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Structural, dielectric, and optical properties of yttrium calcium borate glasses

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Structural and optical properties of stable glasses in the Y2O3−CaO−B2O3 system, containing the same Y/Ca ratio as the YCa4O(BO3)3 (YCOB) crystal, were determined from Raman and reflectance infrared spectroscopy. Changes in optical functions with composition are associated with an increase in the number of non-bridging oxygen and to calcium/yttrium oxides content. Refractive indexes values (from 1.597 to 1.627 at λ=2 μm) are in good agreement with those of the YCOB crystal, an indication that these glasses are potential candidates for optical applications due to their ease of shaping as large bulk samples or fibers. © 2009 American Institute of Physics.

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Calcium oxoborate crystals of the family RECa4O(BO3)3 (RECOB), where RE denotes a trivalent rare-earth ion, are promising laser materials with high potential for the near-infrared range as well as for green emission by self-frequency doubling. In particular, the YCa4O(BO3)3 (YCOB) crystal was shown to be a good candidate for laser operating in the 1.06 μm region, when doped with Nd3+ ions, as well as in the 1.5−1.6 μm region when codoped with Yb3+ and Er3+ ions due to the efficient energy transfer between Yb3+ and Er3+, provided by the high effective photon energy of the borate crystal (1400 cm−1). However, there is no report on the structural and optical investigation of glasses in the system Y2O3−CaO−B2O3 (YCaB). The YCaB glasses, with compositions close to that of YCOB crystal, are promising host matrices for luminescent RE3+ ions, which can substitute Ca2+ or Y3+ cations in the borate network. Moreover, YCaB glasses offer interesting perspectives for applications (e.g., laser, scintillation, and thermoluminescence) as they can easily be shaped as large samples or fibers through low cost processes. The knowledge of local and medium-range order in such glasses and melts is essential to understand more deeply the glass formation process and how composition-dependent structures can lead to dramatic changes in their physical and chemical properties. The microscopic structure of vitreous B2O3 itself is still controversial and has attracted a lot of attention during the past years. There is therefore a need to clarify the structure of such glasses and the relation between the structure and physical properties.

In this framework, we prepared and performed structural investigations by Raman and reflectance infrared (RIR) of yttrium calcium borate (YCaB) glasses with the same atomic ratio ([Y]/[Ca]=1/4) as that of the YCOB crystal. The structure of these materials was analyzed and specified by fitting the RIR bands. The complex dielectric function and complex refractive index were determined using a dielectric function model (DFM).

Three YCaB glass samples with the molar composition x Y2O3−8x CaO−(100−9x) B2O3 (x=4, 5, and 6 mol %) were prepared by the conventional melt quenching technique using a mixture of reagent grade Y2O3, CaCO3, and H3BO3 (>99.9%). Thermal treatments at 500 °C/1 h and 1000 °C/1 h were performed previously to decompose the precursors and to reduce the OH final content. Then the samples were melted between 1250 and 1350 °C, depending on composition, during 1 h, with three stirring steps in the first 30 min, to obtain a homogeneous liquid. For x=4 and 5 mol %, the melts were quenched in preheated graphitic molds (at 500 °C). For x=6 mol %, the melt was splat cooled between two stainless steel plates at room temperature to avoid crystallization. The amorphous state of all samples was verified by x-ray diffraction (not shown). The glass transition (Tg) and glass crystallization (Tv) temperatures were determined by differential thermal analysis (Netzsch STA 409). The Tg values were found between 613 and 649 °C. These glasses present a good thermal stability against crystallization as ΔTv=Tv−Tv varies between 68 and 84 °C. The Tg is maximum for x=4 mol % and decreases as x increases due to the well-known boron anomaly phenomenon.

Raman measurements were performed at room temperature in the wavenumber range from 200 to 1800 cm−1 with a T64000 Jobin-Yvon confocal micro-Raman spectrometer using a 514.5 nm excitation line of a Coherent 70C5 Ar+ laser at 2.8 W. The RIR spectra were recorded over a wide wavenumber range between 25 and 5000 cm−1 under vacuum with a Bruker IFS 113v interferometer.

Figure 1 shows the Raman spectra of the studied glasses. Note that the band intensities of the spectra were reduced using the Bose–Einstein population factor. To get a deeper...
insight into this behavior, we fitted the Raman spectra with a set of Gaussian curves, each one corresponding either to borate groups or modifier cations (Y$^{3+}$ and Ca$^{2+}$), as illustrated in Fig. 1 for the $x=4$ mol % glass composition. We have found that a minimum of twelve Gaussian bands were necessary to fit well the experimental data. The assignment of the band positions was performed by comparison with previous data on other borate glasses and crystals and are displayed in Table I. Shifts in the band positions are observed in Fig. 1 when $x$ is varied. These shifts reflect complex changes in the relative proportions of borate groups. From Gaussian curves fits to Raman spectra, we can then deduce that the addition of calcium oxide to the glass composition increases the amount of orthoborate ($\sim 930$ cm$^{-1}$) and pyroborate ($\sim 1250$ cm$^{-1}$) groups present in the network while the pentaborate ($\sim 500,770$ cm$^{-1}$) amount is decreased. We note a remarkable evolution of the glass structure with composition (increasing $x$) toward that of the YCOB crystal, which presents the most intense Raman band at 930 cm$^{-1}$ due to internal vibrations of (BO$_3$)$^{3-}$ groups.$^{17,18}$

To get a better insight into the structure of the YCaB glasses, we then focused on RIR measurements, which yield complementary structural and optical information.$^{12,19}$ As the RIR spectra were collected in a wide range (from 25 to 5000 cm$^{-1}$), the simultaneous study of both glassy network structure in the mid-infrared (MIR) and cation network interactions active in the far-infrared (FIR) could be considered. As shown in Fig. 2, the spectra were fitted with the DFM proposed by De Sousa Meneses et al.$^{20}$ using the curve fitting software FOCUS.$^{21}$ The Gaussian causal profiles take into account the broadening of the vibration mode due to structural disorder, and the minimum number of bands that well represent the borate groups was deduced from Raman data.

In the inset of Fig. 2, we can observe a shift of the Christiansen point toward lower wavenumber (from 1565 to 1520 cm$^{-1}$) and an increase of the reflectivity in the high wavenumber range, both indicating an increase of the refractive index with the increase of yttrium oxide content. The boron-oxygen arrangements are active in the MIR range (500–1600 cm$^{-1}$), where the 500–850 cm$^{-1}$ region is attributed to the bending vibrations of borate segments. The 850–1200 cm$^{-1}$ region is due to the stretching vibration of structural groups containing B$_2$O$_4$ tetrahedra such as diborate, triborate, tetraborate, or pentaborate groups ($\bigodot$ represents the boron-oxygen units) and an increase of the reflectivity in the high wavenumber range (from 890 to 1250 cm$^{-1}$). The band at 1600 cm$^{-1}$ is due to the stretching vibrations of structural units containing B$_2$O$_4$ tetrahedra such as diborate, triborate, tetraborate, or pentaborate groups ($\bigodot$ represents the boron-oxygen units). According to Ref. 13.

According to Ref. 14.

According to Ref. 15.

According to Ref. 16.

![FIG. 1. (Color online) Normalized Raman spectra of the YCaB glasses. The Gaussian bands associated to the vibration modes are shown for the $x=4$ mol % composition.](image1)

![FIG. 2. (Color online) Experimental RIR spectra of the YCaB glasses. Continuous lines are fits using the dielectric function model. The inset shows the RIR spectra in the large wavenumber range.](image2)
sents a bridging oxygen). Finally, bands in the region between 1200 and 1500 cm\(^{-1}\) arise from the contribution of B–O stretching vibrations in trigonal arrangements such as metaborate chains and rings, pyroborate, and orthoborate groups.\(^7\)\(^{16}\)\(^{22}\)\(^{23}\) The main changes with the addition of metal oxides occurred in the FIR region (100–400 cm\(^{-1}\)) due to Ca\(^{2+}/\)Y\(^{3+}\) oxygen bonding, and in the MIR, which can be assigned to a change in the relative quantity of fourfold and threefold boron coordinated units. The analysis of RIR data corroborates with the evolution of the glass structure obtained from Raman measurements. We can conclude that the complex FIR features of the RIR spectra of YCaB glasses can be related to both differences in coordination of calcium sites and a partial substitution of Ca\(^{2+}\) by Y\(^{3+}\), as found for the RECOB borate crystals\(^3\)\(^{24}\) and calcium borate binary crystal and glasses.\(^7\)

The complex dielectric function, determined using the DFM, directly leads us to the calculation of the complex refractive index of our glasses, displayed in Fig. 3. Illustrating our fitting procedure, we show in the inset of Fig. 3 the imaginary part of the dielectric function (\(\varepsilon''\)), together with the twelve causal Gaussian bands, each associated with vibrations of borate groups or Ca–O and Y–O bonds. In the high wavenumber range (5000 cm\(^{-1}\), i.e., a wavelength of \(\lambda=2\) \(\mu\)m), the calculated refractive index is \(n=1.597\) and 1.627 for the glasses \(x=4\) and 5 mol \%, respectively. For the sake of comparison, we have calculated the refractive indices from the Sellmeier equation for the YCOB crystal obtained by Li \textit{et al.}\(^{25}\) for example, in the near IR region (\(\lambda=2\) \(\mu\)m), \(n_1=1.669\), \(n_2=1.700\), and \(n_3=1.709\). Given the differences in compositions (boron excess in the glasses, which lowers the overall polarizability of the medium) and in structure, the remarkable proximity between refractive indices of the crystal and glasses (average \(\Delta n=0.07\)) implies that the DFM used here is an adequate tool to deduce materials optical properties. Furthermore, the possibility of doping the YCaB glasses with trivalent RE ions opens up interesting perspectives in terms of materials combining the good optical properties of crystals and the ease of glass processing. As an example, we recently showed that neodymium-doped YCaB glasses exhibit a more sensitive thermoluminescent response than the undoped samples.\(^{26}\)

In conclusion, glasses in the YCaB system were prepared and their structure and optical properties were investigated by Raman and RIR spectroscopies. The glasses are formed by a complex borate structure, comprising metaborate chains and rings, pentaborate, diborate, pyroborate, and orthoborate groups. The deconvolution of the RIR spectra with the present DFM is a powerful technique to predict the complex dielectric function and complex refractive index of such materials. We believe that the spectral features in the FIR region (50–400 cm\(^{-1}\)) of these complex constants can be associated with different available Ca\(^{2+}/\)Y\(^{3+}\) sites, as in the case of YCOB and calcium diborate crystals. Regarding the optical and materials properties, the YCaB glasses are promising materials for doping with luminescent trivalent rare-earth ions.

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