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Luminescence and properties of La_2O_3–B_2O_3–M_2O_5:Ln (M=Nb(V) or Ta(V)) and La_2O_3–B_2O_3–M_2O_5–PbO/Bi_2O_3 glasses

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Abstract

New glasses of $(19-y)La_2O_3$–$(81-x)B_2O_3$–xM_2O_5: yLn^{3+} (M= Nb or Ta; Ln= lanthanide ion) and $19La_2O_3$–$(61-z)B_2O_3$–$20Nb_2O_5$–zPbO/Bi_2O_3 composition have been prepared and characterized. Homogeneous transparent glasses are obtained with concentrations up to 20 mol% Nb_2O_5, 10 mol% Ta_2O_5, PbO or Bi_2O_3 and 3 mol% Ln^{3+}. These glasses have large chemical resistance and surface hardness, high refractive indices, excellent transparency in the visible IR region (400–1800 nm), and intense UV absorption. The luminescence of niobate and tantalate MO_6 groups is reported for the first time in glasses. Intense luminescence is observed for Eu^{3+}, Dy^{3+}, Tb^{3+}, or Tm^{3+} in $19La_2O_3$–$61B_2O_3$–$20Nb_2O_5$ glasses upon UV excitation into the MO_6 groups, showing that these materials are interesting hosts for optically active Ln ions. © 1998 Elsevier Science S.A.

Keywords: Glasses; Non-linear optical properties; Niobate luminescence; Lanthanide luminescence

1. Introduction

Non-linear optical materials have become an important scientific and technological frontier due to their potential application in photonics. Inorganic homogeneous glasses with large refractive indices seem to be very promising in this respect, having a long interaction length, high transparency, high chemical and thermal durability, high damage thresholds and relatively high hardness and rigidity [1]. In this work we have developed new glasses of composition $(19-y)La_2O_3$–$(81-x)B_2O_3$–xM_2O_5:yLn^{3+} (M=Nb or Ta; Ln=lanthanide) and $19La_2O_3$–$(61-z)B_2O_3$–$20Nb_2O_5$–zPbO or Bi_2O_3. Although heavy metal oxide and sulfide glasses present the largest known non-linear refractive indices [1,2], they have a very poor chemical resistance. The introduction of Nb(V) in glasses, besides contributing to a large refractive index, has been shown to lead to non-linear optical properties and to increase chemical resistance and hardness [3–6]. Furthermore, since these new glasses contain a large amount of La(III) they may turn out to be interesting hosts for optically active lanthanide ions.

2. Experimental details

Glass samples of $(19-y)La_2O_3$–$(81-x)B_2O_3$–xM_2O_5:yLn^{3+} (M=Nb or Ta; Ln=Eu, Dy, Tb, Tm) and $19La_2O_3$–$(61-z)B_2O_3$–$20Nb_2O_5$–zPbO or Bi_2O_3 composition have been prepared by melting at 1200°C in Pt–5%Au crucibles, followed by quenching and subsequent annealing at temperatures near the glass transition. The samples were cut and polished into plates about 2 mm thick. Homogeneous transparent glasses have been obtained with concentrations up to 20 mol% Nb_2O_5 and 10 mol% Ta_2O_5, PbO or Bi_2O_3. The concentration of Eu^{3+}, Tb^{3+} and Dy^{3+} were varied up to 3 mol% and that of Tm^{3+} up to 1 mol%.

The samples were characterized by differential thermal analysis (Nb glasses only), IR vibrational spectroscopy, UV-Visible–IR absorption spectroscopy (200–1800 nm), luminescence spectroscopy, density and refractive index determination (Brewster angle technique, using a polarized He–Ne laser). The UV-Visible–IR absorption spectra were recorded with a Beckman DU-7500 spectrophotometer (200–800 nm) and an Ando (400–1800 nm). The IR vibrational absorption spectra were measured on a Bruker IF566 FTIR spectrophotometer, using KBr pellet techniques. The luminescence spectra were obtained by using a SPEX Fluorolog DM3000F Spectrofluorometer with double-grating 0.22m SPEX 1680 monochromators, and a 450-W Xe lamp as the excitation source. This set-up is

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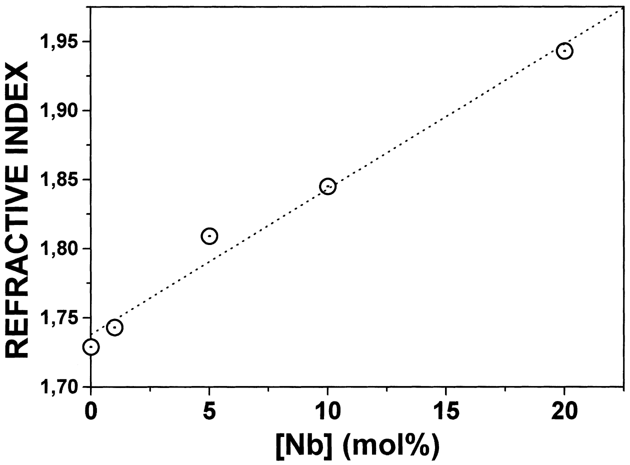

Fig. 1. The dependence of the linear refractive indices of 19La$_2$O$_3$–(81−x)B$_2$O$_3$–xNb2O$_5$ glass samples on the nominal niobium concentration (x=0, 1, 5, 10, 20).

equipped with an Oxford LF205 liquid helium flow cryostat, allowing for measurements down to 4.2 K. The spectra are corrected for the instrumental response.

3. Results and discussion

The glasses have good chemical resistance (no detectable attack after 3 h in 1 M aqueous solutions of HNO_3 or NaOH at 70°C). The surface hardness of the Ta(V)-containing glasses is larger than that for the Nb(V) glasses. The density ρ and the linear refractive index n_0 increase with the Nb(V), Ta(V), Pb^{2+} or Bi^{3+} concentrations: 4.42 g cm^{-3} and 1.784 for 10 mol% Ta_2O_5; 4.50 g cm^{-3} and 1.935 for 20 mol% Nb_2O_5; 5.05 g cm^{-3} and 2.000 for 10 mol% Bi_2O_3; 5.27 g cm^{-3} and 2.015 for 10 mol% PbO (ρ and n_0 values, respectively). As shown in Fig. 1 for Nb glasses, the increase of n_0 with the concentration is almost linear. Preliminary four-wave mixing experiments have shown that the 10-mol% PbO sample is the most promising concerning non-linear optical properties. However, further experiments are needed to provide accurate estimates of n_2.

Table 1 shows the differential thermal analytical data for niobium containing glasses in comparison with a binary La_2O_3–B_2O_3 glass sample. It can be concluded that the increase of the Nb(V) concentration reduces the glass transition temperature T_g and its stability. This indicates that the incorporation of Nb(V) into the glass diminishes the degree of cross-linking between adjacent network chains.

Table 1
Differential thermal analytical data for 19La$_2$O$_3$–(81−x)B$_2$O$_3$–xNb$_2$O$_5$ glass samples

Sample	T_g (°C)	T_x (°C)	T_c (°C)	T_m (°C)
BLA19	684	786	805	1130
BLANB1	660	726	753	1104
BLANB20	636	702	750,768	1020

BLA19, x=0; BLANB1, x=1; BLANB20, x=20; heating rate, 20 K min^{-1}; grain size, 200 mesh; T_g, glass transition temperature; T_x, crystallization onset; T_c, crystallization maximum; T_m, melting temperature.

The IR vibrational spectra (Fig. 2) show that the characteristic BO_3 stretching vibration (1386 cm^{-1} [7]) shifts to lower frequencies as the Nb(V) concentration increases, which is ascribed to a weakening of the B–O bond. Simultaneously, the intensity of the BO_4 stretching vibration (1080 cm^{-1} [7]) decreases, and new peaks, characteristic of Nb–O vibrations [8], appear at 1033, 868, 562 and ~400 cm^{-1}. These observations suggest that the Nb(V) ions are incorporated into the glass network as distorted NbO_6 octahedra, substituting BO_4 groups and giving rise to non-bridging oxygens. The Ta(V) samples behave in a similar way. The IR vibrational spectra of the Pb^{2+}- or Bi^{3+}-containing samples do not show any observable differences relative to the spectra of the glasses without Pb^{2+} or Bi^{3+}.

The introduction of Nb(V) in La_2O_3–B_2O_3 glasses enhances the transmittance in the infrared region to about

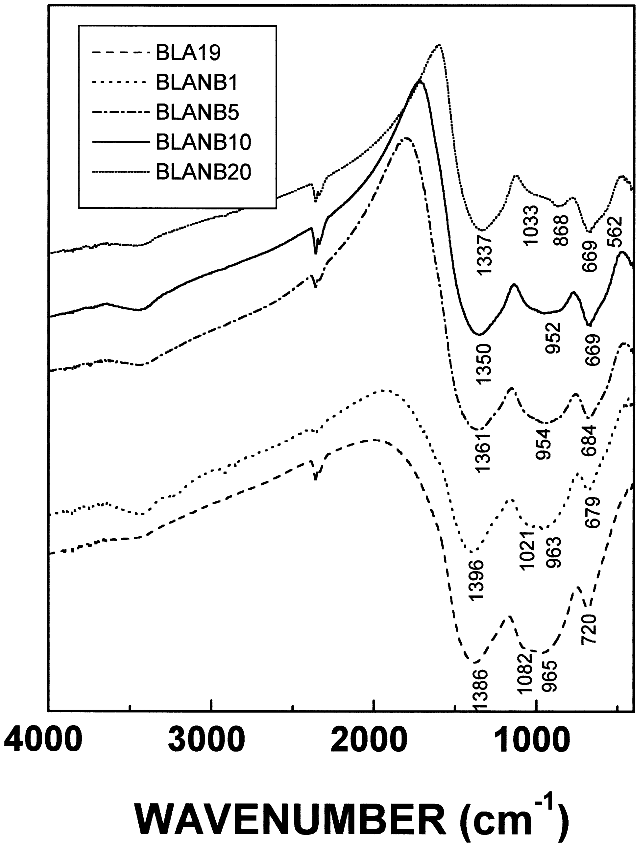

Fig. 2. The infrared vibrational absorption spectra of 19La$_2$O$_3$–(81−x)B$_2$O$_3$–xNb$_2$O$_5$ glass samples (x=0, 1, 5, 10, 20 for samples BLA19, and BLANB1 to BLANB20, respectively). The peak absorption maxima are indicated in the spectra.

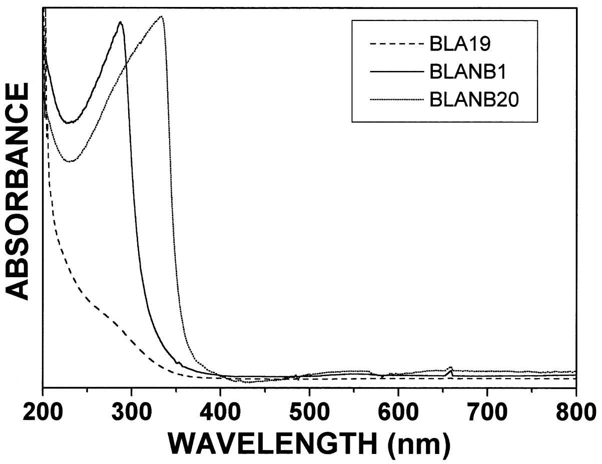

Fig. 3. The UV-Visible absorption spectra for $19La_2O_3$–$(81-x)B_2O_3$–xNb_2O_5 glass samples (x=0, 1 and 20 for BLA19, BLANB1 and BLANB20, respectively).

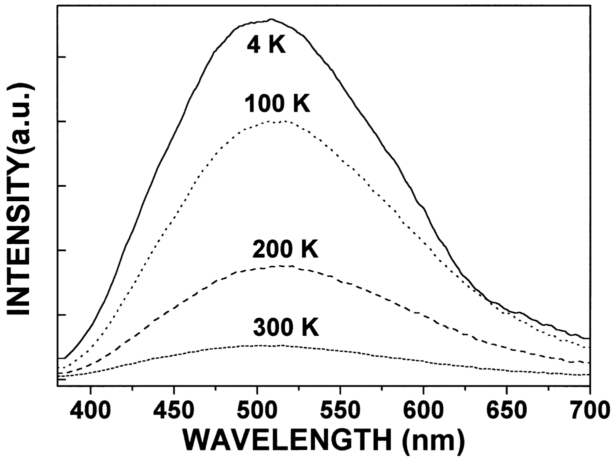

Fig. 5. The luminescence spectra of a $19La_2O_3$–$80B_2O_3$–$1Nb_2O_5$ glass sample at several temperatures, upon UV excitation (260 nm).

97% from 700 to 1700 nm for a sample with 20 mol% Nb(V), and gives rise to a new absorption band in the UV (Fig. 3), which shifts to longer wavelengths as the Nb(V) concentration increases. This band is ascribed to an oxygen→Nb(V) charge transfer transition [9].

The Nb(V)- and Ta(V)-containing glasses show luminescence upon UV excitation (Fig. 4, for 1% Nb: $\lambda_{em(max)}$=490 nm, $\lambda_{exc(max)}$=280 nm, and a 15 300 cm^{-1} Stokes shift, Δ_{ST}; and for 1% Ta: $\lambda_{em(max)}$=420 nm, $\lambda_{exc(max)}$=250 nm, and Δ_{ST}=16 200 cm^{-1}). These emissions are ascribed to NbO_6 and TaO_6 groups [9,10]. Excitation at longer wavelengths gives rise to a weaker emission band shifted to lower energies, which can be ascribed to oxygen-deficient defect groups [10]. Whereas the emission of the Ta(V)-containing glasses shows a small thermal dependence (the emission intensity increases only 70% from 300 to 4.2 K), that of Nb(V)-containing glasses has a very pronounced thermal quenching (Fig. 5). The emission and excitation bands shift to longer wavelengths with increasing Nb(V) or Ta(V) concentration (Fig. 6, $\lambda_{em(max)}$=570 nm, $\lambda_{exc(max)}$=340 nm, Δ_{ST}=11 800 cm^{-1} for 20 mol% Nb(V)), giving rise to energy migration among the MO_6^{-7} groups, and consequent quenching of the luminescence. We note that this shift to lower energies with increasing Nb(V) concentration is also observed in the absorption spectra above (Fig. 3).

Although niobate or tantalate luminescence has never been observed in glasses before, it has been extensively investigated in crystalline materials [9,10], and is known to be strongly dependent on the crystal structure. Isolated and edge- or face-shared MO_6 octahedral groups show efficient luminescence with a large Stokes shift due to a self-trapped exciton state, while corner-sharing of MO_6 groups leads to exciton delocalization, smaller Stokes shift, lower

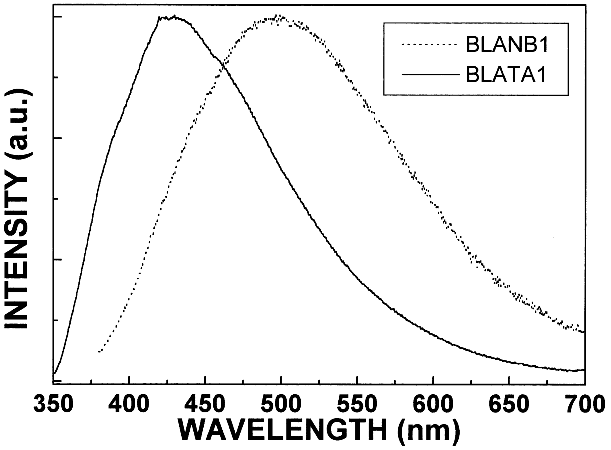

Fig. 4. The luminescence spectra of $19La_2O_3$–$80B_2O_3$–$1M_2O_5$ glasses at 300 K, upon UV excitation (260 nm) for M=Ta (BLATA1) and Nb (BLANB1). The intensities have been normalized.

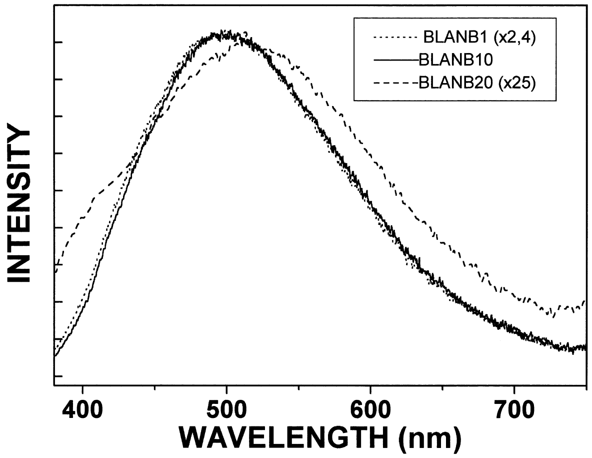

Fig. 6. The luminescence spectra of $19La_2O_3$–$(81-x)B_2O_3$–xNb_2O_5 glass samples (x=1, 10 and 20 for BLANB1, BLANB10 and BLANB20, respectively), upon UV excitation (260 nm). The intensities have been normalized to the intensity of the 10 mol% sample.

energy bands, energy migration and consequent luminescence quenching. Therefore we can conclude that the Nb(V) or Ta(V) ions are incorporated into the glass network as distorted MO_6 octahedra, substituting BO_4 groups and giving rise to non-bridging oxygens. As the M(V) concentration increases, the MO_6 groups condense via corner sharing, giving rise to energy migration and luminescence quenching.

The lanthanide ions Eu^{3+}, Dy^{3+}, Tb^{3+} and Tm^{3+} showed luminescence in the $19La_2O_3$–$61B_2O_3$–$20Nb_2O_5$ glass host (emission colors: Eu^{3+}, red, $^5D_0 \rightarrow {}^7F_J$ transitions, $J=0$–4; Dy^{3+}, whitish-yellow, $^4F_{9/2} \rightarrow {}^6H_J$ transitions, $J=15/2$–11/2; Tb^{3+}, green, $^5D_4 \rightarrow {}^7F_J$ transitions, $J=0$–6; and Tm^{3+}, blue, $^1D_2, {}^1G_4 \rightarrow {}^3H_J, {}^3F_J$ transitions, $J=$ 6–4, 4–2, respectively). A detailed investigation of the luminescence characteristics of optically active lanthanide ions in these new glass hosts is under way, and will be presented in a forthcoming paper.

The introduction of Bi^{3+} in $19La_2O_3$–$61B_2O_3$–$20Nb_2O_5$ gives rise to a new emission, consisting of a broad band with a maximum at 570 nm, upon UV excitation ($\lambda_{exc(max)}=340$ nm). This emission can be ascribed to the so-called D-level [9], based on the strong temperature dependence of the decay times (15 μs at 6 K and 0.6 μs at 300 K), and on the absence of such emission in La_2O_3–B_2O_3:Bi^{3+} glasses. Although the luminescence of Bi^{3+} has been widely investigated and is applied in luminescent materials, especially scintillators, the D-level is not completely understood, and is thought to be a charge-transfer state [9]. In the present case the D-level is likely to be a $NbO_6 \rightarrow Bi^{3+}$ charge transfer state. A more detailed discussion of this point lies beyond the scope of this paper and will be presented elsewhere.

4. Conclusions

The luminescence and properties of new glasses of $(19-y)La_2O_3$–$(81-x)B_2O_3$–xM_2O_5:yLn^{3+} (M=Nb or Ta; Ln=Eu, Tb, Dy, Tm) and $19La_2O_3$–$(61-z)B_2O_3$–$20Nb_2O_5$–$zPbO/Bi_2O_3$ composition are reported. Undoped glasses with low M(V) concentration show efficient broad band luminescence upon UV excitation, which is ascribed to MO_6 octahedral groups. The emission and excitation bands shift to longer wavelengths with increasing Nb(V) or Ta(V) concentration, giving rise to energy migration among the MO_6 groups, making it possible to excite Ln ions via the strong absorption of the MO_6 groups. The lanthanide ions Eu^{3+}, Dy^{3+}, Tb^{3+}, or Tm^{3+} show intense luminescence in $19La_2O_3$–$61B_2O_3$–$20Nb_2O_5$ glasses upon UV excitation in the absorption region of the MO_6 groups. This indicates that these materials are promising hosts for optically active Ln ions. The vibrational, luminescence, absorption and thermal analytical data are consistent with each other and show that Nb(V) and Ta(V) are incorporated into the glass network as distorted MO_6 octahedra, and condense into metalate subnetworks as the MO_6 concentration increases.

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