Optical Properties
of Borate Glass-Ceramics

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Chapter 1

Introduction

The impact of nanoparticles in daily life is increasing and, judging by the speed of miniaturization of electronic and optoelectronic components, they are likely to become ever more important. There is a major interest in studying the interaction of light with matter in the form of such small particles, as they exhibit a discontinuous optical boundary relative to the surrounding. As in the last years a lot of research has been carried out in the search of new materials for photonics application, composites containing small particles have not escaped scrutiny. Glass-ceramics - nanostructured materials composed of a glassy host matrix and optically active nanocrystals - form a new part of this research field.

Nanostructured composites possess interesting electromagnetic properties, which differ greatly from those of bulk material. Optical techniques have been used to investigate the particle size-dependence of linear and third-order optical nonlinearities in nanocrystals and their relation with the effects of quantum confinement. Recently, a novel class of materials, fractal-microcavity composites [1] was discovered. They combine the energy-concentrating effects due to localization of optical excitations in fractals with the strong morphology-dependent resonances of dielectric microcavities.

Research and development in the field of nanostructured nonlinear optical materials showing high performance wavelength conversion, electro-optic effect, and so on, are important in photonics. Glass-related materials have received much attention, because they have a potential for good connectivity with glass fibers [2, 3]. Transparent surface-crystalized glasses and glass-ceramics containing nonlinear optical or ferroelectric crystals have applications in optoelectronics [4, 5, 6]. Several families of rare-earth and / or transition metal ions doped nanocrystals
dispersed throughout a host glass were shown to produce efficient upconversion, fluorescence or luminescence, with potential use for solid-state lasers [7, 8]. The aim of the current work was to prepare and analyze the optical properties of borate based glass-ceramics and their parent glasses.

**Outline of the Dissertation**

The dissertation is structured over eight chapters, starting with the present Introduction.

**Chapter 2** is a general presentation of the glass ceramics. A phenomenological approach, based on the continuous network theory, was used to describe the nucleation and crystal growth processes involved in the glass ceramics preparation. The influence of nucleation agents and the structural difference between the glass and the corresponding crystals are discussed.

The third chapter outlines the theoretical base of the nonlinear light-matter interaction and particularly of second-harmonic generation. The model proposed by R. Boyd [9], to explain the linear and nonlinear optical properties of nanocomposite materials is presented.

The next chapter gives an overview of bismuth borate glasses and crystals properties. The results of SHG powder measurement and the proposed structure of a new bismuth borate phase, BiBO$_3$ are presented. The effects of heat treatments applied to the bismuth borate glasses are discussed.

The optical properties of pure and doped bismuth borate glasses are presented in **Chapter 5**. Optical absorption, luminescence and refractive indices measurements are the main experiments carried out on glasses having various compositions ($x$Bi$_2$O$_3$(1−$x$)B$_2$O$_3$, 0.25 ≤ $x$ ≤ 0.65) and / or dopants (Cr$^{3+}$, Er$^{3+}$, Nd$^{3+}$).

Ferroelectric $x$(Sr$_{0.5}$,Ba$_{0.5}$)Nb$_2$O$_6$ micro crystallites embedded in strontium barium borate glass matrix (1 − $x$)(Sr$_{0.5}$,Ba$_{0.5}$)B$_4$O$_7$ with $x$ = 0.1, 0.2, 0.25, 0.3. are investigated in **Chapter 6**. The effect of Nb$_2$O$_5$ in strontium barium borate glass is studied by means of optical absorption and X-ray diffraction. From the inflection point of the graph of the second-order nonlinear susceptibility as function of temperature, the ferroelectric-paraelectric phase transition temperature is determined.

The presence of second order nonlinearities of Pb$_2$B$_5$O$_9$Br-based glass-ceramics, obtained following bulk nucleation is demonstrated in **Chapter 7**. Absorption and refractive indices measurements for parent glasses are also presented. Moreover, a comparative study of SHG output
of $\text{Pb}_2\text{B}_5\text{O}_9\text{Br}$ and other pentaborate hilgardite-type crystals was performed.

The **Conclusions** chapter summarize the results emerging from the experiments. Finally, the **Appendix** contains detailed descriptions of the experimental setups used and of the thermal treatment conditions employed for the fabrication of the presently-studied glass-ceramics.
Chapter 2

Glass-Ceramics

2.1 Introduction

Glass ceramics materials are polycrystalline solids containing nanometers to micrometers size crystals embedded in a residual glass matrix and are produced by devitrification of glasses. The first step toward this involves conventional techniques for glass production, followed by controlled crystallization; this process leads to the separation of a crystalline phase from the glassy parent phase in the form of tiny crystals, where the number of crystals, their growth rate and their final size are controlled by suitable heat treatment [10].

In 1739, Raumer published a study on the crystallization of silica based glasses. The resulting polycrystalline material (the so-called Raumer porcelain) showed a too low strength for practical application. Products made from fused basalt may also be regarded as forerunner of the glass ceramics, because on cooling of these materials spontaneous recrystallization appears. The positive effects of the fine-grained structure on the properties has also been established for these materials and the term ”crystallization activator” was introduced. The development of glass ceramics was promoted by a systematic study of photosensitive glasses which was the subject of the long-term research conducted by Stookey (1949 - 1954) at Corning Glass Works.

The glass ceramics based on silicates belong to an important class of advanced technological materials, having a wide range of interesting applications. For example, $\beta$-quartz is used for his low thermal expansion, mullite for machinability and spinel for high hardness [11]. Most of the glass ceramics applications use the good mechanical and thermal stability of this materials, but also the electric, magnetic and optic properties are interesting.
CHAPTER 2. GLASS-CERAMICS

Transparent glass ceramics produced from aluminosilicates were used firstly for displays and storage media. But, in recent years an increasing interest in other optical application of glass ceramics can be seen. Transparent fluoride rare earth optical vitroceramics (FROGS), combining the low phonon energy of fluorides with chemical stability of oxides, show large infrared to visible upconversion more efficient than the parent glass, because the rare earth ions are preferentially incorporated into the fluoride crystal [3, 7]. Tick also reports low-loss waveguide based FROGS doped with Tm [12].

In borate systems, recently second harmonic generation in $\beta$-barium borate crystals embedded in borate glass matrix and on surface crystallized glass of LaBGeO$_5$ has been observed [13, 14]. In contrast to sintered ceramics, glass-ceramics are produced from an amorphous material, the glass, which crystallizes applying appropriate thermal treatments. Thus, the opportunity of in-situ oriented crystallization of the glass melt is provided. However, a homogeneous glass, a priori, is isotropic and suitable driving forces have to be supplied in order to obtain anisotropic structures in glass-ceramics. The use of a temperature gradient or an electric or magnetic field during the crystallization process are proven methods to achieve preferred crystal orientations. A further method to obtain anisotropic glass-ceramics is the extrusion process (the unidirectional deformation of a glass melt during extrusion generates shear flow, which causes alignment of structures).

### 2.2 Glasses Nucleation and Crystallization

A glass is defined as "an inorganic product of fusion which has been cooled to a rigid condition without crystallization". The main distinction between glass and crystals is the presence of long range order in the crystal structure [15].

The transition from a viscous liquid to a solid glass is called "glass transition" and the corresponding temperature is $T_g$. The reversible transformation from a glass to a viscous liquid takes place if the glass is heated to a temperature above $T_g$. Since the glass transition occurs as a result of the increase of viscosity and the rate of viscosity increase is dependent on cooling rate, the glass transition temperature, $T_g$, is not always the same. If the chemical composition is the same, $T_g$ usually depends on the cooling rate of a liquid. A volume-temperature diagram showing the cooling behavior of a typical glass-forming melt is provided in Fig. 2.1.

A slow cooling allows enough time for a viscous liquid to alter its local atomic arrangement to attain the minimum free energy at the corresponding temperature, whereas a rapid cooling causes
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Figure 2.1: Left: Volume-temperature relationship of glass-forming liquid and non glass-forming liquid. Right: Temperature dependence of nucleation rate $I$ and crystal growth rate $U$.

An increase of viscosity that is too quick for the local atomic arrangement to follow and results in a transition into a glass at a higher temperature. The structure of a rapidly cooled glass is more open than that of a slowly cooled one because the "freezing-in" of the atomic arrangement occurs at a higher temperature. The properties of a glass are therefore different from glass to glass, depending on the thermal history, even if the chemical composition is the same. A glass whose atomic arrangement lacks regularity over a long range has higher configurational entropy, and hence higher free energy, than a crystalline material of the same composition. Therefore a glass is a thermodynamically metastable material. The transformation of a glass to a crystal proceeds via nucleation and crystal growth under the driving force of the difference in free energy between crystal and glass $\Delta G_v$, which increases with the increase of supercooling $\Delta T_r$. When a solid forms in a liquid there an interface is created. The surface free energy is associated with this interface. As the solid grows, the total surface free energy increases. With decreasing temperature there are two competing effects: the increased difference in free energy between crystals and liquid favors crystallization; the increasing viscosity reduces the tendency to crystallization.

Nucleation is a tri-dimensional process, that involves the formation of longer range atomic order, growth is a bi-dimensional (on the surface of existing crystals).

Nucleation is usually described in terms of the free energy balance between the creation of a new
crystal and new surface(s) associated with the crystal. Forming a nuclei smaller than a critical size causes an initial increase in free energy due to the need to create surface(s) and, therefore, is not thermodynamically favorable. As the nuclei grow larger, the free energy reaches a maximum and becomes negative, leaving stable nuclei. Both nucleation rate $I_0$ and crystal growth rate $U$ are dependent on viscosity $\eta$ as well as on $\Delta G_v$.

The nucleation rate can be described by the following formula:

$$I_0 = \frac{k_1}{\eta} \exp\left(-\frac{g\alpha^3 \beta}{T_r \Delta T_r^2}\right)$$

(2.1)

where $k_1$ is a constant (typically about $10^{30} \text{ dyne cm}$), $g$ is a factor related to the shape of the nucleus ($g = 16\pi/3$ for a spherical nucleus). The reduced temperature is:

$$T_r = \frac{T}{T_m}$$

(2.2)

and

$$\Delta T_r = \frac{T_m - T}{T_m}$$

(2.3)

where $T_m$ is the crystallization temperature (see Fig. 2.1).

The dimensionless parameters $\alpha$ and $\beta$ are given by:

$$\alpha = \frac{(N_A V_C^2)^{1/3} \sigma}{\Delta H_{fM}}$$

(2.4)

and

$$\beta = \frac{\Delta H_{fM}}{RT_m}$$

(2.5)

where $N_A$ is Avogadro’s number, $V_C$ is the molar volume of the crystal, $\sigma$ is the crystal-liquid interface, $\Delta H_{fM}$ is the molar enthalpy of fusion. For typical nonmetals $(\alpha \beta)^{1/3}$ is about 0.5 - 0.7.

Many small crystals form in a system initially but slowly disappear except for a few that grow larger, at the expense of the small crystals. As the larger crystals grow, the area around them is depleted of smaller crystals. This so-called Ostwald ripening denotes the growth of larger crystals from those of smaller size which have a higher solubility than the larger ones. This is a spontaneous process that occurs because larger crystals are energetically more favored than smaller crystals. While the formation of many small crystals is kinetically favored, (i.e. they
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nucleate more easily) large crystals are thermodynamically favored. Thus, from a standpoint of kinetics, it is easier to nucleate many small crystals. However, small crystals have a larger surface area to volume ratio than large crystals. Molecules on the surface are energetically less stable than the ones already well ordered and packed in the interior. Large crystals, with their greater volume to surface area ratio, represent a lower energy state. Thus, many small crystals will attain a lower energy state if transformed into large crystals and this is what we see in Ostwald ripening. The nucleation of a huge number of small crystals, however, also reduces the amount of supersaturation and thus, the thermodynamically favored large crystals sometimes never get a chance to appear.

The crystal growth rate is expressed by the relation:

\[ U = f\left(\frac{RT}{3N_A\pi \lambda^2 \eta}\right)(1 - \exp\left(-\frac{\Delta H_{fM} \Delta T}{RT m}\right)) \]  

(2.6)

where \( f \) is the fraction of the area at which the glass to crystal transition can take place on the crystal surface and \( \Delta T = T_m - T \). The higher the melt viscosity \( \eta \) at the melting temperature, the lower its crystallisability. Qualitatively, this tendency can be explained by an increased inhibition of motion or molecular rearrangement of the basic units of the melt with increasing viscosity.

The crystallization process can be completely controlled if the nucleation and growth rate curves are well separated as in Fig. 2.1.

In the absence of catalyzing agents, most supercooled liquids crystallize heterogeneously from the external surfaces when heated; only a few systems crystallize in the bulk. Most have surface nucleation and if the surface nucleates, crystallites tend to grow rapidly. For homogeneous nucleation it was observed that the reduced glass transition temperature, \( T_{gr} = T_g/T_m \), must have a low value (\( T_{gr} < 0.58 \)) and in this case the maximum nucleation rate is above \( T_g \). It has been demonstrated that stoichiometric glass forming systems can be separated into two classes. The first are able to crystallize in the volume (supposedly by homogeneous nucleation) and their temperatures of maximum homogeneous nucleation rate (\( T_{max} \)) are close to the experimental glass transition temperatures, \( T_g \). The opposite behavior is observed for the other types of glasses, which only crystallize heterogeneously on the surfaces, i.e., the (calculated) temperatures of maximum homogeneous nucleation rate are substantially lower than \( T_g \) (\( T_{max} << T_g \)). For this second family of glasses, the induction periods in the temperature range where nucleation could in principle be detected are too long. As a consequence, the homogeneous nucleation rates could be undetectable low.
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The critical cluster size and the energy needed for a critical cluster formation decreases with the difference $T_m - T$. For this reason, when the glass transition range is reached at relatively high temperatures $T_{gr} > 0.60$, this energy is still too large to allow measurable internal crystallization. However, close to or on interfaces, the energetic barrier for nucleation and the viscosity may be lower than bulk values. Therefore, surface crystallization is more commonly observed than internal crystallization. The transition from glasses demonstrating only surface crystallization $T_{gr} > 0.60$ to glasses showing volume nucleation $T_{gr} < 0.58$ may be qualitatively explained by an increase in nucleation rate with decreasing $T_{gr}$.

Experimentally, it is very difficult to estimate the rates of nucleation and crystal growth because it is impossible to measure most of the parameters. Knowing the glass transition temperature is important when calculating annealing schedules for glass ceramics preparation. By means of DTA measurements it is possible to determine values of glass transition $T_g$, onset of crystallization $T_x$ and melting $T_m$ temperatures. Optical methods are not very suitable for an accurate determination of the glass transition temperature. One of these is the observation of optical modulation of the refractive index in the glass transition temperature range as a peak in the intensity of light scattered at $90^\circ$. Due to the interaction of a low intensity laser beam with a highly unstable glass structure (at $T_g$) diffraction patterns are formed in the bulk [16].

Influence of Nucleation Agents

A nucleation agent promotes nucleation by accelerating phase separation or by lowering the energy barrier of nucleation. Two functional mechanisms may be considered for nucleation agents. Firstly, the heterogeneous nucleation of the oxide phase is induced by adding metallic nucleants such as Au, Ag, Cu, Pt and Pd. During melting the nucleating agents usually pass into solution and are precipitated only at relatively low temperature as a result of a strong decrease in solubility and simultaneous reduction to the metallic form. The metal particle size is roughly 5 to 10 nm. Secondly, the metastable separation mechanism is presumed to be at the origin of nucleation in glasses where oxidic nucleating agents as TiO$_2$, ZrO$_2$, P$_2$O$_5$, Cr$_2$O$_3$ are used. Further highly efficient nucleating agents include fluorides known as opacifiers, and sulphides. In the later cases, the required amount of nucleating agent is considerably higher than in the case of metals.
2.2. GLASSES NUCLEATION AND CRYSTALLIZATION

Influence of Glass and Crystal Structure

Before Zachariasen’s Random Network Theory [17], glass structures were considered to be comprised of nanocrystals 8 - 10 Å size, estimated from the broadening of diffraction patterns. He noted similar mechanical properties between glasses and crystals and so expected similar structural energies. Therefore he suggested that glasses and crystals may have the same building blocks (cation polyhedra) arranged in different patterns, but glasses have broader distributions of bond angles. Both models, the continuous network one and the nanocrystal one, are used nowadays to explain the glassy state.

The nanocrystallite model is supported by the observation that the first devitrification product of a glass may reflect the structural features that are present in glass (Ostwald’s rule of successive reactions). By melting some crystalline phase, on subsequent recrystallization of the glass the same crystalline phase is obtained.

The glass-forming oxides form very viscous liquids; viscosity is related to the structure and bonding that is present. In the crystallization process of such a liquid many strong bonds must break and atomic reorganization must occur. Therefore it is interesting to know if there is a relationship between the structures of glasses and the crystals formed.

The relationship between the homogeneous nucleation behavior and the structure of crystals and of parent glasses was investigated by Muller et al. [18] for silicates. The main assumption is: if the local structure of a glass and its isochemical crystal are similar, only a few interfacial rearrangements will be necessary for crystal nucleation. If these rearrangements are substantial, nucleation can only occur on the external surfaces, assisted by unsaturated bonds and solid impurities at the surface, or, in the volume, only with the aid of nucleating agents. For glasses that only nucleate on the surface, the local order is supposed to be quite different from those of their isochemical crystal phases.

In qualitative terms, the degree of structural similarity between parent glass and resulting crystal should affect the main thermodynamic parameters controlling nucleation, liquid-crystal surface energy and thermodynamic driving force, thus affecting the nucleation ability of the system.

The exact relationships of the structural parameters of glass and crystal with surface energy and driving force are not known. However, there should be some optimum value of similarity.
CHAPTER 2. GLASS-CERAMICS

Transparent Glass-Ceramics

Transparency is an important requirement for optical applications. Heterogeneities like grain boundaries, composition gradients, lattice imperfections cause losses through light scattering. In order to behave as an effective optical medium for light propagation some criteria must to be met: small particle size, interparticle spacing comparable with the crystal size, narrow particle size distribution.

Transmitted light can be represented by the following expression [5]:

\[
T = \exp \left( -3 \cdot r^3 \cdot V_h \cdot d \cdot \frac{n_{\text{crystal}}}{n_{\text{glass}}} - 1 \right) \quad (2.7)
\]

where \( V_h \) volume fraction of the heterogeneity, \( r \) radius of heterogeneity, \( d \) thickness, \( \lambda \) the wavelength of incident light, \( n_{\text{crystal}}, n_{\text{glass}} \) refractive indices of crystal, glass.

Expression 2.7 shows that the attenuation of light depends on the difference in refractive indexes of the glass and crystal, the size and distribution of crystals in the glass. So for a transparent glass ceramic is necessary to grow small crystals in the glass matrix and furthermore, the glassy and crystalline phases must have a similar value of the refractive index.

2.3 Preparation of the Glass-Ceramic Materials

The typical sequence for glass ceramics preparation involves nucleation of a small volume fraction of the glass followed by bulk growth of crystals. The nucleation step is carried out at lower temperatures, presumably to obtain higher driving forces while the growth step is carried out at higher temperatures, in order to obtain higher growth rates due to more rapid diffusion. The initial glasses for the preparation of glass ceramic materials are prepared by cooling the glass forming melt.

The heat treatment schedule is described in Fig. 2.2. The temperature and duration of both holding periods are of great significance. The process schedule is based on the assumption that during the first holding period, both the homogeneous and heterogeneous nucleation will take place simultaneously (the two nucleation processes may have peaks at different temperatures) and large number of nuclei \( 10^{12} - 10^{15} \) nuclei / cm\(^{-3} \) are created. Heating rate is also an important
2.3. PREPARATION OF THE GLASS-CERAMIC MATERIALS

factor, because the glass transition temperature could be higher for a faster ramp rate or lower for a slower ramp rate.

Figure 2.2: Thermal treatment schedule for glass-ceramics: (1) heating the glass from room temperature, (2) nucleation stage, (3) increasing temperature, (4) crystallization stage, (5) cooling down to room temperature.
Chapter 3

Optical Nonlinearities

3.1 Introduction

Materials that exhibit nonlinear optical properties have a large potential for photonic applications and it is important to characterize their behavior. The development of lasers has allowed great progress in the studies of nonlinear optical phenomena. When focused, a laser beam produces an electric field greater than $10^4$ V/cm; this value is considerably larger than that from a conventional light source where the electric fields are in the range of 1 V/cm. The nonlinear interaction of light with matter may be understood as the reaction of the electric dipoles built by electrons and the positively charged atomic cores in the matter under the influence of high electric fields. For small fields the displacement will be small and thus the back driving force will change linearly with the elongation in this first order approach, as in classical mechanics. With strong electric fields the displacement will be increased and the force will become a nonlinear function of the elongation.

3.2 Nonlinear Polarization of the Medium

Electronic polarization is the main mechanism involved in the production of the most important nonlinear optical phenomena: second and third harmonic generation, sum-frequency mixing, optical parametric oscillation, four-photon parametric interaction. The polarization occurs following the distortion of the outer-shell electronic cloud of atoms, ions and molecules compared to the undisturbed state.
Based on Maxwell’s equation the interaction of the matter with the electric field of the light \( E(r', t') \) can be described by the polarization \( P(r, t) \). In the linear case it is described as the linear proportionality between polarization and the electric field’s amplitude \([19, 20, 21]\).

\[
P(r, t) = \varepsilon_0 \int_{-\infty}^{\infty} \chi^{(1)}(r - r', t - t') \cdot E(r', t') dr'dt' \tag{3.1}
\]

where \( \chi^{(1)} \) is the linear susceptibility of the medium. For monochromatic plane waves \( E(k, \omega) = E_0(k, \omega) \exp(ik \cdot r - i\omega t) \), a Fourier transformation applied to Eq. 3.1 yields

\[
P(k, \omega) = \varepsilon_0 \chi^{(1)}(k, \omega)E(k, \omega) \tag{3.2}
\]

with

\[
\chi^{(1)}(k, \omega) = \int_{-\infty}^{\infty} \chi^{(1)}(r, t) \exp(-ikr + i\omega t) dr dt \tag{3.3}
\]

The dependence of \( \chi \) on \( k \) is only weak and can be neglected in all practical cases.

In the nonlinear case, \( P \) can be expanded into a power series of \( E \)

\[
P(k, \omega) = \varepsilon_0 \int_{-\infty}^{\infty} \chi^{(1)}(r - r', t - t') \cdot E(r', t') dr'dt' \\
+ \varepsilon_0 \int_{-\infty}^{\infty} \chi^{(2)}(r - r_1, t - t_1; r - r_2, t - t_2) \cdot E(r_1, t_1) \cdot E(r_2, t_2) dr_1 dt_1 dr_2 dt_2 \\
+ \varepsilon_0 \int_{-\infty}^{\infty} \chi^{(3)}(r - r_1, t - t_1; r - r_2, t - t_2; r - r_3, t - t_3) \cdot E(r_1, t_1) \cdot E(r_2, t_2) \cdot E(r_3, t_3) dr_1 dt_1 dr_2 dt_2 dr_3 dt_3 \\
+ ... \tag{3.4}
\]

where \( \chi(n) \) is the \( n \)-th-order nonlinear susceptibility. As in the linear case, the problem can be treated using the Fourier transformation. For \( E \) a sum of monochromatic plane waves should be assumed

\[
E(r, t) = \sum_i E(k_i, \omega_i) \tag{3.5}
\]

yielding for the polarization

\[
P(k, \omega) = P^{(1)}(k, \omega) + P^{(2)}(k, \omega) + P^{(3)}(k, \omega) + ... \tag{3.6}
\]
3.2. NONLINEAR POLARIZATION OF THE MEDIUM

with

\[ P^{(1)}(k, \omega) = \varepsilon_0 \chi^{(1)}(k, \omega) \cdot E(k, \omega) \]

\[ P^{(2)}(k, \omega) = \varepsilon_0 \chi^{(2)}(k = k_i + k_j, \omega = \omega_i + \omega_j) \cdot E(k_i, \omega_i) \cdot E(k_j, \omega_j) \]

\[ P^{(3)}(k, \omega) = \varepsilon_0 \chi^{(3)}(k = k_i + k_j + k_l, \omega = \omega_i + \omega_j + \omega_l) \cdot E(k_i, \omega_i) \cdot E(k_j, \omega_j) \cdot E(k_l, \omega_l). \]  

(3.7)

The \( \chi^{(n)}(k, \omega) \) can be expressed in a similar way as in the linear case as integrals over the respective \( \chi^{(n)}(r, t) \). \( \chi^{(n)} \) is an \( (n+1) \)-st-rank tensor representing material properties. Using Einstein’s summation convention, the above equations may be rewritten in component form

\[ P^{(2)}_k(\omega) = \varepsilon_0 \chi^{(2)}_{kmn}(\omega = \omega_i + \omega_j) E_m(\omega_j) E_n(\omega_j). \]  

(3.8)

3.2.1 Structural Symmetry of Nonlinear Susceptibilities

The susceptibility tensors must remain unchanged upon symmetry operations allowed for the medium. This reduces the number of independent and nonzero elements. The most important conclusion from this property is that for all centrosymmetric crystals and for all isotropic media (gases, liquids, amorphous solids) all tensor elements of the even-order susceptibility tensors (\( \chi^{(2)}, \chi^{(4)}, \ldots \)) must be zero. Thus no second harmonic generation can be observed in such media.

3.2.2 Permutation Symmetry of Nonlinear Susceptibilities

When tensors are multiplied with vectors, usually the order of the vector multiplication can be changed. In nonlinear optics it should not matter which of the fundamental fields is the first to be multiplied. From this, permutation symmetry for the nonlinear susceptibilities follows, for the second order

\[ \chi^{(2)}_{ijl}(\omega_1, \omega_2) = \chi^{(2)}_{lij}(\omega_2, \omega_1). \]  

(3.9)

A more general permutation symmetry can be defined due to time reversal symmetry resulting in relations like

\[ \chi^{(2)*}_{ijl}(\omega = \omega_1 + \omega_2) = \chi^{(2)}_{jli}(\omega_1 = -\omega_2 + \omega) = \chi^{(2)}_{lij}(\omega_2 = \omega - \omega_1). \]  

(3.10)
Time reversal symmetry can be applied as long as absorption can be neglected. If the dispersion of $\chi$ can also be neglected, then the permutation symmetry becomes independent of the frequencies. Consequently, then a very general permutation symmetry exists between different elements of $\chi$: elements remain unchanged under all permutations of the Cartesian indices. This so-called Kleinman’s conjecture or Kleinman symmetry \[22\] reduces the number of independent elements further. It should be noted that it’s a good approximation only at frequencies far from resonances such that dispersion really can be neglected.

Especially for the susceptibility tensor for second harmonic generation it is common to write it in a different form. As the last two indices can be exchanged, there are 18 different elements left from the full set of 27. These 18 are written as a 2-dimensional matrix $d_{ij}$ \[20, 21, 23\], the last two indices $kl$ of the elements $\chi_{ikl}$ are contracted to one index $j$ such that

$$11 \rightarrow 1, \quad 22 \rightarrow 2, \quad 33 \rightarrow 3, \quad 23, 32 \rightarrow 4, \quad 13, 31 \rightarrow 5, \quad 12, 21 \rightarrow 6. \quad (3.11)$$

### 3.3 Harmonic Generation

One of the most important nonlinear optical processes for technical applications is the generation of harmonics from laser light. Second-harmonic generation is widely used for producing visible and near ultraviolet coherent light from infrared radiation.

#### 3.3.1 Second-Harmonic Generation

Second-harmonic generation (SHG) was first observed experimentally by Franken in crystalline quartz in 1961 \[24\]. The general symmetry arguments have to be adopted in a suitable way for SHG. The responsible tensor is of third rank, materials for SHG thus must be non-centrosymmetric. For practical reasons, usually the $d$-tensor described is used instead of the more general $\chi$-tensor. The local second harmonic polarization can be calculated according to Eq. 3.7. Due to dispersion present in all materials, waves of different frequencies travel at different velocities, yielding a phase-mismatch between second-harmonic waves generated at different positions in a nonlinear material. To get the total second-harmonic intensity produced, we have to integrate over the generated waves taking into account the different velocities. For simplicity we omit all rapidly oscillating factors and calculate only the phase-factors with respect to $x = 0$. $E^{(1)}(x)$ and $P^{(2)}(x)$ can be written as
3.3. HARMONIC GENERATION

Figure 3.1: Fundamental wave $E^{(1)}$, induced second-harmonic polarization $P^{(2)}$, and second harmonic waves $E^{(2)}$, generated at the positions $x_1$, $x_2$, and $x_3$ in a nonlinear material for two different cases. Left: second-harmonic waves travel at the same velocity as the fundamental wave, all are in-phase throughout. Right: different velocities, the usual case, mismatch between the phases of the second-harmonic waves $E^{(2)}$.

\[
E^{(1)}(x) = E^{(1)}(0) \cdot e^{-i k_1 x},
\]

\[
P^{(2)}(x) = \chi \cdot E^{(1)}(x) \cdot E^{(1)}(x) = \chi \cdot E^{(1)}(0) \cdot E^{(1)}(0) \cdot e^{-i 2k_1 x}.
\]

Taking $P^{(2)}$ as driving force in a wave equation for $E^{(2)}$ yields

\[
E^{(2)}(x) = K \cdot P^{(2)}(x) = K \cdot E^{(1)}(0) \cdot E^{(1)}(0) \cdot e^{-i 2k_1 x}
\]  

(3.13)

where the $K$ contains all necessary constants like nonlinear susceptibility or refractive indices.

$E^{(2)}$ now travels through the material with a velocity characteristic for the frequency $\omega_2 = 2\omega_1$ and wave vector $k_2$. Thus at an arbitrary position $x'$ where we could measure the second-harmonic

\[
E^{(2)}(x') = E^{(2)}(x) \cdot e^{-i k_2 (x'-x)} = K \cdot E^{(1)}(0) \cdot E^{(1)}(0) \cdot e^{-i 2k_1 x'} \cdot e^{-i (2k_1 - k_2)x}.
\]

(3.14)

Assuming homogeneous material for $0 < x < L$, $E_{\text{total}}^{(2)}$ can be found integrating Eq. 3.14 over the length of the interaction between the fundamental light and the material.
\[ E_{\text{total}}^{(2)}(x') = K \cdot E^{(1)}(0) \cdot E^{(1)}(0) \cdot e^{-ik_2x'} \int_0^L e^{-i(2k_1-k_2)x'} dx' \]

\[ = K \cdot E^{(1)}(0) \cdot E^{(1)}(0) \cdot e^{-ik_2x'} \cdot e^{\frac{i\Delta k L}{2}} \frac{1}{i\Delta k} \left[ e^{i\Delta k L} - 1 \right] \]

\[ = K \cdot E^{(1)}(0) \cdot E^{(1)}(0) \cdot e^{-ik_2x'} \cdot e^{i\frac{\Delta k L}{2}} \cdot e^{\frac{i\Delta k}{2} L} \frac{1}{i\Delta k} \left[ e^{i\Delta k L} - e^{-i\Delta k L} \right] \]

\[ = K \cdot E^{(1)}(0) \cdot E^{(1)}(0) \cdot e^{-ik_2x'} \cdot e^{i\frac{\Delta k L}{2}} \cdot \sin\left(\frac{\Delta k L}{2}\right) \frac{\sin(\Delta k L/2)}{\Delta k/2} \]

(3.15)

with

\[ \Delta k = k_2 - 2k_1 = \frac{2\pi}{\lambda_2} n(\omega_2) - \frac{2\pi}{\lambda_1} n(\omega_1) = \frac{4\pi}{\lambda_1} (n(\omega_2) - n(\omega_1)). \]

(3.16)

\[ \lambda_1 \text{ and } \lambda_2 = \lambda_1/2 \] are the wavelengths of the fundamental and second harmonic waves, respectively, in vacuum.

The coherence length, \( L_c \), can be defined as the length after which the sine reaches its maximum or the length after which the sine changes sign. Thus it can be written as

\[ \text{either } L_c = \frac{\pi}{\Delta k} \text{ or } L_c = \frac{2\pi}{\Delta k}. \]

(3.17)

The generated second-harmonic intensity depends mainly on the phase mismatch \( \Delta k \), and on the square of the input intensity and the tensor elements involved. For the latter often a so-called effective tensor element is used which is a suitable combination for the geometry considered

\[ I^{(2)} = C \cdot d_{\text{eff}}^2 \cdot I^{(1)^2} \cdot \frac{\sin^2(\Delta k L/2)}{(\Delta k/2)^2} \]

(3.18)

In Eq. 3.18 \( \Delta k \) is in most cases non-zero and the intensity will oscillate in a sine-square way. If, however, \( \Delta k \) approaches zero, we have to calculate the limit

\[ \lim_{\Delta k \to 0} \frac{\sin(\Delta k L/2)}{\Delta k/2} = L. \]

(3.19)

In this case, the second-harmonic intensity increases quadratically with \( L \) - at least as long as we are in the limit of low second-harmonic intensities where \( I^{(1)} \) is unchanged (undepleted fundamental wave approximation). The spatial variation of second-harmonic intensities for some characteristic values \( \Delta k \) are sketched in Fig. 3.2.
3.3. HARMONIC GENERATION

Figure 3.2: Second-harmonic intensities as a function of the position in the nonlinear material for different $\Delta k$.

### 3.3.2 Phase Matching

The fundamental waves generate an oscillating polarization through the medium which oscillates with $\omega$. The polarization wave travels through the medium at a velocity $v(\omega_i, \omega_j)$ for the fundamental frequencies $\omega_i, \omega_j$. The local polarization at every location acts as a source of electromagnetic dipole radiation. The generated free waves travel through the medium at a velocity $v(\omega)$ characteristic for their own frequency $\omega$.

The velocities are defined by the respective refractive indices and - due to the dispersion present in all materials - generally are different. The polarization wave and the generated free wave come out of phase after a typical distance, so-called coherence length. The sum free wave is amplified due to constructive interference up to this coherence length, then attenuated due to destructive interference. No efficient generation of nonlinear radiation seems to be possible.

For an efficient generation of second-harmonic light it is highly desirable to achieve phase matching, $\Delta k = 0$. Usually the refractive indices are governed by normal dispersion which means that in Eq. 3.16 the difference $n(\omega_2) - n(\omega_1)$ is larger than zero, revealing $\Delta k > 0$. One way out is to utilize the birefringence which is present in crystals of all symmetry classes except the cubic one. Uniaxial classes with two different principal refractive indices include the tetragonal, hexagonal and trigonal ones; biaxial classes, where all three principal indices are different, include the orthorhombic, monoclinic and triclinic ones.

Utilizing the birefringence of a material, it may be possible to find propagation directions where the velocities of fundamental and harmonic waves are identical. Drawing the index surfaces
for fundamental and harmonic frequencies, these directions are found as the intersection curves between the index surfaces.

### 3.4 Powder Technique

The powder technique was used for the evaluation of nonlinear optical materials by S. K. Kurtz and T. T. Perry in 1968 [25]. Since that time it is widely used as one of the simplest methods for a rapid classification of new materials.

In the powder sample the light, fundamental and harmonic, is randomly scattered. The scattering leads to an angular distribution, which is similar to that of a planar radiator obeying Lamberts cosine law, with an appreciable amount in backward direction. To collect the light scattered in all directions, an integrating Ulbricht sphere can be used. This angular dependence is sketched in Fig. 3.3.

![Angular distribution of second harmonic generated in a powder sample](image)

**Figure 3.3:** Angular distribution of second harmonic generated in a powder sample (picture taken from [25]). When the powder is immersed in an index-matching liquid, a narrow angular distribution in forward direction shows up, otherwise a broad angular distribution in forward and in backward direction is found.
3.4. POWDER TECHNIQUE

The generated harmonic intensity depends in a characteristic way on the average particle size in the powder. This size dependence is different for materials which are phase matchable and those which are not. For small particles, with size smaller than the coherence length, $\hat{r} << l_c$, the intensity of the SHG signal increases linearly with the size of powders: $I^{2\omega} \propto \hat{r}$. For larger particles, in the case of phase matchable materials the intensity remains constant, but for non phase matchable materials an inverse relation between intensity and particle size is observed: $I^{2\omega} \propto 1/\hat{r}$. The two dependencies are schematically sketched in Fig. 3.4.

![Graph showing particle-size dependencies for phase-matchable and non-phase matching materials.](image)

Figure 3.4: Particle-size dependencies for phase-matchable and non-phase matching materials.

SHG intensities from powders at small particle size, $\hat{r} << l_c$, can be described by

$$I^{2\omega} \simeq \langle d^2_{ijk} \rangle \frac{L}{l_c^2} \hat{r}$$

(3.20)

where $L$ is the thickness of the powder sample and $\langle d^2_{ijk} \rangle$ the directionally averaged nonlinear coefficients.

SHG intensities from powders, at larger particle sizes, can be approximated using the following expressions:

$$I^{2\omega} \simeq \frac{\langle d_{ijk} \rangle}{(n+1)^6} \cdot \frac{l_c^2}{2\hat{r}} \quad \text{non - phase matchable}$$

(3.21)
CHAPTER 3. OPTICAL NONLINEARITIES

\[ I^{2\omega} \simeq \frac{d_{PM}^2}{(n + 1)^6} \cdot \frac{\sin \theta_m}{\sin \rho} \cdot \sin \theta_m \sin \rho \text{ phase-matchable} \]  \hspace{1cm} (3.22)

where \(\rho\) is walkoff angle, \(\theta_m\) the angle between the phase-matching direction and optic axis and \(d_{PM}\) the coefficients for which phase matching occurs.

Directionally averaged nonlinear coefficients, \(\langle d_{ijk}^2 \rangle\) can be estimated from powder SHG measurements relative to a standard (in our case \(\text{SiO}_2\)) through the relation:

\[ \langle d_{ijk} \rangle = A d_{111} \cdot \left( \frac{n + 1}{n_{\text{SiO}_2} + 1} \right)^3 \cdot \sqrt{\frac{I^{2\omega}}{I_{\text{SiO}_2}^{2\omega}}} \] \hspace{1cm} (3.23)

where \(A\) is geometrical factor close to unity, \(d_{111} = 0.364 \text{ pm/V}\), \(n, n_{\text{SiO}_2}\) the refractive indices for the substances and quartz. The samples to be compared must have equal average particle sizes, smaller then the coherence length of the quartz standard.

A test for phase matching can be made using several particle sizes which have to be larger than the average coherence length. Comparing different materials - known and unknown ones - it is also possible to get a rough estimate about the magnitude of the effective tensor elements of the SHG tensor, responsible for phase-matching.

Using the powder technique, materials can be classified into different categories at a very early state of the investigations. These categories include: Centrosymmetric - No second-harmonic intensity found by the powder technique; Phase Matchable - Constant second-harmonic intensity at increasing particle sizes; Non Phase Matchable - Second-harmonic intensity decreasing as a function of the particle size.

3.5 Nonlinearities in Composite Materials

3.5.1 Introduction

Glasses are optically isotropic media that theoretically cannot exhibit second order optical non-linearities. However, many attempts have been undertaken during the last decade to induce optical non-linearity in glasses by bulk or surface nanostructuring with non-centrosymmetric crystals or by poling. The possibility of inducing large and permanent second order nonlinearities in glasses by poling has attracted much attention in the last years. The most used methods are: thermal poling - high voltage DC-electric field applied at temperatures about 100 - 400 °C,
3.5. NONLINEARITIES IN COMPOSITE MATERIALS

Laser poling - high power infrared laser beam, UV - poling - ultraviolet laser beam coupled with a high voltage DC-electric field. The observed SHG is usually attributed to a second-order susceptibility located in a thin near-surface region of about 10 µm at the anodic side of a poled plate. An efficient method to produce nonlinearities in bulk centrosymmetric media is photoinduced second harmonic generation (PISHG). The photoinduced processes are created by the intense radiation of an ultrashort pulsed UV laser. It has been found that PISHG is more efficient in amorphous materials in comparison to the single-crystalline ones due to the presence of trapping levels originating from the disordered clusters [26].

In contrast to glasses, nanocrystals can be viewed as a class of large molecules, composed of a limited number of bulk-like unit cells. An additional feature of the nanocrystal size regime, with possible significance for their second-order nonlinear optical response, is the enhancement of the ratio of surface atoms to volume atoms. Second harmonic generation is forbidden in centrosymmetric media within the dipole approximation, but at an interface, the centrosymmetry intrinsically brakes. As a result, second-order nonlinear optical spectroscopies such as second harmonic generation, have found widespread usage as probes of bulk surfaces and interfaces.

3.5.2 Optical Properties of Composites

Boyd and Sipe [9] have given an overview of linear and nonlinear optical properties of composite materials. In this model it is assumed that the size of particles and the distance between them are much smaller than the light wavelength, so the scattering is negligible. But the particles contain many atoms and therefore are large enough to use the macroscopic dielectric constants.

Commonly encountered structures are depicted in Fig. 3.5. The Maxwell Garnett geometry consists of small inclusions ε_i embedded in a host material ε_h. The second topology, Bruggeman, consists of two intermixed components ε_a and ε_b (nonlinear liquids impregnated into porous glass). The latest is made of ordered layered structure.

Figure 3.5: Composite material structures: Maxwell Garnett, Bruggeman and layered [9].

The propagation of light in such structures can be described by effective values of optical con-
stants after volume averaging the local optical response of the material. In order to determine the effective medium properties from those of the constituent media properties the nature of mesoscopic fields must be studied and spatial averages over them have to be performed to identify the values of the macroscopic field.

A lattice of atoms, each characterized by the polarizability \( \alpha \), could be used as physical model for the Maxwell Garnett geometry. The atomic polarizability relates the dipole moment \( p \) induced in an atom to the local electric field. This differs from the macroscopic electric field \( E \) because the field of a given dipole moment contributes to the macroscopic field but not to the field to which the dipole responds:

\[
    p = \alpha (E + \text{local field corrections}) \tag{3.24}
\]

The integral of the electric field \( e \) over a sphere surrounding a charge distribution with a dipole moment \( p \) is given by:

\[
    \int e \, dV = -\frac{4\pi}{3} p \tag{3.25}
\]

If the lattice consists of \( N \) atoms in a volume \( V \), introducing this equation in Eq. 3.24

\[
    p = \alpha \left[ E - \left( -\frac{4\pi}{3} \frac{p}{V} \right) \right] \tag{3.26}
\]

The dipole moment per unit volume \( P \) is given by:

\[
    P = \frac{N}{V} \alpha \left( E + \frac{4\pi}{3} \frac{P}{V} \right) \tag{3.27}
\]

From the Eq. 3.26 and constitutive relations the so-called Clausius-Mossotti equation is obtained:

\[
    \epsilon - 1 \over \epsilon + 2 = \frac{4\pi N}{3 V} \alpha \tag{3.28}
\]

also referred to as the Lorentz-Lorenz relation when the relation between the refractive index and dielectric constant \( \epsilon = n^2 \) is used.

The polarization in an inclusion is given by:

\[
    P_i = \frac{\epsilon_i - 1}{4\pi} E_i \tag{3.29}
\]
3.5. NONLINEARITIES IN COMPOSITE MATERIALS

where $E$ is the field within the inclusion.

Due to the depolarization filled in the sphere, the electric field inside the inclusion $E_i$ differs from the external electric field $E_0$ and the polarization has the following expression:

$$P_i = \frac{3}{4\pi} \frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i + 2\varepsilon_h} E_0$$  (3.30)

The dipole moment of the sphere inclusion in the host medium is:

$$p_i = \frac{4\pi}{3} a^3 P_i = a^3 \frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i + 2\varepsilon_h} E_0$$  (3.31)

where $a$ is the radius of the sphere and an effective polarizability can be assumed as:

$$\alpha = a^3 \frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i + 2\varepsilon_h}$$  (3.32)

Using this relations and taking into account that the inclusion spheres are not in vacuum but in a host material $\varepsilon_h$, the effective dielectric constant $\varepsilon_{\text{eff}}$ is given by:

$$\frac{\varepsilon_{\text{eff}} - \varepsilon_h}{\varepsilon_{\text{eff}} + 2\varepsilon_h} = f \frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i + 2\varepsilon_h}$$  (3.33)

where the fill fraction of the inclusion

$$f = \frac{4\pi N}{3} a^3$$  (3.34)

For metallic inclusions when $\varepsilon_i + 2\varepsilon_h \rightarrow 0$ the Maxwell Garnett expression leads to a surface plasmon resonance.

The nonlinear optical properties are characterized by a nonlinear polarization $P_{i\text{NL}}$:

$$P_{i\text{NL}} = A_i (E_i \cdot E_i^*) \cdot E_i + \frac{B_i}{2} (E_i \cdot E_i) E_i^*$$  (3.35)

where $A_i$ and $B_i$ are constants specifying the nonlinear optical response of an isotropic medium.

An analog relation can be written for the host.

In the effective medium approximation the nonlinear response of the composite is given by:

$$D = \varepsilon_{\text{eff}} E + 4\pi P_{\text{eff}}$$  (3.36)

with
\( P_{\text{NL}}^{\text{eff}} = A_{\text{eff}} (\mathbf{E} \cdot \mathbf{E}^*) \cdot \mathbf{E} + \frac{B_{\text{eff}}}{2} (\mathbf{E} \cdot \mathbf{E}) \mathbf{E}^* \) \hspace{1cm} (3.37)

where \( A_{\text{eff}} \) and \( B_{\text{eff}} \) characterize the nonlinear optical response of the composite as an effective medium.

If the nonlinearity is considered only in the inclusions, the simplest case, then the linear field in the inclusion is uniform:

\[ \mathbf{E}_i = \frac{\varepsilon_{\text{eff}} + 2\varepsilon_h}{\varepsilon_i + 2\varepsilon_h} \mathbf{E} . \] \hspace{1cm} (3.38)

If the nonlinearity is weak the coefficients \( A_{\text{eff}} \) and \( B_{\text{eff}} \) are proportional to the fourth power of \( (\varepsilon_{\text{eff}} + 2\varepsilon_h)/(\varepsilon_i + 2\varepsilon_h) \) as:

\[ A_{\text{eff}} = f \left| \frac{\varepsilon_{\text{eff}} + 2\varepsilon_h}{\varepsilon_i + 2\varepsilon_h} \right|^2 \left( \frac{\varepsilon_{\text{eff}} + 2\varepsilon_h}{\varepsilon_i + 2\varepsilon_h} \right)^2 A_1 \] \hspace{1cm} (3.39)

\[ B_{\text{eff}} = f \left| \frac{\varepsilon_{\text{eff}} + 2\varepsilon_h}{\varepsilon_i + 2\varepsilon_h} \right|^2 \left( \frac{\varepsilon_{\text{eff}} + 2\varepsilon_h}{\varepsilon_i + 2\varepsilon_h} \right)^2 B_1 . \] \hspace{1cm} (3.40)

For \( \varepsilon_i/\varepsilon_h < 1 \) the effective nonlinearity rises fast as a function of \( f \), explained by an increase of the nonlinear material fraction, but their values will be always smaller than that of the pure inclusion material. If the host medium is nonlinear and \( \varepsilon_i/\varepsilon_h > 1 \) there will be an enhanced nonlinear polarization.

The particle shape plays an important role in the enhancement of nonlinearities in composite materials. Theoretical calculations for structures with inclusions of different forms (ellipsoid instead of spheres) have been proposed by Gao et al. [27].
Chapter 4

Structure and Properties of the Bismuth Borate System

4.1 Bismuth Borate Crystals

4.1.1 Introduction

In crystalline form, borates with various compositions are of exceptional importance due to their interesting linear and nonlinear optical properties (for a recent review see Ref. [28]). The theory of anionic groups proposed by Chen is a model for inorganic (borate) materials that is analogous to the principles used for organic NLO materials to calculate bulk NLO coefficients from molecular nonlinearities. The anionic groups are considered to be the most basic structural units responsible for optical nonlinearities of borates. The wide variability of borate crystal chemistry allows the creation of very different structure types. Among all borate structures until now 36 % are non-centrosymmetric. In nonlinear optics, the aim is to create new borate compounds with high SHG coefficients by the application of the theory of anionic groups leading to compounds with nearly planar \([\text{BO}_3]^3\) groups as basic structural units, either as isolated triangular \([\text{BO}_3]^3\) or coupled to pairs of \([\text{B}_2\text{O}_5]^4\) groups. From the viewpoint of crystal chemistry there are numerous structural types of promising borates due to their tendency to form various complex polyanions.
4.1.2 The $\text{Bi}_2\text{O}_3$-$\text{B}_2\text{O}_3$ System

The binary system $\text{Bi}_2\text{O}_3$-$\text{B}_2\text{O}_3$ investigated by Levin and McDaniel contains five Bi-B-O compounds. The phase diagram is sketched in Fig. 4.1.

![Phase Diagram of Bi$_2$O$_3$-B$_2$O$_3$ System](image)

The system $\text{Bi}_2\text{O}_3$-$\text{B}_2\text{O}_3$ contains four congruently and one incongruently melting compounds. The Table 4.1 summarizes some of their properties.

The monoclinic bismuth borate $\text{BiB}_3\text{O}_6$ shows up remarkably large linear and nonlinear optical coefficients [30, 31]. Calculations indicate that this can be mainly attributed to the contribution of the $[\text{BiO}_4]^{5-}$ anionic group [37, 38]. For the linear properties (refractive index) this anionic group should act in a similar way even in amorphous $\text{BiB}_3\text{O}_6$ [39]. Due to an ultraviolet cutoff wavelength at 276 nm, $\text{BiB}_3\text{O}_6$ has a wide band gap and therefore is applicable in a wide spectral region. $\text{BiB}_3\text{O}_6$ crystallizes in space group C2 and consists of $[\text{B}_3\text{O}_6]^{3-}$ rings forming sheets of corner sharing $\text{BO}_3$ triangles and $\text{BO}_4$ tetrahedra with a ratio 2:1, linked by six-coordinated bismuth cations. A lone-pair electron is located at the bismuth cation. In Fig. 4.2 the unit cell of the $\text{BiB}_3\text{O}_6$ crystal is drawn.
4.1. BISMUTH BORATE CRYSTALS

<table>
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<tr>
<th>Properties</th>
<th>BiB$_3$O$_6$</th>
<th>Bi$_2$B$<em>8$O$</em>{15}$</th>
<th>Bi$_3$B$<em>5$O$</em>{12}$</th>
<th>Bi$_3$B$_2$O$_9$</th>
<th>Bi$_2$B$_2$O$_9$</th>
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Table 4.1: Crystals in Bi$_2$O$_3$-B$_2$O$_3$ system.

Figure 4.2: BiB$_3$O$_6$ crystal structure - the blue spheres represent the Bismuth ions, the red ones the Oxygen and the green are the Boron atoms.
4.2  Bismuth Borate Glasses

4.2.1  Introduction

Borate glasses are composed of structural groupings (see Fig. 4.3) as boroxol, tetraborate, diborate, etc, that are also identifiable in borate crystals and are linked by bridging oxygens. Jan Krogh-Moe [40], investigating borate glasses and crystals by infrared technics, has postulated a general rule to identify the structural grouping in these compounds. Youngman et al. [41] have proposed a structural model of B\textsubscript{2}O\textsubscript{3} glass, in which the glass consists of microdomains rich or poor in boroxol rings which are considered as ordered in an intermediate range.

Adding alkali oxides in borates the viscosity increases and the so-called "boron oxide anomaly" appears. This is a gradual change in the coordination number of boron from 3 to 4 as alkali oxide is added. If the alkali impurity creates non-bridging oxygen, the connectivity of the B\textsubscript{2}O\textsubscript{3} network decreases; however, if an alkali impurity causes boron to become tetrahedrally coordinated, the connectivity of the network increases. Because the connectivity of a B\textsubscript{2}O\textsubscript{3} glass is greatly altered by either of these structural changes, the glass properties are also subject to change. Usually, the property changes resulting from the creation of non-bridging oxygen are directly opposite of the property changes caused by an increase in boron coordination. This interesting structural phenomenon is known as the boron anomaly.

Whereas the structure of SiO\textsubscript{2} glass is inherently three-dimensional, that of B\textsubscript{2}O\textsubscript{3} is largely planar. Vitreous borates contain a significant fraction of boroxol rings, in contrast to the crystalline B\textsubscript{2}O\textsubscript{3}. Glassy B\textsubscript{2}O\textsubscript{3} contains two boron sites, in a ratio of about 3:1; the more populated site is due to boron in boroxol rings, while the less populated site is due to connecting BO\textsubscript{3} groups [42]. Vitreous B\textsubscript{2}O\textsubscript{3}, studied by Raman spectroscopy shows that near the glass-transition temperature
the boroxol rings breaks up leading to a more open structure; above the melting point, when the viscosity is low, a regrouping of atoms occurs which results in a low density random network structure [43]. The more open structure of a glass profoundly affects its behavior as a host, allowing greater flexibility so that sites can accommodate metal ions over a much wider range of size and coordination number. Glass transition temperature decreases with increasing network fluidity.

4.2.2 $x \text{Bi}_2\text{O}_3(1-x)\text{B}_2\text{O}_3$ Glasses

The role of Bi$^{3+}$ in glasses may be compared with that of Pb$^{2+}$ ions, due to similarity of Bi$^{3+}$ and Pb$^{2+}$ ions, in atomic weight, ionic radius and electronic configuration and in possessing extensive glass forming regions. Similar to the lead borate system it has relatively low liquidus temperature. Relatively low melting point of the compound is a consequence of the high polarizability of the ion. It has been pointed out by Heynes [44] that a compound in which the ratio of the bond strength to the melting point is high is more likely to form a glass. Strong short range interaction in the bismuth borate glasses results from the triple charged Bismuth ion. They are highly polarizable and cations may exist in the glass network in $[\text{BiO}_3]$ pyramidal units in the presence of conventional glass forming cations like Boron. The shift of the 1380 cm$^{-1}$ absorption band in the IR spectra to lower frequencies with increasing bismuth oxide shows the perturbation of the B-O-B linkage by the Bismuth ion by increasing the interaction of the network oxygen with Bismuth [45]. Bi$_2$O$_3$ does not form glass by itself. The melt becomes transparent at 850 °C, but on cooling it fully crystallizes [46]. Heynes [44] has observed that if Bi$_2$O$_3$ is melted in silica crucible, it can dissolve enough silica to form a stable glass, therefore it can be assumed that in this case it behaves as a network former. However, bismuth oxide forms glasses with known glass formers as SiO$_2$, B$_2$O$_3$, P$_2$O$_5$, GeO$_2$, but not with TiO$_2$ or TaO$_2$.

Preparation

Bismuth borate glasses with different Bi$_2$O$_3$/B$_2$O$_3$ ratios ($x\text{Bi}_2\text{O}_3(1-x)\text{B}_2\text{O}_3$, where 0.25 $\leq x \leq$ 0.65) were fabricated from oxide melts with the respective compositions. The melts were thoroughly homogenized at a temperature of 700-800 K and then cooled down to room temperature at a rate of 100 K per hour. It is important to pre-react the mixed powders in solid state to avoid the separation of the melting components and the deposition of Bi$_2$O$_3$ at the bottom of the
crucible, due to the high viscosity and great difference of the densities of the components. The evaporation of $\text{B}_2\text{O}_3$ near the surface could cause the formation of bismuth rich phases.

### 4.3 Crystallization of Bismuth Borate Glasses

Most of the crystals in the $\text{Bi}_2\text{O}_3$-$\text{B}_2\text{O}_3$ system are congruently melting, at the respective stoichiometric composition, therefore they can be grown from stoichiometric melts. Borate glassy melts are characterized by high viscosity and a steep negative slope of its temperature dependence [47]. Therefore, it is expected that the rate of nucleation and crystal growth processes to be very small. As discussed in Section 2.2, the reduced glass transition temperature $T_{gr} = T_g/T_m$, can give us an indication about the glass ability to nucleate homogeneously or heterogeneously.

In 2004, Becker et al. [48] have determined experimentally the glass transition temperature, $T_g$, liquidus temperature $T_{liq}$, and the crystallization onset, $T_x$, for bismuth borate glasses. This values are plotted in Fig. 4.4. The variation of the reduced glass transition temperature with bismuth oxide content in the glass is also shown. The high values of $T_{gr} > 0.72$, indicate that only heterogeneously nucleation (on surfaces or nucleating agents) will take place in these glasses.

Figure 4.4: Left: Glass transition temperature, $T_g$, liquidus temperature, $T_{liq}$, and crystallization onset, $T_x$, for bismuth borate glasses [48]. Right: Reduced glass transition temperature ($T_{gr} = T_g/T_{liq}$) variation with bismuth borate glass composition calculated using data from [48].

This condition for nucleation was proposed after extended studies performed on silicates, but not for the special case of borates. Therefore, it is interesting to study the nucleation and crystalliza-
4.3. CRYSTALLIZATION OF BISMUTH BORATE GLASSES

ion behavior of bismuth borate glasses and the influence of nucleation agents.

In order to obtain microcrystals in the glass matrix, two approaches were used. For the first, described in the Section 2.3, a two stage heat treatment was employed. The second method uses the spontaneous nucleation in some melts, followed by rapid cooling and freezing of the grown crystals.

The glasses, prepared as described before, were polished. This provide a clean and defect-free surface that lowers the influence of heterogeneous nucleation at the surfaces. During heating stage, samples transparency is checked under an optical microscope, therefore only micrometer-size crystals could be observed. The crystallized phase is determined by powder diffraction.

In order to compare the crystallized samples with the parent glass, X-ray diffraction spectra were performed. Due to the disordered structure, the X-ray diffraction pattern of the glass consists of a few broad diffuse haloes. Fig. 4.5 shows the spectra of prepared glasses.

![Figure 4.5: Diffraction patterns of glasses $x\text{Bi}_2\text{O}_3(1-x)\text{B}_2\text{O}_3$, where $0.25 \leq x \leq 0.65$.](image-url)

The powder diffraction patterns of crystallized samples exhibit sharp peaks. The crystallized glasses for compositions $x = 0.25$ and $x = 0.45 - 0.55$ will be presented in the next section. At $x = 0.35$, $\text{Bi}_3\text{B}_5\text{O}_{12}$ crystals are formed by surface nucleation (see Fig. 4.6). The highest bismuth content melt of bismuth borate glasses, exhibit a strong tendency to crystallization. Even in this
case, the glass nucleation is initiated at the surface and the Bi$_4$B$_2$O$_9$ crystallites are obtained (see Fig. 4.6).

The main part of the study was focused on BiB$_3$O$_6$ and BiBO$_3$(II) phases of the bismuth borate system.

### 4.3.1 BiB$_3$O$_6$ Glass-Ceramics

As presented in the previous section, crystalline BiB$_3$O$_6$ has strong nonlinearities and is therefore suitable for various applications in nonlinear optics. The $x = 0.25$ glass undergoes a phase separation and crystallizes in the BiB$_3$O$_6$ neighbor phases, but adding 1000 ppm Chromium forces the growth of bismuth triborate. The X-ray diffraction patterns are plotted in Fig. 4.7.

Different heat schedules were performed, but in all cases, the nucleation appears on few sites at the surface. These nuclei grow fast until the sample fully crystallizes. Therefore we used various methods to increase the number of nucleating centers.

One of this methods consists on seeding the glass with polycrystalline BiB$_3$O$_6$. A fine grounded mixture of BiB$_3$O$_6$ crystals and glass ($x = 0.25$) melted at 900$^\circ$C, forms an obtained transparent and homogeneous glass. After a two step heat treatment ($T_1 = 430^\circ$C, $t_1 = 72$ h, $T_2 = 640^\circ$C, $t_2 = 10$ min) small monoclinic-like crystals appear on the surface. Their shape, presented in Fig. 4.8 is similar with that of the BiB$_3$O$_6$ crystals (see Fig. 4.2). In contrast to non seeded samples, where the nucleation appears from 2-3 centers on the surface, the number of nuclei is larger and
4.3. CRYSTALLIZATION OF BISMUTH BORATE GLASSES

Figure 4.7: Left: Glass with \( x = 0.25 \), Bi\(_2\)O\(_3\) crystallizes in the phases Bi\(_3\)B\(_5\)O\(_{12}\) (blue squares) and Bi\(_2\)B\(_8\)O\(_{15}\) (yellow triangles). Right: BiB\(_3\)O\(_6\) crystals are obtained for glass \( x = 0.25 \) Bi\(_2\)O\(_3\) doped with 1000 ppm Cr\(^{3+}\).

In order to induce bulk nucleation, TiO\(_2\) and ZrO\(_2\) were added to the melt. It was observed that 1 mol\% ZrO\(_2\) is not soluble in the bismuth borate melt and precipitates at the bottom of the crucible. Low concentration, 1 mol\% TiO\(_2\) has no influence on the recrystallization process. The

Figure 4.8: Surface crystallized BiB\(_3\)O\(_6\) crystals.
glass containing high TiO$_2$ content (10 mol%) recrystallizes as a mixture of Bi$_3$B$_5$O$_{12}$ and an unknown phase. The Fig. 4.9 shows the X-ray pattern of this phases.

Lithium tetraborate was used to produce more non-bridging oxygens and also to promote the phase separation in a BiB$_3$O$_6$ rich-phase and a Li$_2$B$_4$O$_7$ phase. The mixture melted at 800 °C on cooling became a transparent glass. After heating at 600 °C surface crystallization occurs. The main phase is Bi$_3$B$_5$O$_{12}$.

![X-ray pattern of Bi$_3$B$_5$O$_{12}$ phase](image)

Figure 4.9: BiB$_3$O$_6$ glass containing 10 mol % TiO$_2$ (left) and 20 mol % Li$_2$B$_4$O$_7$ (right). The crystallized phase is Bi$_3$B$_5$O$_{12}$.

### 4.3.2 BiBO$_3$ (II) Microcrystals

For glasses with compositions varying from $x = 0.45 - 0.55$, three phases exists: the stable Bi$_4$B$_2$O$_9$, a high temperature metastable BiBO$_3$ (I) and a low temperature metastable BiBO$_3$ (II). The first two were obtained as single-crystals and some properties were investigated [35, 36].

Recently, Becker et al. [36] have obtained single-crystals of the high temperature metastable bismuth orthoborate BiBO$_3$ (I). The micrometer sized crystals were grown by heating the glass with $x = 0.5$ composition at 450°C for 48 h. After the first 24 h of this schedule they obtained the BiBO$_3$ (II) phase; this transforms during an additional heating period into BiBO$_3$ (I). They noted that this transformation can take place at room temperature too.
4.3. CRYSTALLIZATION OF BISMUTH BORATE GLASSES

4.3.2.1 BiBO$_3$ (II) Preparation

The Fig. 4.10 shows the X-ray diffraction spectrum of crystallized glasses with $x = 45$ and $x = 55$ compositions. The BiBO$_3$ (II) phase occurs in both cases.

![X-ray diffraction spectrum](image)

Figure 4.10: Left: Glasses $x = 0.45$ Bi$_2$O$_3$ crystallize as BiBO$_3$(II). Right: Glasses $x = 0.55$ Bi$_2$O$_3$ crystallize Bi$_4$B$_2$O$_9$ (triangles) and BiBO$_3$ (dots).

The glasses subjected to heat treatment crystallize always on the surface. The image from cross-polarized (used to enhance the image contrast) microscope of surface crystallized BiBO$_3$ (II) is presented in Fig. 4.11. The different sized grains can be observed.

![Microscope image](image)

Figure 4.11: Left: BiBO$_3$ (II) obtained by surface crystallized glasses $x = 0.5$. Right: BiBO$_3$ (II) powder diffraction pattern. The dot stems represents the BiBO$_3$ (II) spectrum from PDF Nr.27-0320.
CHAPTER 4. STRUCTURE AND PROPERTIES OF THE BISMUTH BORATE SYSTEM

Adding nucleation agents as 1\%mol TiO\textsubscript{2} or ZrO\textsubscript{2} the number of surface nucleating sites increases. The same effect has been observed for doped samples with Er\textsuperscript{3+}, Nd\textsuperscript{3+} and Cr\textsuperscript{3+}. The later case is presented in Section 5.2.4.

The BiBO\textsubscript{3} (II) microcrystalline powder was obtained heating a glass with $x = 0.5$ for 24 h at 400 °C. The X-ray diffraction spectra of the obtained powder is presented in Fig. 4.11. It is similar the with the BiBO\textsubscript{3} (II) spectrum (PDF Nr.27-0320). This powders are used in the SHG measurements described in Section 4.3.2.3.

A fine grained ceramic was also prepared by pouring the melt at 600 °C on a steel plate. In all cases, the BiBO\textsubscript{3} (II) phase is stable and exhibit a strong second order harmonic intensity.

4.3.2.2 BiBO\textsubscript{3} (II) Structure Determination

The Werner trial-and-error indexing algorithm (based on a permutation of Miller indices for base lines) was used for the identification of cell parameters of BiBO\textsubscript{3} (II) crystals.

Method

In the powder spectrum only the information of interplanar spacings and no information on the angles between crystal planes are present. Therefore, indexing is in principle a trial-and-error procedure and the correctness of the unit cell found is based on the exact match of the calculated and observed peak positions.

The underlying physical principle of indexing is the reconstruction of the 3-dimensional reciprocal lattice from the radial distribution of the lengths $d$ of reciprocal-lattice vectors. The basic relation used for indexing a powder diffraction pattern is obtained by squaring the $d$ vector [49]

$$Q(hkl) = d^2 = h^2A + k^2B + l^2C + 2klD + 2hlE + 2hkF$$  \hspace{1cm} (4.1)

where $A = \mathbf{a} \cdot \mathbf{a}$, $B = \mathbf{b} \cdot \mathbf{b}$, $C = \mathbf{c} \cdot \mathbf{c}$, $D = \mathbf{b} \cdot \mathbf{c}$, $E = \mathbf{c} \cdot \mathbf{a}$ and $F = \mathbf{a} \cdot \mathbf{b}$. The vectors defining the reciprocal unit-cell are $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ and $hkl$ the Miller indices.

This equation cannot be solved by ordinary algebra because the number of unknown variables is always greater than those known. Moreover, the solution strongly depends on the precision and completeness of data.
It has been shown that the interdependence of these features and the reliability of a solution can be evaluated by a figure of merit which takes into account the average discrepancies between $Q_{\text{obs}}$ and $Q_{\text{cal}}$, $<\Delta Q>$, or the average angular discrepancy, $<\Delta(2\theta)>$, and the size of the unit cell, through the number of calculated lines $N_{\text{cal}}$ up to the $N^{th}$ observed line. The most widely used criterion for indexing is the de Wolff figure of merit defined as

$$M_N = \frac{Q_N}{2 <\Delta Q> N_{\text{cal}}} \quad (4.2)$$

The determination of the space group is based on the extinction rules for reflections. A major problem is an extensive overlap of reflection positions at higher diffraction angles, which prevents finding out which reflections are absent.

**Results**

The maximum figure of merit value, $FOM = 12.5$, was obtained for a monoclinic structure with cell parameters $a = 7.696 \text{ Å}$, $b = 9.950 \text{ Å}$, $c = 7.033 \text{ Å}$, $\beta = 117.47^\circ$ and the volume $V = 477.8 \text{ Å}^3$. Applying a refinement procedure, the maximum FOM is 24.8 for the space group C2. In this case the Durbin-Watson serial correlation is 2.039.

### 4.3.2.3 BiBO$_3$ (II) SHG Powder Measurements

**Experimental Setup**

The experimental setup, drawn in Fig. 4.12 used to measure the powder SHG signal is similar to that used by S. K. Kurtz [25]. The IR beam of an pulsed YAG:Nd laser excites the second harmonic in the powder sample (S), placed in the center of a Ulbricht sphere (US). The scattered second harmonic light is focused, with a high aperture lens (L), on a photomultiplier. The incident laser beam is removed by the filter (F) placed in front of the detector. The SHG signal is measured by an oscilloscope. The data are collected via the serial interface by a computer.

The powder samples were separated into particle size fractions using sieves of different mesh size.
Results

The BiBO₃ microcrystals illuminated by an YAG:Nd infrared laser, exhibit a strong second harmonic signal. Due to the small size of the crystals, the SHG powder measurement is the most suitable method to estimate the directionally averaged nonlinear coefficients $<d_{ijk}>$. Using the relation 3.23 and quartz as reference, the value of the $<d_{ijk}> \approx 3.85 \pm 0.5$ pm/V is obtained.

The powder SHG intensity variation with particle size, plotted in Fig. 4.12, proves that this crystal is phase matchable for a fundamental wavelength of 1064 nm.
Chapter 5

Optical Properties of Bismuth Borate Glasses

5.1 Optical Properties of Pure Bismuth Borate Glasses

5.1.1 Refractive Index

Refractive indices of bismuth borate glasses were first reported in 1962, but only for one wavelength by oil immersion \[45\] and recently for compositions \(0.20 \leq x \leq 0.42\) \[48\] (\(x\) as defined in the preceding chapter).

Our measurements of the refractive indices cover the whole composition range, they were carried out on a high resolution goniometer using the prism method with an accuracy of \(\pm 0.002\). In the near UV and the visible spectral region, a HgCd lamp with spectral lines in the range 404.7 - 643.8 nm was used. In the infrared two laser diodes at 790 nm and \(\sim\)1500 nm and an infrared camera for detection were used. The samples were cut in prism form, the surfaces polished for optical quality. The angles of the prisms were determined using the autocollimation method. From the minimum deflection angles \(\varphi\) for the discrete spectral lines of the light sources, the refractive indices are calculated according to:

\[
n = n_{\text{air}} \frac{\sin(\gamma/2 + \varphi/2)}{\sin(\gamma/2)} .
\]

In this equation \(\gamma\) denotes the prism angle (\(\approx 35^\circ\)), the refractive index of air \(n_{\text{air}}\) is calculated
using Edlén’s approximation \[50\]

\[
n_{\text{air}} - 1 = 10^{-8} \left[ 6432.8 + \frac{2949810}{146 - \lambda^{-2}} + \frac{25540}{41 - \lambda^{-2}} \right] . \tag{5.2}
\]

Figure 5.1: Refractive index of glass bismuth borate BiB\(_3\)O\(_6\). Squares indicate measured data, the thick line is a Sellmeier approximation to the data. Thin lines represent the refractive indices of crystalline BiB\(_3\)O\(_6\) (dashed: average of the three crystal indices).

Fig. 5.1 shows a typical measurement for a composition where also crystalline Bismuth borate exists \((x = 0.25)\). Except that the steep ultraviolet increase is shifted to longer wavelengths, the refractive index of the glassy material is nearly identical to the average index of the crystalline one. This average was derived using the data given in Ref. [31]. Unfortunately, a comparison to the index data calculated by Lin et al. \[38\] is hardly possible, as these authors based their calculations on the crystal coordinate system instead of the optical one.

The measured values can be described by a Sellmeier dispersion relation:

\[
n^2(\lambda) = A + \frac{B}{\lambda^2 - C} - D\lambda^2 \tag{5.3}
\]

where \( A = 3.2141, \ B = 0.0456, \ C = 0.0349, \ D = 0.0235 \).

The high refractive index makes the glass suitable for applications where a glass material exhibiting an index of approximately 1.85 is needed. Measurements of the dispersion for different compositions \(xBi_2O_3(1-x)B_2O_3\), where \(0.25 \leq x \leq 0.65\), show that the refractive indices increase with increasing Bismuth content (Fig. 5.2).
5.1. OPTICAL PROPERTIES OF PURE BISMUTH BORATE GLASSES

Figure 5.2: Refractive index for various compositions. Dots indicate measured data for various compositions, lines are Sellmeier approximation to the data.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_0$</td>
<td>1.90598</td>
</tr>
<tr>
<td>$A_1$</td>
<td>5.78900</td>
</tr>
<tr>
<td>$A_2$</td>
<td>-2.22010</td>
</tr>
<tr>
<td>$B_1$</td>
<td>0.16995</td>
</tr>
<tr>
<td>$C_0$</td>
<td>0.02116</td>
</tr>
<tr>
<td>$C_1$</td>
<td>0.09230</td>
</tr>
<tr>
<td>$D_0$</td>
<td>0.01857</td>
</tr>
</tbody>
</table>

Table 5.1: Values for the Sellmeier coefficients in Eq. 5.4.

A Sellmeier fit covering the full composition range can be obtained with the following function:

$$n^2(\lambda, x) = A_0 + A_1 \cdot x + A_2 \cdot x^2 + \frac{B_1 \cdot x}{\lambda^2 - C_0 - C_1 \cdot x} - D_0 \cdot \lambda^2.$$  (5.4)

The coefficients are presented in Table 5.1. The measured data and the fit function are shown in Fig. 5.2.
5.1.2 UV-VIS and near IR Absorption

For absorption measurements, a Bruins Omega 10 spectrometer working in the near ultraviolet, visible, and near infrared spectral region was employed. A broadband lamp is typically used as the light source. The incident beam, after passing through a grating monochromator, is directed into the sample and the reference channels by a switchable mirror. The sample absorbs, scatters, transmits, and/or reflects portions of the light, and the intensity of the light emerging from the sample is measured by a detector. The ratio of the final light intensity to the initial light intensity is the transmittance of the sample for that particular wavelength. For a homogeneous and transparent sample, without scattering centers and after reflection corrections, it is assumed that the measured reduction of transmitted light is due to absorption.

Figure 5.3: Optical absorption of bismuth borate glasses with Bi$_2$O$_3$ content of 0.25, 0.35, 0.55, 0.65 (left to right). The inset shows the position of the short wavelength absorption edge ($\alpha=10$) as a function of the Bi$_2$O$_3$ content and the position of the ultraviolet oscillator as defined by the generalized Sellmeier relation.

The attenuation of a beam of intensity $I_0(\nu)$ by a sample of thickness $d$ is given by Lambert-Beer’s law:

$$I(\nu) = I_0(\nu) \cdot \exp(-\alpha(\nu) \cdot d)$$  \hspace{1cm} (5.5)
where $I(\nu)$ - intensity of transmitted light and $\alpha(\nu)$ is the absorption coefficient. The values of absorption coefficients, corrected for multiple reflections at normal incidence using the measured refractive indices are given by:

$$\alpha = -\frac{1}{d} \ln \left( -g + \sqrt{g^2 + \frac{1}{R^2}} \right)$$ (5.6)

where

$$g = \frac{(1 - R)^2}{2TR^2}$$ (5.7)

and $\alpha$ is the absorption coefficient, $d$ the thickness of the sample along the light propagation direction, $T = I/I_o$ the transmission, $R = (n - 1)^2/(n + 1)^2$ with $n$ denoting the refractive index.

Fig. 5.3 shows the absorption spectrum of bismuth borate glass for various compositions. Compared to crystals [31], the absorption edge is slightly shifted towards longer wavelengths. This feature is typical for amorphous materials, where a broadened random distribution of gap energies must be assumed. A similar strong dependence on the Bi$_2$O$_3$ content as for the refractive index is found for the position of the short wavelength absorption edge of the glasses. Increasing the Bi$_2$O$_3$ content the short wavelength absorption edge shifts to longer wavelengths. For an absorption coefficient of $\alpha = 16$, a linear fit of this shift yields

$$\lambda_{\alpha=16} = 0.316 + 0.187 \cdot x \ (\lambda \ \text{in} \ \mu\text{m})$$ (5.8)

This can be compared with the position of the ultraviolet oscillator defined in the Sellmeier equation 5.4

$$\lambda_{0,UV} = (C_0 + C_1 \cdot x)^{1/2}$$ (5.9)

which is the line plotted in the inset for $n \longrightarrow \infty$. A linear fit of the ultraviolet oscillator position yields

$$\lambda_{0,UV} = 0.165 + 0.186 \cdot x \ (\lambda \ \text{in} \ \mu\text{m})$$ (5.10)

i.e. the identical slope as in Eq. 5.8. This shows that the linear optical properties of bismuth borate glasses in the short wavelength region can be assumed to be predominantly governed by one oscillator in the UV which is strongly connected to the the bismuth oxide content.
5.2 Chromium Doped Bismuth Borate Glasses

5.2.1 Introduction

Transition metal ions have incomplete $3d^n$ ($n < 10$) shells and have a number of low lying energy levels between which optical transitions may occur. Since the optically active $3d$ electrons are outside the ion core, they interact strongly with the electric fields of neighborhood ions. Therefore transitional metals can be used as spectroscopic probes of the effect of spatial confinement in crystals connected with the modification of their environment. The transition metal ion can modify its immediate surrounding arranging a coordination polyhedron, presumably of non-bridging oxygens, around itself (metal-ligand complex). Anions or oriented dipoles known as ligands surround the dopant cation, which together form a complex. These complexes could be either tetrahedral or octahedral depending on the bonding requirements of the particular transition metal ion. The absorption spectra of these elements may be explained in terms of ligand field theory. The ligand fields cause degenerate energy levels in the outer $d$ shell to split; consequently, an electron may be excited between two outer $d$ energy levels. This excitation requires energy from the visible spectrum, therefore, the selective absorption of incoming visible light produces the appearance of color in the glass.

In most glasses, Cr$^{3+}$ ions occupy sites which have nearly octahedral symmetry because of the strong ligand-field stabilization energy of Cr$^{3+}$ in a sixfold coordination. The $3d$ electrons are on the outside of the ion and are very sensitive to the effects of the crystalline environment. The energy level diagram of the $3d^3$ electronic configuration in an octahedral field is plotted in Fig. 5.4.

The ground energy level of free Cr$^{3+}$ ions is $^4F$ and the excited levels are $^4P, ^2G, ^2F$ etc. In octahedral crystal fields the energy levels of Cr$^{3+}$ split into ground level $^4A_2$ and excited levels $^2E, ^2T_1, ^2T_2, ^4T_2, ^4T_1, ^2A_1$ (the new crystal field levels are classified by irreducible representations of the $O_h$ group). The excited levels could exchange their position depending on the strength of the crystal fields.

The absorption and emission of Cr$^{3+}$ arises from the parity forbidden electronic transitions in the $3d$ electronic shell. The relative positions of the excited $^4T_2$ and $^2E$ states depend on the crystal-field strength (see Fig. 5.4). For $Dq/B < 2.3$ (low-field case), $^4T_2$ is the lowest excited state and the emission arises from the $^4T_2 \rightarrow ^4A_2$ spin-allowed transition. These $^4T_2 \rightarrow ^4A_2$ broad absorption and emission bands are of interest for applications in lasers and solar concen-
5.2. CHROMIUM DOPED BISMUTH BORATE GLASSES

Figure 5.4: Tanabe Sugano diagram for Cr\textsuperscript{3+} ions in octahedral crystal fields. Values of \( E/B \) are plotted as a function of \( Dq/B \) with \( C/B = 4.5 \). [51]

For \( Dq/B > 2.3 \) (high-field case), emission spectrum takes the form of a narrow band, the so-called R-line (well-known in ruby lasers), corresponding to \( \text{^2E} \rightarrow \text{^4A}_2 \) transition. For intermediate values of crystal field \( Dq/B \approx 2.3 \), a mixture of these two transition are observed.

5.2.2 Absorption of Cr\textsuperscript{3+} in Bismuth Borate Glasses

The typical absorption spectra of Cr\textsuperscript{3+} consist of several broad spin-allowed absorption bands due to transitions like \( \text{^4A}_2 \rightarrow \text{^4T}_2, \text{^4T}_1 \) and a series of sharp lines due to the spin forbidden transitions \( \text{^4A}_2 \rightarrow \text{^2E}, \text{^2T}_1 \). The peak position of the broad bands depend on crystal field, but that of sharp lines do not, because the energy levels \( \text{^2E} \) and \( \text{^2T}_1 \) do not depend much on the crystal field.

As compared with the absorption spectra of pure bismuth borate glass, chromium ions shifts the onset of the absorption edge to longer wavelengths and an absorption shoulder around 0.623 µm appears. The effect of adding chromium oxide to glass, for different glass composition \((x = 0.25\)
Figure 5.5: Absorption in the blue and red spectral region of bismuth borate glass with Cr$^{3+}$ doping for 0.25 Bi$_2$O$_3$ (left) and 0.5 Bi$_2$O$_3$ (right).

and $x = 0.5$ Bi$_2$O$_3$) is shown in Fig. 5.5. The absorption spectrum shows two broad bands due to the spin-allowed but parity-forbidden transitions from the $^4A_2$ ground state to the $^4T_2$ ($\approx 0.623 \mu$m) and to the$^4T_1$ ($\approx 0.390 \mu$m) excited states. The widths of these bands imply strong electronic coupling to vibrations of the local environment. The dip in the absorption spectrum at around 0.700 $\mu$m is the so-called Fano antiresonance, between the $^4T_2$ band and $^2E_2$ and $^4T_1$ levels (this appears when a broad band and a narrow band are superimposed in the same energy region). Since this spin and parity forbidden transitions are only weakly coupled to the vibrational spectrum they appear as narrow lines superimposed on the $^4T_2$ band.

The knowledge of local order and detailed structural information on the neighboring atoms of impurity ions in borate glasses leads to a better understanding of absorption and luminescence mechanisms. The Racah parameters $B$, $C$ describing the electron-electron interaction and the ligand field intensity $Dq$ for a transition element ion as Cr$^{3+}$ are found to be useful parameters, sensitive to the nature of local symmetry and distortions. The experimental energies of the absorption bands may be used to determine the strength $Dq$ of the octahedral crystal field and the Racah parameters [51]:

$$Dq = \frac{E(^4T_2) - E(^4A_2)}{10}.$$  \hspace{1cm} (5.11)

The value of the Racah $B$ parameter can be estimated from the position of the two lowest lying absorption bands:
5.2. CHROMIUM DOPED BISMUTH BORATE GLASSES

\[
\frac{Dq}{B} = \frac{15(x - 8)}{x^2 - 10x}\tag{5.12}
\]

where

\[
x = \frac{E(4A_2 \rightarrow 4T_1) - E(4A_2 \rightarrow 4T_2)}{Dq}\tag{5.13}
\]

\[
\frac{C}{B} = \frac{1}{3.05} \cdot \left[ \frac{E}{B} - 7.9 + 1.8 \cdot \left( \frac{B}{Dq} \right) \right].\tag{5.14}
\]

Because of the disorder due to the glass structure the values of Racah parameters represent an average over the distribution of sites occupied by the Cr$^{3+}$ ions in the glass. The calculated $Dq/B$ value, for 0.25 Bi$_2$O$_3$ glasses, is 2.4.

5.2.3 Luminescence of Chromium in Bismuth Borate Glass

The $Dq/B$ value of 2.4, as calculated in previous section, shows that these glasses provide intermediate-field sites for Cr$^{3+}$ ions in which the effect of admixing $^2E$ and $^4T_2$ energy levels results in a luminescence spectrum consisting of sharp R-line at 0.710 μm ($^2E \rightarrow ^4A_2$) and a broad band, centered around 0.850 μm ($^4T_2 \rightarrow ^4A_2$).

Experimental setup

The experimental setup used for luminescence measurements is drawn in Fig. 5.6. The second harmonic of a YAG-Nd laser at $\lambda = 0.532$ μm was used to excite the Chromium emission in the glass sample (S). A part of the incident light is directed by a beam splitter (BS) to a fast photodiode (PD) and the main part of the beam directed into the sample. The luminescence light is focused using a $f = 70$ mm lens to the entrance slit of a TRIAX monochromator and detected by a photomultiplicator with extended sensitivity range in infrared region (Hamamatsu R636-10). The cutoff filter (F) was used to isolate the scattered light from the pump source. The photomultiplier signal is recorded by a MSA-200 photon counter card, which is triggered from the photodiode output. The monochromator is controlled remotely by a computer via the serial port. A program was written in Visual C to combine the data acquisition with the selection of the wavelength where the measurement is performed.
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Results

In Fig. 5.7 the steady state photoluminescence spectra for 0.25 Bi$_2$O$_3$ content glasses and different Cr$^{3+}$ concentration (1000 ppm and 3000 ppm) are plotted. The luminescence output is expressed in arbitrary units due to the difficulty in calibrating the detection system accurately.

Time-resolved luminescence spectrum of 1000 ppm in 0.25 Bi$_2$O$_3$ borate glass recorded immediately after laser excitation and 40 µs and 80 µs later, shows the slower decay of the $^2E$ level. This opens also the possibility to study separately the temporal behavior of the two emission bands.

The decay curves for the R-line and the broadband emission are plotted in Fig. 5.8 on a logarithmic scale, for various glass compositions and doping concentration.

Discussion

The steady-state luminescence spectra of Cr$^{3+}$ doped bismuth borate glasses exhibits a high intensity of the R-line emission relative to the broad band. The high value of $R = I(^2E)/I(^4T_2)$ indicates a tightly packed oxygen network for bismuth borate glasses.

Henderson et al. [52] have studied the role on the anion packing densities in glasses and have observed that this increases along the series of fluorides $\rightarrow$ silicates $\rightarrow$ borates. In the same time,
5.2. CHROMIUM DOPED BISMUTH BORATE GLASSES

Figure 5.7: Left: Steady-state luminescence spectra of 0.25 Bi$_2$O$_3$ borate glasses with 1000 ppm and 3000 ppm Cr$^{3+}$ doping. Right: Time-resolved luminescence of 1000 ppm in 0.25 Bi$_2$O$_3$ borate glass immediately after laser excitation and 40 $\mu$s and 80 $\mu$s later.

Figure 5.8: Left: Luminescence decay curves for 1000 ppm and 3000 ppm Cr$^{3+}$ doped 0.25 Bi$_2$O$_3$ borate glass, plotted on a logarithmic scale. Right: Luminescence decay curves for 1000 ppm Cr$^{3+}$ doped 0.5 Bi$_2$O$_3$ borate glass plotted on a logarithmic scale.

a larger modifier ions, as Bi$^{3+}$, results in a more open structure glasses, lowering the oxygen packaging density and increasing the the predominance of low-filed sites. The high value of $R$ indicates a stronger boron influence in the bismuth borate matrix and a tight packing oxygen network.

At higher doping concentration, the intensity of the emission due to the R-line relative to the intensity of the broad band is lower. The R-line emission, at 0.710 $\mu$m is superposed on the broad absorption band, centered at 0.632 $\mu$m, therefore is stronger reabsorbed than the emission
coming from the broad band (see the absorption spectrum in Fig. 5.5).

The time-resolved emission spectrum given in Fig. 5.7 shows that as the delay time increases the intensity of the broadband, associated with low field sites decreases and is almost zero for a delay of 80 µs.

The decay measurements (Fig. 5.8) confirms the larger decay time of the R-line (compared with the broadband decay). The emission at 0.850 µm has a rapid decay because the radiationless processes have a high probability.

For 0.25 Bi₂O₃ doped with 1000 ppm Cr³⁺, the second part of the ⁴T₂ curve shows the same decay rate as the ²E. This suggest energy transfer from the ²E level to the ⁴T₂. After 2 µs this level is still emitting because it is populated by the ²E level. Increasing the doping concentration to 3000 ppm, the R-line has almost the same decay rate, but the broadband decrease sharply.

For glasses with higher bismuth concentration the decay of the R-line deviates from an exponential behavior. The non-exponential decay curves indicate a multi-site occupancy by Cr³⁺ ions and/or interaction between the optical centers.

If we assume an exponential decay, \( I = I₀ \cdot exp(-t/τ) \), the inverse of the slope of curves in Fig. 5.8 represents an estimation of the decay time \( τ \). The glass with 0.25 Bi₂O₃ content and 3000 ppm chromium doping, values are for ²E \( \rightarrow \) ⁴A₂ transition \( τ₁ ≈ 5µs \) and \( τ₂ ≈ 0.4 \mu s \) for the broadband transition ⁴T₂ \( \rightarrow \) ⁴A₂.

### 5.2.4 Luminescence of Chromium in Crystallized Glass

The variable environment of an amorphous material makes transition metal ions inefficient as luminescent ions in glasses, as non radiative processes are favored. But in crystalline hosts this ions are well known as optically active dopants for broadband lasers, like for example Ti³⁺ doped Al₂O₃ or Cr⁴⁺ doped Y₃Al₅O₁₃ or as saturable absorbers. Glass-ceramics can combine the advantages of glass (easy of fabrication in fiber forme) and crystals (high luminescence efficiency). Cr³⁺ has potential use in tunable lasers and solar concentrators.

The transition metal ions act at the same time as efficient nucleating agents and as structural fluorescent probes. It was reported that in Ni doped silica based glasses absorption spectra are shifted to shorter wavelength after heating, because the Ni ions environment changes from a low field site (glass) to a high field one [2].
Small quantities of transition metal ions can strongly influence the nucleation process, and the nanoscale size restriction may enhance the homogeneous line broadening of the optical transitions. The local environment around the optically active ion can be very different depending on the glass composition, the nucleating agent, the method used to induce nucleation and the size of the crystallites. Different sites are available for the luminescent ion in a glassy ceramic: the sites of the glassy phase, the sites inside the nanocrystallites, the sites at the crystal-glass interface. The spectral characteristics of the luminescent ions (especially in the case of transition metal ions) are strongly dependent on the local environment.

Results
After a heat treatment was applied to the Chromium doped bismuth borate glasses only surface crystallization was observed. As compared with undoped samples, the nucleation centers increase. For the glass with 0.25 Bi₂O₃, the surface got opaque as crystals had grown to micrometer size. For the 0.5 Bi₂O₃ glass the surface became red, but no changes on measured absorption spectra could be observed, maybe due to the small fraction of crystallized material. The crystals grown on the surface are presented in Fig. 5.9.

Figure 5.9: Surface crystallized 0.50 Bi₂O₃ borate glass doped with 10000 ppm chromium.

To investigate the crystallites in the 0.5 Bi₂O₃ containing glass, we used a confocal microscope, Leica TCS SL. It could be shown that the crystallites exhibit photoluminescence in the
orange spectral region under laser excitation ($\lambda = 488$ nm). The emission spectrum plotted in the Fig. 5.10 shows a maximum intensity at 0.520 $\mu$m.

![Figure 5.10: Confocal image (left) of photoluminescence in a Cr$^{3+}$ doped crystallized glass for 0.50 Bi$_2$O$_3$ content and the corresponding photoluminescence spectrum (right).](image)

**Discussion**

Following the crystallization process, it is expected that the chromium ions will occupy the high field sites and the emission spectra will consist only of the R-line. Because this emission occurs at 0.690 $\mu$m, it cannot explain the spectra with a maximum emission 0.520 $\mu$m. Furthermore, the bismuth ions have no emission bands in visible. The emission could be attributed to a change in the oxidation state of the chromium ions after crystallization.

Chromium ions can exist in more than one oxidation state Cr$^{n+}$ ($n = 2-6$). The tetravalent ion has emission only in infrared region and the hexavalent at 0.714 $\mu$m. The Cr$^{5+}$ in six-fold coordination is observed in the luminescence spectra of sol-gel silicate glasses at 0.655 $\mu$m after 0.457 $\mu$m wavelength excitation [53]. The chromate ion, CrO$_4^{2-}$ (VI) exhibit broad emission around 0.500 $\mu$m. Therefore it can be assumed that the emission of chromium ions in the crystallized samples is due to the change of the chromium oxidation state from (III) to (VI).

The 3D image gained by the confocal microscope indicates a monoclinic structure of the BiBO$_3$
5.3 Rare Earth Absorption and Luminescence

5.3.1 Introduction

Paramagnetic ions - depending upon size and valence state - enter a glass as a network modifier cation (in the case of rare earth ions) or substitutionarily for a network forming cation. Due to the shielding provided by the outer closed shells of \(5p\) and \(5s\) electrons, the \(4f^N\) electronic states exhibit a strong atomic character that makes them of particular interest for both fundamental research and optical applications. The electric dipole transitions between two states of \(4f^N\) configuration of rare earth ions, which are forbidden for free ions, become allowed in the crystal field by mixing into the \(4f^N\) configuration another configuration \(4f^{N-1}5d^1\) having opposite parity. The matrix elements of the electric dipole operator are calculated by considering the crystal field as a first-order perturbation.

The magnitude of crystal field effects in rare earth ions is small due to the screening of the optically active levels. According to the Judd-Ofelt theory [54, 55], from the measurement of absorption, refractive index and density, the strength parameters \(\Omega_{2,4,6}\), which describe the effect of the crystal field of the glassy matrix around the doping ion, can be calculated. The probability of a radiative transition, emission or absorption, between the initial state \((S, L, J)\) and final level \((S', L', J')\) is proportional to the square of the matrix elements \(U\) of the appropriate operator \(p\) for electric dipole transitions and \(m\) for magnetic dipole transitions) and this quantity is called the strength of the transition. The line strength for the electric dipole, \(S^{ed}\) and magnetic dipole \(S^{md}\) transition are given by:

\[
S^{ed}[(S, L)J; (S', L')J'] = \sum_{t=2,4,6} \Omega_t |\langle (S, L)J || U^{(t)} || (S', L')J' \rangle|^2
\]

\[
S^{md}[(S, L)J; (S', L')J'] = \frac{1}{4m^2c^2} |\langle (S, L)J || L + 2S || (S', L')J' \rangle|^2
\]

where \(\Omega_t\) are the Judd-Ofelt parameters, \(J\) and \(J'\) represent the total angular momentum of initial and final states, \((S, L)\), \((S', L')\) define all other quantum numbers needed to specify the states.

The intensity of an absorption band is measured by its oscillator strength, which is directly proportional to the area under the absorption curve. The line strength for both electric and magnetic
dipole transitions are related to the integral absorbance [56]:

\[ \int \alpha_{\text{band}} d\lambda = \frac{8\pi^3 e^2}{3ch(2J + 1)n^2} \cdot (\chi_{\text{ed}} S_{\text{ed}}^a + \chi_{\text{md}} S_{\text{md}}^a) \]  

(5.17)

where \( c \) is speed of light, \( \alpha_{\text{band}} \) the absorption coefficient, \( \lambda \) the mean absorption wavelength, \( e \) electron charge, \( \rho \) erbium concentration, \( h \) Planck constant and \( (2J + 1) \) the multiplicity of the ground level. The effective field correction at the rare earth ion site in the glassy matrix is related to the refractive index by:

\[ \chi_{\text{el}} = \frac{n(n^2 + 2)^2}{9}, \]  

(5.18)

\[ \chi_{\text{md}} = n^3. \]  

(5.19)

Since the reduced matrix elements are constant characteristic to each transition, the three parameters can be obtained experimentally from the line strength of at least three absorption bands. The numerical values of the reduced matrix elements for Er\(^{3+}\) and Nd\(^{3+}\) ions have been calculated by Weber [57] and Carnall [58]. A least-square analysis is used to calculate the optimum set of the three parameters from the Eq. 5.17.

The spontaneous emission probability \( A(aJ, bJ') \) for the dipole-dipole transitions from an initial excited state \( aJ \) to a final state \( bJ' \) is calculated from:

\[ A(aJ, bJ') = \frac{64\pi^4 e^2}{3h(2J + 1)} \cdot \frac{n(n^2 + 2)^2}{9} \cdot S_{\text{ed}} \]  

(5.20)

where \( (2J + 1) \) is the multiplicity of the excited state. The total radiative emission probability is the sum of the \( A(aJ, bJ') \) terms calculated over all terminal states \( b \):

\[ A_T(aJ) = \sum_{bJ'} A(aJ, bJ') \]  

(5.21)

The fluorescence branching ratio:

\[ \beta_R = \frac{A(aJ, bJ')}{A_T(aJ)}. \]  

(5.22)

With the measured lifetime of an emission band \( \tau_f \) and the calculated radiative lifetime \( \tau_R = A_T^{-1}(aJ) \), from Eq. 5.20, the non radiative decay rate, \( W_{NR} = \tau_{NR}^{-1} \) and total quantum efficiency, \( \eta \), can be calculated by:
5.3. RARE EARTH ABSORPTION AND LUMINESCENCE

\[ W_{NR} = \tau_f^{-1} - A_T(aJ) \]  
(5.23)

\[ \eta = \tau_f A_T(aJ) \]  
(5.24)

The three intensity parameters \( \Omega_t \) are characteristic of a given rare earth ion in a given matrix and are related to the radial wavefunctions of the states \( 4f^N \), the admixing states \( 4f^{N-1}5d \) and the ligand field parameters that characterize the matrix. They are given by:

\[ \Omega_t = (2t + 1) \sum_{s,p} |A_{s,p}|^2 \Xi^2(s, t)(2s + 1)^{-1} \]  
(5.25)

where \( A_{s,p} \) are the crystal field parameters of rank \( s \) and are related to the structure of the host. \( \Xi(s, t) \) are related to the radial wavefunctions of \( 4f \) and admixing levels \( 5d \) and the energy difference between these two levels. It has been suggested that \( \Xi(s, t) \) is proportional to the nephelauxetic parameter \( \beta = \nu_c/\nu_a \), where the \( \nu_c \) and \( \nu_a \) are the energies of the corresponding transitions in the complex and in the aqua ion. This ratio indicates the degree of covalency of the RE-O bond. The bonding parameter is defined as \( \delta = 100(1 - \bar{\beta})/\bar{\beta} \), where \( \bar{\beta} = (\sum_1^N \beta)/N \) and \( N \) represents the number of levels used to compute \( \beta \).

5.3.2 Erbium Doped Bismuth Borate Glasses

5.3.2.1 Absorption

Results

Fig. 5.11 shows the absorption spectrum of bismuth borate glasses doped with 1 mol\% Er\(^{3+}\) and the assignments of the excited states.

The Judd-Ofelt analysis is used to establish a correlation between glass host and rare earth spectroscopic properties in bismuth borate glasses. The calculated Judd-Ofelt parameters are shown in Fig. 5.12 and the bonding parameter, \( \delta \), as function of the glass composition.

The absorption spectra obtained by doping the 0.25 Bi\(_2\)O\(_3\) glass with 1, 3 and 10 % mol Er are shown in Fig. 5.13. At high erbium concentrations, interaction between erbium ions is an
important gain limiting effect. One of these processes is co-operative upconversion which will be discussed in Section 5.3.2.3.
Figure 5.13: 1, 3, 10 % mol Er$^{3+}$ absorption spectra of bismuth borate glasses for 0.25 Bi$_2$O$_3$.

Discussion

The Judd-Ofelt coefficients have relatively high values. All coefficients decrease as the Bi$_2$O$_3$ content increases, this effect being most pronounced with $\Omega_2$. The $\Omega_2$ parameter is reported to be related to the structural changes around the Er ions (due to short range effects) and $\Omega_4$ and $\Omega_6$ are related to long range effects.

The $\Omega_2$ parameter has the greatest variation with glass composition. The dependence of $\Omega_2$ on composition is due to the change of the local symmetry of rare earth ions in glass. A lower value of this parameter is an indication of a more symmetric site, therefore we can assume that higher bismuth content results in more symmetric environment for erbium ions. Due to the large bismuth ion, the average distance Er-O increases resulting in a weaker field around Er ions reflected in a lower value of $\Omega_2$ for high bismuth concentration.

The $\Omega_6$ value slightly decreases with Bi$_2$O$_3$ content. The value at $x = 0.5$ is comparable with that reported by Tanabe et al. in [59]. The relative high value of $\Omega_6$ can be explained by the low basicity of the glass. The $\Omega_6$ parameter varies inversely proportional with the covalency of the Er-O bond, this being related to the local basicity of the rare earth site. The boron oxide is the most acidic oxide; the electronegativities of Bi, B and O elements are about 1.8, 2.0 and 3.5 respectively. As a result, the covalency of the B-O bond is stronger than that of the Bi-O bond.
and the influence of the B-O bond on the local ligand environment around erbium ions increases with the boron concentration. Also, the covalency of the Er-O decreases and $\Omega_6$ should increase. The bonding parameter $\delta$ variation with bismuth content $x$ confirms the increasing of the Er-O covalency when more Bi$_2$O$_3$ is added in the borate glass.

The intensities of the absorption lines of the 1, 3, 10 % mol Er$^{3+}$ bismuth borate doping are proportional to the erbium concentration. The high dopant level indicates a high Er solubility in the bismuth borate matrix. By contrast, for crystalline BiB$_3$O$_6$ it is reported that only a small amount of rare earth concentration (1000 ppm) can be incorporated in the crystal matrix [60], therefore a glass matrix is more suitable for incorporating a higher amount of impurities. This is very important in application as fiber amplifier where the demand for a high amplification in a smaller propagation path imposes higher rare-earth doping concentrations.

5.3.2.2 Luminescence

Rare earth doped fiber lasers are an interesting class of lasers which combine the guiding properties of optical fibres with the broadband luminescence associated with rare earth ions in a glass host to produce a widely tunable system operating over several wavelength bands. In order to overcome loss in fibre transmission systems, rare-earth doped fibers can be used as the gain medium.

Increasing the relative contribution of the electric dipole transitions favors a flat emission spectrum. The cross section of the magnetic-dipole transition is independent of ligand field and contributes to a sharp peak in the spectra at 1.53 $\mu$m, what is varied with the host composition is the electric dipole transition. The silica based erbium-doped-fiber amplifier (EDFA) has a narrow spectrum at 1.55 $\mu$m due to a high contribution of the magnetic-dipole transition in the $^4I_{12/2} - ^4I_{15/2}$ band.

Results

Erbium can be pumped directly into the first excited level using a 1.48 $\mu$m diode laser (at the $^4I_{13/2}$ level), or via one of the higher excitation states, for example using a 0.800 $\mu$m diode laser.

The absorption and emission bands at 1.5 $\mu$m of 1 mol\% Er$^{3+}$ in glasses with different bismuth content are plotted in Fig. 5.14.
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Figure 5.14: Left: 1 mol% Er$^{3+}$ absorption spectra at 1.5 µm. Right: Emission at 1.5 µm under 1.48 µm excitation.

Peak value and FWHM of absorption and emission variation at 1.5 µm are compared in Fig. 5.15.

Figure 5.15: Peak value (left) and FWHM (right) of absorption (red diamonds) and emission (blue circles) at 1.5 µm for 1 mol% Er$^{3+}$ doped borate glasses variation.

After excitation using a 0.800 µm diode laser, the erbium relaxes rapidly into the first excited state and emission at 1.5 µm is observed (see Fig. 5.16). Emissions at 0.900 µm and 1.100 µm are observed only for 3% mol Er in 0.25 Bi$_2$O$_3$. 

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CHAPTER 5. OPTICAL PROPERTIES OF BISMUTH BORATE GLASSES

Discussion

The bismuth borate glasses exhibit at 1.5 $\mu$m a broader ($\approx 100$ nm in comparison with 40 nm of silica based glasses) and flat luminescence spectrum. With increasing bismuth content the inhomogeneous broadening of the absorption and emission band decreases and the peak value of the band is red-shifted. Increasing the boron content, we can assume that more borate groups are formed, resulting in a more inhomogeneous distribution of Er$^{3+}$ sites. This leads to a more inhomogeneous broadening of the emission spectra.

The lower the phonon energy of the glass host, the more phonons are needed to bridge the energy gap between the $^4I_{13/2}$ level and $^4I_{15/2}$ and the lower is the probability for a nonradiative transition. Because the phonon energy of Bi$_2$O$_3$ is at 500 cm$^{-1}$, adding Bi$_2$O$_3$ must lead to a decrease in the phonon energy of the glasses and a longer lifetime of the upper level. Besides this, according to the Judd-Ofelt theory, the calculated radiative lifetime decreases with increasing refractive index of the host. In Bismuth-based silica glasses it was observed that the refractive index has much more influence than the phonon energy [61].

The lifetime of the $^4I_{13/2}$ level is very low because of its large nonradiative transition probability. The value of the decay time couldn’t be measured because it was lower than the rise time of the photodiode used as detector (2 $\mu$s).

By 0.800 $\mu$m excitation, emissions at 0.900 $\mu$m and 1.100 $\mu$m are observed only for 3 mol %Er in $x = 0.25$ Bi$_2$O$_3$ content glass. For the other compositions it is assumed that the rapid multiphonon decay promotes more efficiently the population of the $^4I_{13/2}$ level due to high phonon...
energy (B-O 1400 cm\(^{-1}\)).

### 5.3.2.3 Upconversion

The conversion of long-wave light to shorter wavelength radiations in rare-earth-doped materials has stimulated interest in the development of optical devices such as visible laser sources pumped by an infrared line excitation, optical fibres, sensors. Glasses are attractive due to the fact that large quantities of RE ions can be incorporated in these host lattices, and also they present the advantage that they can be used in optical fibre technology. However, the up-conversion efficiency is influenced by the ligand field, the multiphonon relaxation processes and optical properties of the host material.

The up-conversion is a rather unusual process since low energy photons are "converted" to higher energy photons. At least two NIR photons are required to generate one VIS photon. Up-conversion can efficiently occur only in materials in which multiphonon relaxation processes are not predominant, thus allowing more than one metastable excited state with sufficient population. In erbium ions, the \(4f\) electrons are efficiently shielded and thus not strongly involved in the metal-to-ligand bonding. As a consequence, electron-phonon coupling to \(f - f\) transitions is reduced, and multiphonon relaxation processes are less competitive.

### Results

In order to study the up-conversion, the Er-doped glass samples were illuminated by an infrared laser at about 0.800 \(\mu\)m. The recorded emission spectra of a sample with \(x = 0.25\) and 1 mol% Er in the visible region are plotted in Fig. 5.17.

The expected red emission, around 650 nm, due to transition from \(4F_{9/2}\) to \(4I_{15/2}\) and blue emission \(2H_{9/2}\) to \(4I_{15/2}\), around 410 nm, were not observed. Instead, a broad green emission near 555 nm, due to the transition from \((2H_{11/2}, 4S_{3/2})\) to \(4I_{15/2}\) was intense enough to be seen by naked eyes. An image of this luminescence is presented in Fig. 5.18.

The relative intensity of the green up-converted emission has been measured versus the pump power at 800 nm. The power dependence of this intensity is plotted in a logarithmic scale in Fig. 5.17. It follows from the slope of this plot that the green emission is a two-step up-conversion process.
Figure 5.17: Left: Up-conversion spectra for different laser intensities. Right: Variation of the maximum emission peak with incident laser intensity.

Figure 5.18: Left: Image of the up-conversion emitted in a bismuth borate glass sample. Right: Decay of up-conversion luminescence in bismuth borate glasses.

The decay of the upconversion luminescence is presented in Fig. 5.18. The intensity is plotted in a logarithmic scale versus time.

**Discussion**

Since the 0.800 µm pump laser excites the $^4I_{9/2}$ level which is lower than $^4S_{3/2}$, an erbium ion cannot obtain enough energy from a single pump photon to reach this upper levels. Therefore it must obtain additional energy from nearby erbium ions or from absorption of a second pump
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Basically, there are two up-conversion processes, excited-state absorption (ESA) and energy-transfer up-conversion (ETU). In the case of higher Er concentrations, both ESA and ETU are active. At low concentrations, for example 1 mol%, the dominant mechanism is ESA as the Er-Er distances are far too large for effective energy transfer to take place. As the concentration is increased, there are more Er ions available and thus, substantial energy transfer can occur and ETU becomes the dominant mechanism.

In the ETU process, energy migrates from a donor to an acceptor in an isolated ion pair and/or in a cluster, raising the latter ion into a higher energy excited state.

In ESA, upconversion occurs through absorption of a photon by an excited erbium ion, promoting it to a higher energy state. In this process the erbium ion is excited to the $^4I_{9/2}$ level, then decays nonradiatively to $^4I_{11/2}$ level, after which a second photon from the pump beam brings the ion to the $^4F_{7/2}$ level and then nonradiative relaxation populates the $^4S_{3/2}$ level.

The upconversion wasn’t observed in 3 mol% Er$^{3+}$ doped $x$ Bi$_2$O$_3$ glasses. Therefore we can assume that at low erbium doping (1 mol%) excited state absorption is responsible for the upconversion luminescence and at higher doping (10 mol%), the energy transfer.

The slope of the decay curve indicates a time constant of $\tau \approx 2.5$ ms. This is a relatively high value.

5.3.3 Neodymium Doped Bismuth Borate Glasses

In addition to the comprehensive study of Er-doped bismuth borate glass, the absorption and luminescence properties of bismuth borate glasses doped with Nd$^{3+}$ were studied.

In the Fig. 5.19 the absorption spectra of 1 and 3 mol % Nd$^{3+}$ doped $x$Bi$_2$O$_3$(1 $-x$)B$_2$O$_3$, $x = 0.25$, are presented. Following the procedure described in the first part of this chapter, the Judd-Ofelt parameters for dipole dipole transition were calculated and the obtained values are: $\Omega_2 = 2.186 \times 10^{-24}$ m$^{-2}$, $\Omega_4 = 7.489 \times 10^{-24}$ m$^{-2}$ and $\Omega_6 = 0.584 \times 10^{-24}$ m$^{-2}$.

The emission spectrum under 0.800 $\mu$m laser excitation is plotted in Fig. 5.20. The three emission bands centered at 900 nm, 1066 nm and 1341 nm correspond respectively to the following...
transitions: $^4F_{3/2} \rightarrow ^4I_{9/2}$, $^4F_{3/2} \rightarrow ^4I_{11/2}$ and $^4F_{3/2} \rightarrow ^4I_{13/2}$. The spectral linewidth of the fluorescent emission spectrum at 1066 nm was measured to be approximately 40 nm. This is a rather value larger than in other Nd:glass systems where the linewidth usually is 30 nm. Thus Nd-doped bismuth borate glasses may provide suitable active media for short pulse lasers.

Figure 5.19: 1, 3 mol% Nd$^{3+}$ absorption in $x = 0.25$ bismuth borate glasses.

Figure 5.20: 1 and 3 mol% Nd$^{3+}$ emission in bismuth borate glasses.
Chapter 6

Ferroelectric Microcrystals in Glass Matrix

6.1 Introduction

Ferroelectrics, due to their spontaneous polarization, have very important nonlinear optical and electrical properties. Single crystals or polycrystalline ferroelectric ceramics form the most important class of materials used for sensors, transducers, actuators etc., based on electric signals. Future photonic applications will require transparency, therefore transparent ferroelectric glass ceramics appears as potential material for this use. H. Jain [62] has summarized the most important results on transparent ferroelectric glass-ceramics. The melts of common ferroelectrics do not form glass on cooling, so they must be mixed with glass forming oxides. Therefore, the heat treatment schedule will be complicated by the formation of undesired non-ferroelectric phases. This can be avoided by choosing the composition in such a way that all other possible crystallized phases must have a lower tendency to devitrification. Experimentally, in the DTA spectra, the crystallization temperatures must be well separated in temperature.

Silica was the first matrix used in the early attempts to obtain ferroelectric glass-ceramics. Borrelli [4, 63] reports transparent materials which contain ferroelectric nanometer size phases in a silica matrix. He observed that the electrooptical effect is small and that the ferroelectric hysteresis is absent due to the very small size of the crystals. Size effects on the ferroelectric phase transition have been investigated by Känzig et al. [64]. KDP fine particles show no ferroelectric phase if the size is less than 150 nm. They attributed the change of the ferroelectric properties to the presence of domain walls or surface layers. The
suppression of the ferroelectric behavior for small size crystals is further weakened when the particles are mechanically confined within a dielectric glass matrix. On cooling below $T_c$ the crystallites are subjected to stress from the ferroelectric phase transition as from the difference in thermal contraction from that of the matrix.

### 6.2 Strontium Barium Niobate Glass-Ceramics

Sr$_x$Ba$_{(1-x)}$Nb$_2$O$_6$ (SBN) is a ferroelectric solid solution between BaNb$_2$O$_6$ and SrNb$_2$O$_6$. SBN crystals possess a ferroelectric phase $4mm$ at room temperature and undergo a transition to a paraelectric phase $4/mmm$ at higher temperatures. SBN belongs to the tungsten bronze family (has tetragonal tungsten bronze structure - TTB) and can be grown in a range $0.32 < x < 0.82$ [65]. As the material shows strong relaxor properties of the phase transition, a Curie region instead of a distinct Curie temperature must be defined.

Nanometer size ferroelectric SBN has being already prepared by different chemical methods. SBN ultrafine powders were prepared using sol-gel and hydrolysis aging processes [66]. The crystallite size of SBN powders subjected to different thermal treatments, between 700 and 1200 °C, varied from 73.1 to 211.7 nm. Variation of Sr/Ba ratios had no effect on the crystallites size. Moreover, the phase transition temperature was lower than that of the bulk material and decreases as the crystallites size increases (in the nanometer range).

Thin films of SBN made by sol-gel were obtained via two-step heat treatment at 550 °C for 5 h and between 700 - 1000 °C for 1 h. They are also dependent on the substrate: an amorphous substrate lacks nucleation sites and the two step process is needed [67]. In this case the ferroelectric phase begins to form at 800 °C.

SBN single crystals have high melting temperatures which can be lowered by using fluxes. Because the TTB structure has many unoccupied sites where different ions can be accommodated, the flux must be made from ions that cannot be included in the TTB structure. Whipps has used strontium barium tetraborate as solution for SBN growth [68].

We used this method to obtain $x$(Sr$_{0.5}$,Ba$_{0.5}$)Nb$_2$O$_6$ crystallites embedded in strontium barium borate glass matrix $(1 − x)$(Sr$_{0.5}$,Ba$_{0.5}$)B$_4$O$_7$ with $x = 0.1, 0.2, 0.25, 0.3$. The oxides Nb$_2$O$_5$ and B$_2$O$_3$ and SrCO$_3$, BaCO$_3$ were the starting materials. The melt has high viscosity and the compounds are very volatile so deviations from the initial stoichiometry are expected.
6.2. STRONTIUM BARIUM NIOBATE GLASS-CERAMICS

The strontium barium tetraborate melt became transparent at 1150 °C, by adding Nb_2O_5 this temperature increases slightly to 1250 °C. Also the tendency to crystallization increases.

Absorption measurements, Fig. 6.1, show that the absorption edge (defined as the wavelength corresponding to an absorption coefficient $\alpha = 8$) is considerably shifted to lower energies by adding niobium oxide, from 0.270 nm for Sr_{0.5}Ba_{0.5}B_4O_7 glasses to 0.320 nm for glasses with $x = 0.1$. Furthermore, increasing the Nb_2O_5 content the absorption edge is slightly shifted from 0.320 nm ($x = 0.1$) to 0.340 nm ($x = 0.3$). This values are comparable with that of the SBN crystals, observed at $\approx$ 370 nm [69].

For $x = 0.3$, keeping the melt for 30 min. at 1150 °C, micrometer sized star-like crystals are formed (see Fig. 6.2), that exhibit strong second order nonlinearities.

Due to the small proportion of crystalline phase in the glass matrix, no X-ray diffraction measurement could be used for the crystal structure identification. Instead, the temperature dependence of the second order nonlinear susceptibility was measures. On heating the sample, the intensity of the second harmonic signal decreases from a nearly constant value at temperatures up to 120 °C to approximately zero at temperatures above 200 °C (Fig. 6.1). Because the temperature of the phase transition (the inflection point of the curve) is comparable with that of SBN single crystals [70] and there are not other ferroelectric crystals that can be obtained from the used composition, it can be concluded that the crystallized phase is SBN. The temperature of the
inflection point of 150 °C corresponds to a strontium content of 0.4. The transition temperature region (≈ 100 °C) is broader than that of single crystal (≈ 20 °C) [70] due to a larger distribution in composition of the crystals in the glass.

Figure 6.2: Images of SBN microcrystals growth from spontaneous nucleation in the melt.

For \( x = 0.25 \), cubic-like non-centrosymmetric microcrystals are formed in the melt when treated at 1000 °C for 30 min.

Fig. 6.3 presents a picture of this crystals and the X-ray diffraction spectrum. The structure of this crystals is unknown, because they could not be identified from the used X-ray powder diffraction database.

The previous microcrystals were obtained by spontaneous nucleation and growth in the melt. Amorphous glasses were obtained from rapid cooling of the melt (at 1250 °C) containing no microcrystals. In this case, after the two step heat treatment, summarized in the Table C.1, only surface crystallization occurs. On heating the samples below 740 °C, no microcrystals are observed. If only the high temperature step is applied the number of nuclei is very small and bigger crystals can be grown without being distorted by the other neighbor crystals (Fig. 6.4). On heating the sample at higher temperature the crystals are growing faster and the sample fully crystallizes.

There are a large number of possible crystallized phases in this system (strontium borate, barium borate or other borate mixture). The diffraction pattern of strontium barium borate fully
6.2. STRONTIUM BARIUM NIOBATE GLASS-CERAMICS

![Image of cubic-like microcrystals and their X-ray diffraction spectrum.](image1)

Figure 6.3: Image of cubic-like microcrystals and their X-ray diffraction spectrum.

![Figure 6.4: Surface crystallized glasses for two steps and one step heat treatment.](image2)

![Surface crystallized glasses for two steps and one step heat treatment.](image3)

Figure 6.4: Surface crystallized glasses for two steps and one step heat treatment.

crystallized glasses changes to a spectra similar to the SBN crystal by increasing the SBN content in the glass (Fig. 6.5). The surface crystallized non-centrosymmetric crystals (intense SHG signal observed) are not SBN, because they appear in the strontium barium borate glasses too. Therefore one can assume that a low temperature phase crystallizes on the surfaces and at higher temperature it transforms in SBN.

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6.3 Strontium Bismuth Tantalate Glass-Ceramics

These results are a preliminary study on the influence of starting materials and conditions of preparation for strontium bismuth tantalate (SBT) glass-ceramics.

Previously, Varma et al.\textsuperscript{[6]} have obtained strontium bismuth tantalate nanometer-size crystals in lithium tetraborate glasses by one step heat treatment at 500 °C for 8 h.

We have prepared $x\text{SrBi}_2\text{TaO}_9$ in $(1 - x)\text{LiBO}_2$ and/or $\text{Li}_2\text{B}_4\text{O}_7$ glasses ($x = 0.1, 0.15, 0.2$) by melting the mixture at 1100 °C and rapidly cooling it to room temperature by splat quenching. In our experiments we have used commercial fluxes as matrix for SBT. The preparation of SBT required a solid state reaction for 48 h at 1000 °C. This yields a stable material, otherwise, a phase decomposition process takes place.

On cooling, the composition with $x = 0.1$ in lithium tetraborate crystallized and no controllable process took place. Using a mixture of $\text{Li}_2\text{B}_4\text{O}_7$ and LiBO\textsubscript{2}, for $x = 0.1$, a transparent and homogeneous glass was obtained. The molten glass was kept at 1200 °C for 1 h, then it was splat quenched. Spontaneous nucleation in the volume of the glass yielded sparse microcrystals. A heat treatment (10 minutes at 600 °C) was applied and it had induced further growth of the microcrystals. The frozen structure obtained is displayed in Fig. 6.6.
Such experiments with SBT are showing a promising study direction, as spontaneous nucleation took place in the volume of the glass during the applied heat treatments. More experiments are required in order to study the crystals size variation with respect to different heat treatment conditions.
Chapter 7

Hilgardite type Pb$_2$B$_5$O$_9$Br

Glass-Ceramics

7.1 Introduction

The mineral family of hilgardites includes three polymorphs with the formula Ca$_2$[B$_5$O$_9$]Cl·H$_2$O, Ca$_2$[B$_5$O$_9$]OH·H$_2$O (tyretskite) and CaSr[B$_5$O$_9$]Cl·H$_2$O (kurgantaite). Several other compounds of the composition M$_2$[B$_5$O$_9$]X (M = Ca, Sr, Ba, Eu, Pb and X = Cl, Br) have been obtained during attempts to prepare boracite-type structures [71, 72]. Zeolite-like structure, second harmonic generation and piezoelectric properties have been observed for hilgardites. In the recent years the crystal structure of Ba$_2$[B$_5$O$_9$]Cl·0.5H$_2$O was reported and two more Pb-containing phases in the hilgardite family, Pb$_2$[B$_5$O$_9$]OH·H$_2$O and Na$_{0.5}$Pb$_2$[B$_5$O$_9$]Cl(OH)$_{0.5}$, have been synthesized [73, 74, 75].

7.2 Pb$_2$B$_5$O$_9$Br Crystals

7.2.1 Pb$_2$B$_5$O$_9$Br Structure

Transparent small single crystals Pb$_2$B$_5$O$_9$Br (and similar Pb$_2$B$_5$O$_9$OH·H$_2$O, Pb$_2$B$_5$O$_9$OH·0.5H$_2$O) have been obtained from low-temperature hydrothermal solutions at 250-270 °C under a pressure of 50-300 atm, for 14 and 20 days, using as starting materials B$_2$O$_3$, Pb$_2$CO$_3$ and PbBr$_2$. Depending on the amount of PbBr$_2$ in the solutions, three forms of crystals are usually ob-
tained, all of them presenting hilgardite type structure. In the case of small amounts of PbBr₂ in the solution only monoclinic modifications of hilgardite structure have been synthesized, Pb₂B₅O₉OH·H₂O and Pb₂B₅O₉OH·0.5 H₂O, both of them having centrosymmetric structures. Excess of PbBr₂ in the solution leads to the formation of anhydrous orthorhombic Pb₂B₅O₉Br with non-centrosymmetric structure. The crystals were grown by the group of S. Y. Stefanovich at the Karpov Institute of Physical Chemistry, Moscow, Russia. There, these crystals were previously prepared using other techniques such as solid-state reactions, gas transport reactions synthesis and flux growth [76, 77].

The crystal structure of orthorhombic Pb₂[B₅O₉]Br was solved based on powder [76] and single crystal X-ray diffraction data [78]. Their structure consists of intercrossing anionic and cationic frameworks, as sketched in Fig. 7.1; the anionic part is builded from three BO₄ tetrahedra (bright blue) and two BO₃ triangles (dark blue). The cationic part consists of BrPb₄ tetrahedra (yellow), that are unstable unless they are in the cage formed by the 4 anionic groups around them. Rod-like shape Pb₂[B₅O₉]Br crystals, grown by hydrothermal solutions are shown in Fig. 7.1.

Figure 7.1: Left: Polyhedral drawing of intercrossing anionic and cationic frameworks of Pb₂[B₅O₉]Br crystals [78]. Right: Pb₂[B₅O₉]Br crystals grown by hydrothermal solutions.
7.2.2 Linear Optical Properties of Pb$_2$B$_5$O$_9$Br and Pb$_2$B$_5$O$_9$OH·0.5H$_2$O Crystals

Transparency at smaller wavelength is important for the generation of higher harmonics. The measured values of the absorption edge are 230 nm for Pb$_2$B$_5$O$_9$OH·0.5H$_2$O and 310 nm for Pb$_2$B$_5$O$_9$Br crystals. There are slight differences between hydrothermally and vapor grown Pb$_2$B$_5$O$_9$Br crystals. Both have the same value of the absorption edge, but the latter seem to be more transparent in the visible and have a steeper absorption edge, properties related to the non-twinned character of this crystal.

Due to the small size of the available crystals, no prisms could be fabricated for refractive index measurements. Instead, the refractive indices were calculated from the physical and optical thickness of platelet sample. The optical thickness is the product of the refractive index and the physical thickness of an optical material. For an anisotropic material there will be different optical thicknesses corresponding to different refractive indices. This can be determined under a polarizing microscope focusing the objective on the top and the bottom of the crystal. The refractive indices of these crystals were measured in optical uniaxial approximation. Because the crystal structure is almost tetragonal, due to a similar value of $a$ and $b$ unit cell parameters, only two refractive indices are measured: ordinary $n^o$ and extraordinary $n^e$, where both polarizers are parallel, respectively perpendicular to the $c$ axis. The results are summarized in Table 7.1. They show that the investigated crystals exhibit high birefringence, which makes them suitable for phase matched harmonic generation.

<table>
<thead>
<tr>
<th>Refractive index</th>
<th>Pb$_2$B$_5$O$_9$Br</th>
<th>Pb$_2$B$_5$O$_9$OH·H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n^o$</td>
<td>1.95±0.02</td>
<td>1.70±0.03</td>
</tr>
<tr>
<td>$n^e$</td>
<td>1.75±0.02</td>
<td>1.53±0.03</td>
</tr>
</tbody>
</table>

Table 7.1: Refractive indices of Pb$_2$B$_5$O$_9$Br and Pb$_2$B$_5$O$_9$OH·H$_2$O crystals.

7.2.3 Second Order Nonlinearities of Pentaborate Hilgardite-Type Crystals

The halogen pentaborates M$_2$[B$_5$O$_9$]XX’ (M = Ca, Sr, Ba, Pb; X, X’ = Cl, Br, OH, H$_2$O), related to hilgardite structure show high second order nonlinearities. As previously reported [79], SHG
values increase with the change of the metal substitution as Ca < Sr < Ba < Pb and for the halogen substitution as Cl < Br.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SHG (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>13</td>
</tr>
<tr>
<td>Pb₂<a href="OH">B₅O₉</a>·0.5H₂O</td>
<td>15</td>
</tr>
<tr>
<td>Pb₂[B₅O₉]Br</td>
<td>600</td>
</tr>
<tr>
<td>Pb₂[B₅O₉]Cl</td>
<td>160</td>
</tr>
<tr>
<td>Ba₂[B₅O₉]Br</td>
<td>84</td>
</tr>
<tr>
<td>Ba₂[B₅O₉]Cl</td>
<td>27</td>
</tr>
<tr>
<td>Sr₂[B₅O₉]Br</td>
<td>15</td>
</tr>
<tr>
<td>Sr₂[B₅O₉]Cl</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 7.2: Powder SHG results for hilgardite type crystals \( \langle L \rangle \simeq 3 \ \mu m \).

A confirmation of this behavior is presented in Table 7.2. The intensity of the SHG signal of order of magnitude of \( I_{SiO₂} \) observed for centrosymmetric Pb₂[B₅O₉](OH)·0.5H₂O may be explained by small amount of Br present in these samples. For Pb₂[B₅O₉]Br, the application of the Eq 3.23 leads to a value \( \langle d \rangle = 3.0 \pm 0.5 \ \text{pm/V} \), rather large, exceeding those for other of nonlinear borates and approximately half of that for BiB₃O₆.

### 7.3 Pb₂B₅O₉Br Based Glasses

Glasses were prepared by melting Pb₂B₅O₉Br and Pb₂B₅O₉(OH)·0.5H₂O crystalline powders in a closed platinum crucible.

From the DTA measurements (made at Moscow State University), plotted in Fig. 7.4 it can be seen that the Pb₂[B₅O₉]Br crystals melt at approximate 800 °C. At this temperature the loss of Br is about 10 wt.%. The temperature and duration of melting was a compromise between two requirements: first to avoid Br evaporation and second to obtain a homogeneous glass without crystalline inclusions. Details of the melting conditions are presented in Table 7.3. The first column contains an identification code of glasses which will be used further.

Using a TS1500 heating stage under the microscope there could be observed the liquidus (when the crystal is complete melted) and solidus temperatures of this crystals (appearance of first liquid droplets). Table 7.4 summarize these results. Moreover, the dehydration temperature of
### Table 7.3: \( \text{Pb}_2\text{B}_5\text{O}_9\text{Br} \) based glass preparation.

<table>
<thead>
<tr>
<th>Code</th>
<th>Melting</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>805 (20 min)</td>
<td>yellow</td>
</tr>
<tr>
<td>12</td>
<td>798 (30 min)</td>
<td>weak yellow</td>
</tr>
<tr>
<td>13</td>
<td>755 - 802 (gradual heating 40 min)</td>
<td>colorless</td>
</tr>
<tr>
<td>21</td>
<td>740 - 795 (gradual heating 20 min) 795 (15 min)</td>
<td>weak lemon - yellow</td>
</tr>
<tr>
<td>22</td>
<td>790 (15 min) 790 - 795 (gradual heating 15 min)</td>
<td>lemon - weak yellow</td>
</tr>
</tbody>
</table>

### Table 7.4: Liquidus and solidus temperatures for \( \text{Pb}_2\text{B}_5\text{O}_9\text{Br} \) and \( \text{Pb}_2\text{B}_5\text{O}_9\text{OH-H}_2\text{O} \) crystals.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( \text{Pb}_2\text{B}_5\text{O}_9\text{Br} )</th>
<th>( \text{Pb}_2\text{B}_5\text{O}_9\text{OH-H}_2\text{O} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{\text{liquidus}} )</td>
<td>793±2</td>
<td>730±5</td>
</tr>
<tr>
<td>( T_{\text{solidus}} )</td>
<td>740±10</td>
<td>680±10</td>
</tr>
</tbody>
</table>

\( \text{Pb}_2\text{B}_5\text{O}_9\text{OH-H}_2\text{O} \) crystals can be detected at 570±20 °C as complete loss of transparency.

In the case of \( \text{Pb}_2\text{B}_5\text{O}_9\text{OH-H}_2\text{O} \) based glasses, the absorption edge is shifted from 230 nm, in crystalline form, to 300 nm in glassy form, for \( \text{Pb}_2\text{B}_5\text{O}_9\text{Br} \) based ones from 310 nm to 390 nm. The absorption edge value of the former one seems to be independent from preparation conditions. The refractive indices of glasses prepared for longer time at high temperature (11 and 12) is smaller (due to loss of Br) than that for the glasses prepared for shorter time. The behavior of the absorption edge and the refractive indices of \( \text{Pb}_2\text{B}_5\text{O}_9\text{Br} \) based glasses are presented in Fig. 7.2.

It was necessary to check the chemical composition of glasses in order to know the component losses by heating at high temperature. The investigations were carried out with a Cameca SX40 Electron Probe Micro-Analyzer, at the Chemical Department of Osnabrück University, by Dr. Bernd Gather. A \( \text{Pb}_2\text{B}_5\text{O}_9\text{Br} \) single crystal was used as standard. The microprobe spectra for the standard and two glasses (11 and 13 - see Table 7.3 for preparation conditions) are plotted in Fig. 7.3.

The decreasing intensities shows that both Br and Pb evaporate following the melting of the polycrystalline powder. The compositions of the resulting glasses, assuming that the boron content remains unchanged, are: \( \text{Pb}_{0.91}\text{B}_5\text{O}_{8.2}\text{Br}_{0.36} \) (glass 13) and \( \text{Pb}_{0.48}\text{B}_5\text{O}_{7.9}\text{Br}_{0.13} \) (glass 11). This indicates a considerable deviation from the initial stoichiometric composition.
7.4 \( \text{Pb}_2\text{B}_5\text{O}_9\text{Br} \) Crystallized Glasses

Great similarity in short-range structures of \( \text{Pb}_2\text{B}_5\text{O}_9\text{Br} \) in crystalline and glassy form rises the possibility to obtain glass-ceramics, due to a lower energy used for structural rearrangements at the transition from glass to crystal (see also the discussion in the section 2.2). It can be observed...
a good resemblance between crystal and glass IR spectra, Fig. 7.4, reflecting the existence of the same structural units.

Figure 7.4: Left: Infrared spectra of crystal (1) and glasses annealed for 14 h at 456 °C (2), 448 °C (3), as-quenched glass (3). Right: DTA spectra for glasses as quenched (1) and annealed for 14 h at 425 °C (2), 435 °C (3), 448 °C (4), 452 °C (5) [77].

Pb₂B₅O₉Br is the only phase crystallized after heat treatment. In Fig. 7.5 the X-ray diffraction pattern of crystallized glasses is shown. It is identic with that of the powder spectra reported in literature [76]. The absence of sharp peaks in the parent glass spectrum demonstrates its amorphous state.

The DTA spectra show that the glass transition temperature is at about \( T_g = 445 °C \), the glass crystallization temperature \( T_x = 572-580 °C \) and melting temperature 780-790°C. It is reported that the annealing at \( T_g \) is the best solution for bulk nucleation of this type of glasses [77].

In order to initiate and control the crystallization behavior of these glasses, a two stage heat treatment was used. For the first step, intended to induce bulk nucleation, the glasses were held at 20 - 80 °C below \( T_g \), for max. 24 h. Due to a very high crystallization rate, at the second stage the samples were heated only for few minutes at \( T_x \). For longer times the samples fully crystallize and become opaque. The heat treatment parameters are listed in Table 7.5.

Surface crystallization is always present, but bulk crystallization is clearly observed after repol-
CHAPTER 7. HILGARDITE TYPE Pb$_2$B$_5$O$_9$Br GLASS-CERAMICS

Figure 7.5: X-ray diffraction spectra of glasses (left) and crystallized Pb$_2$B$_5$O$_9$Br based glasses (right).

ishing the sample, as shown in Fig. 7.6.

Figure 7.6: Images of Pb$_2$B$_5$O$_9$Br based glass-ceramics at two different focussing points inside the sample.

The initial glass shows no SHG output, but the crystallized glasses exhibit rather high second order nonlinear effect. In Table 7.5 these values are presented in comparison with quartz.

The most important result is related to the latest sample (2b), where microcrystals cannot be observed under the microscope, but the SHG output has a value comparable with quartz.
### Table 7.5: SHG output of Pb$_2$B$_5$O$_9$Br glasses heat treated at various temperatures before and after repolishing.

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Heat treatment</th>
<th>SHG (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Std:</td>
<td>$\alpha$-SiO$_2$ single crystal</td>
<td>3.5 no sphere</td>
</tr>
<tr>
<td>Std</td>
<td>$\alpha$-SiO$_2$ thin powder (3 $\mu$m)</td>
<td>7.4 - 7.6 with sphere</td>
</tr>
<tr>
<td>1a</td>
<td>380 C + 530 C (5 min)</td>
<td>280 no sphere</td>
</tr>
<tr>
<td>2a</td>
<td>325 C, 380 C + 530 C (5 min)</td>
<td>464 no sphere</td>
</tr>
<tr>
<td>3a</td>
<td>380 C (18 h) + 550 C (2 min)</td>
<td>920 no sphere</td>
</tr>
<tr>
<td>1b</td>
<td>320 C (18 h) - 380 (24 h) + 530 C (3 min)</td>
<td>3 with sphere</td>
</tr>
<tr>
<td>2b</td>
<td>320 C (18 h) - 380 (24 h) + 530 C (3 min)</td>
<td>148 no sphere</td>
</tr>
<tr>
<td></td>
<td></td>
<td>376 with sphere</td>
</tr>
<tr>
<td>1b</td>
<td>320 C (18 h) - 380 (24 h) + 530 C (3 min)</td>
<td>1.7 - 1.8 with sphere; after repolishing</td>
</tr>
<tr>
<td>2b</td>
<td>320 C (18 h) - 380 (24 h) + 530 C (3 min)</td>
<td>240 - opaque region; no sphere; after repolishing</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14 - 17 - transparent region; no sphere; after repolishing</td>
</tr>
</tbody>
</table>

Table 7.5: SHG output of Pb$_2$B$_5$O$_9$Br glasses heat treated at various temperatures before and after repolishing.
Chapter 8

Conclusions and Outlook

The main contributions of this work to the field of optical properties of bismuth borate-based glass-ceramics, ferroelectric glass-ceramics and Pb$_2$B$_5$O$_9$Br glass-ceramics are summarized in this chapter.

8.1 Conclusions

Bismuth Borate Glasses and Glass-Ceramics

Optical properties of glasses in the binary system bismuth oxide (Bi$_2$O$_3$) - boric oxide (B$_2$O$_3$) are measured for the composition range $x$Bi$_2$O$_3$(1 − $x$)B$_2$O$_3$, 0.25 ≤ $x$ ≤ 0.65. Samples with different Bi$_2$O$_3$/B$_2$O$_3$ ratios were prepared by melt quenching. Absorption measurements and refractive indices measurements were performed over the UV-VIS - near IR range for all prepared samples. They show that the refractive indices increase as the Bi$_2$O$_3$ fraction is increasing. Also the ultraviolet absorption edge was shown to shift to longer wavelengths. From these measurements a generalized Sellmeier formula was derived to describe the refractive indices for the whole composition range and a wide wavelength range.

A new stable phase BiBO$_3$ (II) was prepared in powder form. X-ray diffraction was used to determine the structure. It was shown that the structure is a monoclinic one, with cell parameters $a = 7.696\text{Å}$, $b = 9.950\text{Å}$, $c = 7.033\text{Å}$, $\beta = 117.47^0$ and the volume $V = 477.8 \text{Å}^3$. The SHG intensity variation was studied as a function of particle size, and it demonstrates that this crystal is phase matchable.
Applying heat treatments to the prepared bismuth borate glasses in order to obtain glass ceramics leads in most cases to surface nucleation. It was proved that dopants increase the number of nucleating sites on the surfaces. After thermal treatment, the glasses obtained by melting polycrystalline powders crystallize in the same phase as the crystals used.

On erbium-doped samples absorption and luminescence measurements were made. A Judd-Osfield analysis of the typical Erbium bands was performed for the absorption spectra recorded. It revealed comparably high Judd-Osfield coefficients ($\Omega_2 \approx 6$, $\Omega_4 \approx 2.5$, $\Omega_6 \approx 1.5$). All coefficients were shown to decrease as the $\text{Bi}_2\text{O}_3$ content increases, this effect being most pronounced with $\Omega_2$. The luminescence at 1.55 $\mu$m reveals a broad and flat band which is narrowing with the increase in $\text{Bi}_2\text{O}_3$ content. The green upconversion was observed and the temporal behavior of the emission at 550 nm was investigated.

The absorption and emission spectra of chromium-doped bismuth borate glasses were measured. The $\text{Cr}^{3+}$ ions occupy both high field and low field sites and therefore the emission consists of a broad band, centered around 0.850 $\mu$m $^{4}\text{T}_2 \rightarrow ^{4}\text{A}_2$ and a sharp band at 0.710 $\mu$m $^{2}\text{E} \rightarrow ^{4}\text{A}_2$. The decay time of the R-line is larger that that of the broad band at 0.800 $\mu$m. It is suggested that energy transfer from the $^2\text{E}$ level to the $^{4}\text{T}_2$ occurs. On surface crystallized glasses, for $x = 0.5$ $\text{Bi}_2\text{O}_3$ and high $\text{Cr}^{3+}$ concentration content, luminescence of chromate ions $\text{CrO}_4^{2-}$ doped $\text{BiBO}_3$ microcrystals was observed.

**Ferroelectric Glass-Ceramics**

Strontium barium niobate microcrystals embedded in strontium barium borate matrix were obtained by spontaneous nucleation in the melt and rapid quenching. The phase transition temperature region ($\approx 100 ^\circ\text{C}$), determined by second harmonic generation measurements, is broader than that of the single crystal ($\approx 20 ^\circ\text{C}$) due to a larger distribution in composition of the crystals in the glass.

Preliminary results on $x\text{SrBi}_2\text{TaO}_9$ crystals in $(1-x)\text{LiBO}_2$ and/or $\text{LiB}_4\text{O}_7$ ($x=0.1$, 0.2) glass are presented.

**Pb$_2$B$_5$O$_9$Br Glass-Ceramics**

Optical properties of $\text{Pb}_2\text{B}_5\text{O}_9\text{Br}$ based glass were also investigated. The heat treatment applied leads to the formation of small nanocrystals inside the glass. The X-ray diffraction pattern
confirms the crystallization of the Pb$_2$B$_5$O$_9$Br structure, despite the loss of bromide during the heating process. Although under the microscope the crystals are not seen, the high intensity of SHG signal indicates that noncentrosymmetric crystalline structures at nanometer scale are formed.

8.2 Outlook

The study of transparent glass-ceramics is a relatively new research field. It aims to provide the industry with new materials with special optical properties. These sought-for materials are microcrystals embedded in glass matrixes, and, as it was demonstrated, they can combine the easiness of processing glass with the strong nonlinear properties of crystals.

Bismuth Borate Glasses and Glass-Ceramics

Strong nonlinearities of bismuth based glasses makes them interesting materials for applications in photonics. The structural and optical properties of the BiBO$_3$ (II) crystal are unknown, because it was never obtained as a single crystal. This makes the growth of this crystal and the study of its properties, an interesting research direction. Moreover the crystallized $x = 0.5$ bismuth borate composition doped with chromium has shown interesting luminescence features. The mechanism by which the chromium oxidation state changes from trivalent to hexavalent has not been yet explained.

Ferroelectric Glass-Ceramics

A suitable glass matrix in which the SBN crystals to be the first crystallized phase should be found. The optical and dielectric properties of nanosized crystals are interesting to investigate. Also a correlation with a theoretical model would be useful for a better understanding of the optical nonlinearities and of the phase transition behavior.

Pb$_2$B$_5$O$_9$Br Glass-Ceramics

Glasses with compositions near to the stoichiometric composition should be prepared and their crystallization behavior studied. At this time more research is required for obtaining smaller size Pb$_2$B$_5$O$_9$Br crystals embedded in the glass matrix.
Appendix A

Experimental Details

This appendix describes some of the devices used for experiments in this thesis.

**TRIAX 180 Spectrometer** *(Jobin Yvon Inc.)*, was used in experimental setup for visible luminescence. The scanning range, corresponding to a spectral dispersion grating with 1200 lines/mm, is 310-1400 nm. The resolution is 0.3 nm and the focal length 0.19 m. The start and end wavelengths, as well as the scan speed and wavelength increment between datapoints are programmed, via the serial interface, by a PC.

**Metrospec Spectrometer** *(AMKO GmbH)*, was employed for infrared luminescence experiments. The scanning range is between 175-2200 nm, for a grating with 600 lines/mm. The focal length of the spectrometer is 0.2 m.

**TS1500 heating stage** *(Linkam Scientific Instruments)*, performs the schedule for glass-ceramics preparation. It enables to heat up the samples to 1500 °C from room temperature at maximum 130 °C/min. The sample chamber, with 8 mm diameter and 6 mm high, is water cooled. The temperature is measured with a S-type platinum/rhodium thermocouple accurately controlled by the TMS94/1500 programmer.

**1064 nm Nd-YAG Laser**, model EPO-5000 *(Continuum)* was used for second harmonic measurements. The pulsed laser, with pulses of 5 ns, has a repetition rate of about 1 KHz and approximately 10 KW peak power.
532 nm frequency doubled Nd-YAG Laser (Soliton GmbH), was used for red and IR luminescence of chromium doped samples. The pulses are of 20 ns, a repetition rate of about 50 Hz, wavelength of 532 nm and approximately 40 mJ/pulse.

800 nm Laser Diode, was used for IR luminescence and visible upconversion in rare earth doped samples. For decay measurements, the diode current was modulated by a squared signal from a pulse generator. The 200 Hz frequency was choused. The diode intensity can be varied from 0 to 230 mA.

1.478 µm Laser Diode, Model AF4A00PX, (Anritsu Corporation), was used for excitation of the luminescence in rare earth doped samples. The output power is 154 mV.

MSA-200 gated photon counter, (Becker & Hickl GmbH) was used to record the photomultiplier signal from luminescence measurements. It is a 200 MHz (5 ns) multiscaler card with capacity of memory location 8 bits (or 255 counts) and maximum recording time 2.6 ms (512k points). The device counts all pulses whose amplitude is greater than a selectable discriminator threshold and stores them into subsequent memory locations.

STOE X-ray powder diffractometer, (STOE & CIE GmbH), was employed for the identification of crystallized phases. The scan mode was transmission 2Theta:Omega. A curved Germanium monochromator supplies a monochromatic CuKα1 beam at 1.540598 Å. The powdered samples were prepared between two thin foils and this sandwich is inserted into the rotating sample holder.

Chemicals employed for glass preparation and doping are: Nd₂O₃, Er₂O₃, Cr₂O₃ supplied from Alfa Aesar and B₂O₃, Bi₂O₃, SrCO₃, BaCO₃, from Aran Isles Chemicals.

MATLAB software, Version 6.5 - Release 13, was used to compute the experiments results and to plot the graphics.
Appendix B

Bismuth Borate Heat Treatment

<table>
<thead>
<tr>
<th>Schedule</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>↑ 430 C (72 h) ↑ 640 C (10 min)</td>
<td>surface monoclinic like crystals</td>
</tr>
<tr>
<td>↑ 400 C (1 h) ↑ 430 C (30 min) ↑ 600 C (20 min)</td>
<td>surface crystallized</td>
</tr>
<tr>
<td>↑ 500 C (10 h)</td>
<td>surface crystallized</td>
</tr>
<tr>
<td>↑ 470 C (3 h) ↑ 500 C (2 h)</td>
<td>surface crystallized</td>
</tr>
<tr>
<td>↑ 450 C (3 h) ↑ 520 C (1 h)</td>
<td>10 mol%TiO\textsubscript{2} ; nothing</td>
</tr>
<tr>
<td>↑ 500 C (30 min) ↑ 600 C (1 h)</td>
<td>10 mol%TiO\textsubscript{2} ; crystallized</td>
</tr>
<tr>
<td>↑ 450 C (13 h) ↑ 620 C (30 min)</td>
<td>10 mol%Er\textsuperscript{3+} ; nothing ; at 650 C begin to melt</td>
</tr>
<tr>
<td>↑ 400 C (2 h) ↑ 460 C (3 h) ↑ 470 C (3 h) ↑ 550 C (3 h)</td>
<td>1 mol%Er\textsuperscript{3+} ; nothing</td>
</tr>
<tr>
<td>↑ 460 C (1 h) ↑ 530 C (1 h) ↑ 540 C (3 h) ↑ 600 C (10 min)</td>
<td>1 mol%Er\textsuperscript{3+} ; surface</td>
</tr>
<tr>
<td>↑ 450 C (16 h) ↑ 600 C (1 h)</td>
<td>10 mol%Er\textsuperscript{3+} ; nothing</td>
</tr>
<tr>
<td>↑ 460 C (10 h) ↑ 470 C (10 h) ↑ 480 C (2 h) ↑ 490 C (3 h) ↑ 510 C (6 h)</td>
<td>10 mol%Er\textsuperscript{3+} ; nothing</td>
</tr>
<tr>
<td>↑ 450 C (2 h) ↑ 500 C (2 h)</td>
<td>1000 ppm Cr\textsuperscript{3+} ; surface crystallized</td>
</tr>
</tbody>
</table>

Table B.1: Thermal treatment for $x = 0.25$ bismuth borate glass.
### APPENDIX B. BISMUTH BORATE HEAT TREATMENT

<table>
<thead>
<tr>
<th>Schedule</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>↑ 397 C (3 h) ↑ 410 C (5 h) ↑ 500 C (30 min)</td>
<td>surface crystallized</td>
</tr>
<tr>
<td>↑ 350 C (3 h) ↑ 470 C (1 h) ↑ 500 C (30 min)</td>
<td>nothing</td>
</tr>
<tr>
<td>↑ 300 C (5 h) ↑ 350 C (20 h) ↑ 420 C (20 h)</td>
<td>nothing</td>
</tr>
<tr>
<td>↑ 410 C (2 h) ↑ 430 C (3 h) ↑ 500 C (1 h)</td>
<td>1000 ppm Cr$^{3+}$; surface crystallized</td>
</tr>
<tr>
<td>↑ 410 C (2 h) ↑ 430 C (3 h) ↑ 480 C (1 h)</td>
<td>1000 ppm Cr$^{3+}$; surface crystallized</td>
</tr>
<tr>
<td>↑ 402 C (10 h) ↑ 450 C (5 h) ↑ 480 C (3 h)</td>
<td>1000 ppm Cr$^{3+}$; surface crystallized</td>
</tr>
<tr>
<td>↑ 300 C (2 h) ↑ 470 C (1 h)</td>
<td>1000 ppm Cr$^{3+}$; surface crystallized</td>
</tr>
<tr>
<td>↑ 350 C (3 h) ↑ 470 C (4 h)</td>
<td>1000 ppm Cr$^{3+}$, surface crystallized</td>
</tr>
<tr>
<td>↑ 400 C (36 h) ↑ 420 C (4 h)</td>
<td>1000 ppm Cr$^{3+}$, surface crystallized</td>
</tr>
<tr>
<td>↑ 390 C (65 h)</td>
<td>10000 ppm Cr$^{3+}$, nothing</td>
</tr>
<tr>
<td>↑ 395 C (24 h) ↑ 410 C (1 h) ↑ 420 C (2 h) ↑ 430 C (10 h)</td>
<td>1000 ppm Cr$^{3+}$; surface crystallized</td>
</tr>
<tr>
<td>↑ 400 C (2 h) ↑ 470 C (6 h)</td>
<td>10 mol%TiO$_2$, nothing</td>
</tr>
<tr>
<td>↑ 410 C (72 h) ↑ 420 C (4 h)</td>
<td>5 mol%TiO$_2$, nothing</td>
</tr>
<tr>
<td>↑ 390 C (20 h) ↑ 470 C (4 h)</td>
<td>5 mol%TiO$_2$, surface crystallized</td>
</tr>
<tr>
<td>↑ 390 C (24 h) ↑ 420 C (7 h)</td>
<td>10 mol%Er$^{3+}$, after 1 h begin to crystallize on surface; after 7 h the surface is all crystallized</td>
</tr>
<tr>
<td>↑ 350 C (36 h) ↑ 400 C (7 h)</td>
<td>10 mol%Nd$^{3+}$, nothing</td>
</tr>
</tbody>
</table>

Table B.2: Thermal treatment for $x = 0.5$ bismuth borate glass.
Appendix C

Ferroelectric Glass-Ceramics

<table>
<thead>
<tr>
<th>x</th>
<th>Schedule</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>↑ 500 °C (10 C/min) → 500 °C (2h) ↑ 840 °C (1 C/min)</td>
<td>surface crystallization</td>
</tr>
<tr>
<td>0.3</td>
<td>↑ 500 °C (10 C/min) → 500 °C (2h) ↑ 800 °C (1 C/min) → 800 °C (30 min)</td>
<td>surface crystallization</td>
</tr>
<tr>
<td>0.3</td>
<td>↑ 650 °C (10 C/min) ↑ 800 °C (1 C/min) → 800 °C (4h)</td>
<td>surface crystallization; shg weak</td>
</tr>
<tr>
<td>0</td>
<td>↑ 500 °C (10 C/min, 1h) ↑ 700 °C (10 C/min, 1h) ↑ 800 °C (10 C/min, 10 min)</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>↑ 500 °C (10 C/min, 1h) ↑ 700 °C (10 C/min, 1h) ↑ 870 °C (10 C/min, 10 min)</td>
<td>small crystals</td>
</tr>
<tr>
<td>0</td>
<td>↑ 600 °C (10 C/min, 2h) ↑ 650 °C (20 C/min, 1h) ↑ 750 °C (10 C/min, 30 min)</td>
<td>at 700 °C nothing; small crystals</td>
</tr>
<tr>
<td>0</td>
<td>↑ 600 °C (10 C/min, 1h) ↑ 650 °C (10 C/min, 2h) ↑ 700 °C (1 C/min, 1h) ↑ 710 °C (1 C/min, 30 min) ↑ 740 °C (1 C/min, 30 min) ↑ 800 °C (1 C/min, 30 min)</td>
<td>surface crystallization</td>
</tr>
<tr>
<td>0</td>
<td>↑ 600 °C (10 C/min, 1h) ↑ 700 °C (1 C/min, 1h) ↑ 750 °C (1 C/min, 8h)</td>
<td>after 2 h appear small crystals</td>
</tr>
<tr>
<td>0</td>
<td>↑ 700 °C (10 C/min, 3h) ↑ 710 °C (1 C/min, 5h)</td>
<td>nothing</td>
</tr>
<tr>
<td>0</td>
<td>↑ 700 °C (10 C/min, 2h) ↑ 710 °C (1 C/min, 6h)</td>
<td>nothing</td>
</tr>
<tr>
<td>0</td>
<td>↑ 710 °C (10 C/min) ↑ 720 °C (1 C/min, 1h) ↑ 740 °C (1 °C/min)</td>
<td>small crystals</td>
</tr>
</tbody>
</table>

Table C.1: Thermal treatment for $x$(Sr$_{0.5}$,Ba$_{0.5}$)Nb$_2$O$_6$ in $(1-x)$(Sr$_{0.5}$,Ba$_{0.5}$)B$_4$O$_7$ Glass (x=0-0.3).
Appendix D

Rare Earth - Energy Levels Scheme

Figure D.1: Left: Er$^{3+}$ energy levels. Right: Nd$^{3+}$ energy levels.
Bibliography


BIBLIOGRAPHY


S. Tanabe. Broad-band 1.5$\mu$m emission of Er$^{3+}$ ions in bismuth-based oxide glasses for potenstial WDM amplifier. *Journal of Luminescence*, 87:670, 2000.

P. Becker and C. Wickleder. Crystal growth and spectroscopic characterization of BiB$_2$O$_6$:RE$^{3+}$ (RE$^{3+}$ = Pr$^{5+}$, Nd$^{3+}$, Gd$^{3+}$, Er$^{3+}$, Tm$^{3+}$). *Crystal Research and Technology*, 36:27, 2001.


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Eidesstattliche Erklärung

Hiermit erkläre ich an Eides Statt, die vorliegende Abhandlung selbständig und ohne unerlaubte Hilfe verfasst, die benutzten Hilfsmittel vollständig angegeben und noch keinen Promotionsversuch unternommen zu haben.

Osnabrück, 14.01.2005
Isabella - Ioana Oprea