Luminescence and energy transfer in La$_2$O$_3$–Nb$_2$O$_5$–B$_2$O$_3$:M^{3+} (M = Bi, Eu, Dy) glasses

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Abstract

The luminescence and energy transfer processes in La$_2$O$_3$–Nb$_2$O$_5$–B$_2$O$_3$:M^{3+} (M = Bi, Eu, Dy) glasses were investigated using luminescence spectroscopy (excitation and emission, down to 4.2 K) and decay time measurements at room temperature. The observation of niobate luminescence implies a considerable degree of short- and intermediate-range order in these glasses. Energy transfer from the niobate groups to the lanthanide ions was observed for Eu^{3+}, but not for Dy^{3+}, suggesting that the energy transfer process occurs to the charge-transfer state of the Eu^{3+} ion, rather than to its f-levels. Inter-Eu^{3+} energy transfer was negligible in the concentration range investigated (up to 3 mol%). In contrast, cross-relaxation processes between Dy^{3+} ions were active at concentrations as low as 0.5 mol%. In the Bi^{3+} doped glasses the energy transfer was observed from the Bi^{3+} excited levels to the oxygen deficient niobate groups.
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1. Introduction

Niobium containing glasses have several interesting properties, such as large non-linear optical susceptibilities [1–3]. Nevertheless, the structural role of the Nb(V) cation is still not fully understood. Recently, we have developed new glasses of composition 19La$_2$O$_{3-x}$M$_2$O$_5$–(81−x)B$_2$O$_3$ (M = Nb or Ta; x = 0−20) [4]. These glasses have showed high chemical resistance, surface hardness

and refractive indices (up to 1.935 for x = 20), excellent transparency in the visible-IR region and intense UV absorption [4]. Their most striking property, however, is the occurrence of niobate and tantalate luminescence upon UV excitation [4], and as far we know, this is still the first and only observation of niobate and tantalate luminescence in glasses. The vibrational, luminescence, absorption and thermal analytical data are consistent with each other, and indicate that the Nb(V) and Ta(V) ions are incorporated into the glass network as MO$_6$ octahedra, condensing into subnetworks as the M(V) concentration increases [4].

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In this work, we have investigated the possibility of energy transfer between the niobate groups and optically active ions, namely, Bi^{3+}, Dy^{3+}, and Eu^{3+}. The lanthanide ions Dy^{3+} ($4f^9$) and Eu^{3+} ($4f^6$) were chosen because both present efficient luminescence in the visible region and have similar ionic radius, but differ with respect to the excited states resonant with the niobate states. For instance, the Dy^{3+} ion has only 4f states, whereas the Eu^{3+} ion has charge-transfer states in addition to the 4f states [5]. The Bi^{3+} ion was chosen for it's closed-shell $6s^2$ configuration, which is known to strongly influence the luminescence of d^0-complexes, such as the niobate group [5]. Furthermore, the effects of the composition on the niobate luminescence were investigated in order to yield quantitative information on the energy transfer processes.

2. Experimental

Glasses with the following designation and composition (i) [xBLANBy:zLn]: $(x-z)La_2O_3$–yNb_2O_5–$(100-x-y)B_2O_3$:zLn ($x = 19$ or 25; $y = 1-20$; $z = 0-5$; $Ln = Eu^{3+}$ or Dy^{3+}); (ii) [BLANBw:Bi]: $24.5La_2O_3$–wNb_2O_5–$(75-w)B_2O_3$: $0.5Bi_2O_3$ ($w = 10-20$); (iii) [BLA]: $(20-a)La_2O_3$–$80B_2O_3$:aLn; and (iv) [BLACN]: $4CaO$–$2Na_2O$–$(19-a)La_2O_3$–$75B_2O_3$:aLn ($a = 0-5$) were prepared from La_2O_3 (Alfa, 99.999%), Ln_2O_3 (Aldrich, 99.99%), Bi_2O_3 (Riedel, 99.99%), B_2O_3 (Alfa, 99.999%) or H_3BO_3 (Merck Suprapur), $CaCO_3$ (Alfa, 99.95%), Na_2CO_3 (Alfa, 99.95%) and Nb_2O_5 (Alfa, 99.9985%) by melting 5 g batches in uncovered Pt crucibles at $1200°C$ for 1 h, and subsequently quenching by pouring onto Pt plates at room temperature. An excess of 12 wt% of B_2O_3 was added to compensate for evaporation losses. In this way the glasses are within $\pm 1\%$ of the nominal composition.

The luminescence spectra were obtained by using a SPEX DM3000F Spectrofluorometer with double-grating 0.22 m SPEX 1680 monochromators and a 450 W Xe Lamp. This setup was equipped with an Oxford LF205 liquid Helium flow cryostat. The spectra were corrected for the instrumental response. Excited state decay-time

measurements were performed at 298 K using the third harmonic of a Nd-YAG laser (10 Hz) as the excitation source. The emission was detected with a modified 1P28 photomultiplier tube, after dispersion through a 0.25 m monochromator. The signal was then analyzed on a boxcar. The temporal resolution of the overall system is ca. 50 ns.

3. Results and discussion

The luminescence of 19BLANB glasses have already been reported [4] and consist of broad band emission upon UV excitation. The emission and excitation bands shifted to longer wavelengths with increasing Nb(V) concentration, for instance, the maxima of the emission ($\lambda_{em(max)}$) and excitation ($\lambda_{exc(max)}$) were 490 and 280 nm, respectively, for 1 mol% Nb_2O_5, and 570 and 340 nm for 20 mol% Nb_2O_5 [4]. Furthermore, the energy difference between the emission and excitation maxima, the so-called Stokes shift (Δ_{ST}), decreased from 15,300 to 11,800 cm^{-1} when the Nb(V) concentration increased from 1 to 20 mol%. The emission intensity decreased by ca. ten times from when the Nb(V) concentration increased from 1 to 20 mol% Nb_2O_5. Excitation at longer wavelengths resulted in a shift of the emission band to lower energies. This shift was more pronounced for higher concentrations. The luminescence intensity decreased 10–100 times when the temperature increased from 4.2 to 300 K [4].

The luminescence of 25BLANB glasses was very similar to that of 19BLANB glasses [4] in all aspects except for the excitation bands. As a representative example, Fig. 1 shows the excitation and emission spectra of the 25BLANB10 and 19BLANB10 samples at 4.2 K. Although the emission maximum occurred at about the same position (viz. 510 nm), the excitation maximum of 25BLANB10 is shifted to much shorter wavelengths (265 nm) compared to 19BLANB10, and thus leading to a large Δ_{ST} (18,000 cm^{-1}). Another difference is the presence in the emission band for 25BLANB10 of a shoulder at 570 nm, whose intensity increases upon excitation at longer wavelengths.

The niobate luminescence has been extensively investigated in crystalline materials [5–9], and is strongly dependent upon the crystal structure. The most efficient luminescence occurs in niobyl groups [7], i.e., an Nb–O group with a short bond distance, approximately 0.17 nm. Structurally isolated NbO_6 octahedra, such as in ordered perovskites and in $MgNb_2(P_2O_7)_3$, are not efficient luminescent centers [10], whereas isolated distorted niobate groups, such as in $LaNbO_4$, where the Nb(V) has a $4+2$ coordination, provide very efficient centers [6]. Edge- or face-shared NbO_6 octahedral groups show efficient luminescence with a large Δ_{ST}, while corner-sharing of NbO_6 groups leads to shift of the optical absorption to
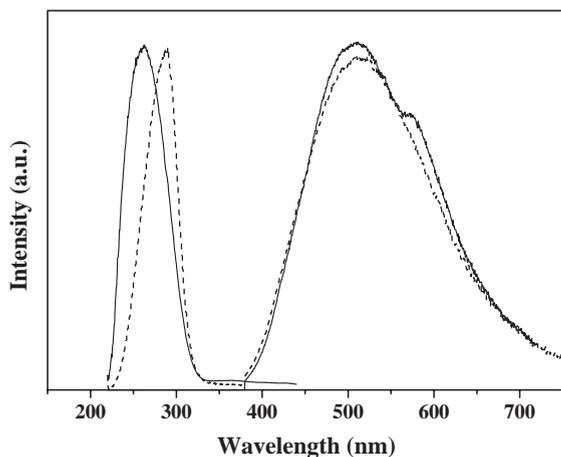

Fig. 1. Emission ($\lambda_{exc} = 260$ nm) and excitation ($\lambda_{em} = 500$ nm) spectra of $25La_2O_3$–$10Nb_2O_5$–$65B_2O_3$ (solid line) and $19La_2O_3$–$10Nb_2O_5$–$71B_2O_3$ (dashed line) glasses at 4.2 K. The intensities have been normalized.

lower energies, exciton delocalization, smaller Δ_{ST}, lower quenching temperatures, energy migration and consequently luminescence quenching [6]. The closer the Nb–O–Nb angles are to $180°$ the more pronounced the effects of the NbO_6 condensation become [6]. Furthermore, cation disorder, such as in $ScNbO_4$ and $MgNb_2O_6$, drastically decreases the luminescence quantum yields and increases the concentration of extrinsic niobate groups, i.e., groups with oxygen deficiency or excess positive charge [6]. These extrinsic groups have been observed in several niobates and present emission and excitation spectra at much longer wavelengths than the intrinsic groups. Some selected spectroscopic properties and their dependence upon the structure are presented in Table 1.

The observation of niobate luminescence thus implies a considerable degree of short- and intermediate-range order in BLANB glasses. Considering the absorption and luminescence spectra [4], and the literature data for crystalline niobates [9] presented in Table 1, it is suggested that at 1 mol% Nb_2O_5 the NbO_6 groups might be condensed into single chains of corner-sharing octahedra with uneven Nb–O bond lengths (0.177 vs. 0.210 nm) leading to approximately isolated NbO_5 units [9]. As the Nb(V) concentration increases these single chains and/or the NbO_5 units can condensed into double chains of corner-sharing octahedra NbO_6 connected in pairs by edge-sharing [9]. This increase in the chains causes a shift of the absorption to lower energies and an increase in energy migration, consistent with the observed values for the emission and excitation wavelengths for the 19BLAN1, 19BLAN10 and

Table 1
Spectroscopic and structural properties of niobate crystals and glasses

Structure	$\lambda_{abs(max)}$	$\lambda_{em(max)}$	$\lambda_{exc(max)}$	Δ_{ST}
α-$LaNb_3O_9$-double chains of corner-sharing octahedra NbO_6 connected in pairs by edge-sharing with Nb–O–Nb $= 130$–$150°$ [9].	320	535	310	14,000
α-$NbPO_5$-corner-sharing octahedra NbO_6 with Nb–O $= 0.177$ nm (niobyl) and O–Nb $= 0.210$ nm leading to approximately isolated NbO_5 [9].	—	490	260	18,000
19BLANB1 [4]	282	490	280	15,300
19BLANB10 [4]	—	510	290	14,800
19BLANB20 [4]	330	570	340	11,800
25BLANB10 [this work]	—	510	265	18,100

Maxima absorption, $\lambda_{abs(max)}$, emission, $\lambda_{em(max)}$, and excitation, $\lambda_{exc(max)}$, wavelengths (nm) and Stokes shift, Δ_{ST} (cm^{-1}).

19BLAN20 samples (Table 1). The luminescence can be attributed to the trapping of the migrating energy by some NbO_6 groups within the niobate subnetwork, although most of the groups will decay non-radiatively. The emission at longer wavelengths can be ascribed to extrinsic groups [6] (niobate groups lacking oxygen or at sites surrounded by borate groups). Due to the glass long-range disorder there will be many chain segments and extrinsic groups with slightly different geometries, giving rise to a dependence of the emission on the excitation wavelengths. As far as the luminescence is concerned, the increase in the La^{3+} concentration seems to partially disrupt the double chains into single corner-sharing chains, giving rise to some niobyl groups and NbO_6 groups with off-center Nb(V) ions, which is partially consistent with the luminescence results for the 19BLAN10 and 25BLAN10 samples (Table 1).

The Ln^{3+} doped BLANB samples presented the characteristic Ln^{3+} luminescence, namely, the $^5D_0 \rightarrow {}^7F_J$ transitions, $J = 0-14$ for Eu^{3+} and $^4F_{9/2} \rightarrow {}^6H_J$ transitions, $J = 15/2-11/2$ for Dy^{3+} upon UV excitation, in addition to the niobate emission. Representative results for these emission spectra are illustrated in Fig. 2 with the respective transition assignments. Samples of BLA:Ln^{3+} and BLACN:Ln^{3+} glasses were also investigated for comparison. The emission spectra of the Ln^{3+} ions are essentially identical in BLA, BLACN and BLANB glasses.

The excitation spectra of the Eu^{3+} emission in BLACN and 25BLANB10 glasses are shown in Fig. 3, and consist of several f–f lines and a broad band in the UV region. The spectral resolution of these spectra and those of Fig. 4 was limited by the nature of the samples (glasses), since the inhomogeneous broadening is very large for transitions of optically active ions, such as Eu^{3+} and Dy^{3+}, in glasses. For Eu^{3+} in BLA and BLACN glasses, Fig. 3a, the observed broad band is ascribed to a charge-transfer transition, which has been shown to play the role of a quenching state [10]. For Eu^{3+} in BLANB glasses, Fig. 3b, however, the broad band cannot be assigned only to the charge-transfer transition of Eu^{3+}. A comparison with the excitation spectrum of the niobate emission in
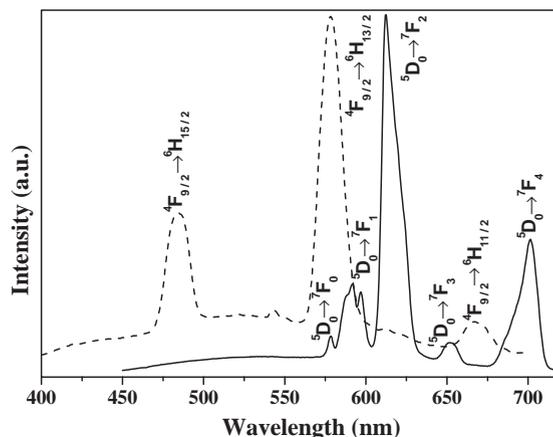

Fig. 2. Luminescence spectra at 4.2 K of Eu^{3+} in $24La_2O_3$–$18Nb_2O_5$–$57B_2O_3$:$1Eu_2O_3$ (solid line) and of Dy^{3+} in $19La_2O_3$–$20Nb_2O_5$–$60B_2O_3$:$1Dy_2O_3$ (dashed line) upon excitation at 290 nm.
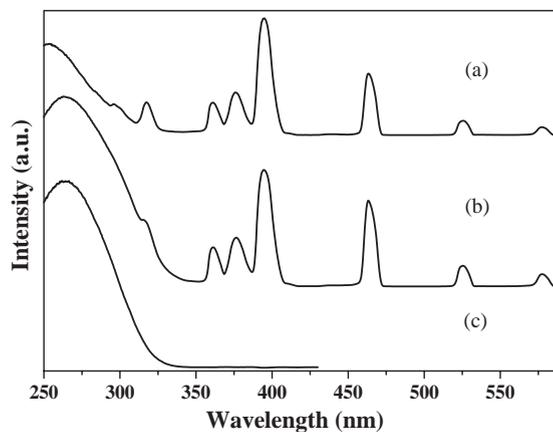

Fig. 3. Excitation spectra at 4.2 K of the: (a) $^5D_0$ emission ($\lambda_{em} = 615$ nm) of Eu^{3+} in $4CaO$–$2Na_2O$–$18La_2O_3$–$75B_2O_3$:$1Eu_2O_3$ glass; (b) $^5D_0$ emission ($\lambda_{em} = 615$ nm) of Eu^{3+} in $24La_2O_3$–$10Nb_2O_5$–$65B_2O_3$:$1Eu_2O_3$ glass; and (c) niobate emission ($\lambda_{em} = 500$ nm) in $24La_2O_3$–$10Nb_2O_5$–$65B_2O_3$:$1Eu_2O_3$ glass.

the same glass sample, Fig. 3c, shows that the broad band observed in the excitation spectrum of the Eu^{3+} emission in 25BLANB10 glass closely resembles the excitation band of the niobate groups. This clearly indicates that there is energy transfer between the niobate groups and the Eu^{3+} ions in BLANB glasses, although the process does
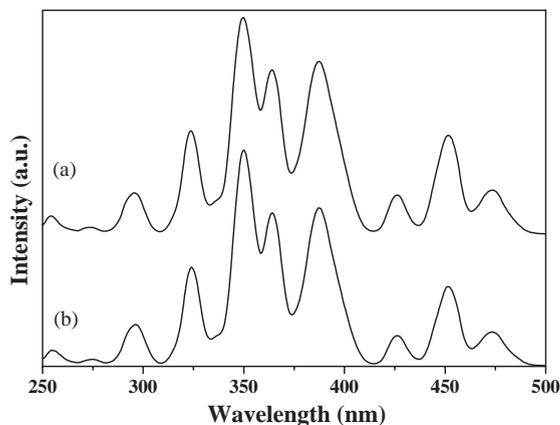
Fig. 4. Excitation spectra at 4.2 K of the $^4F_{9/2}$ emission ($\lambda_{em} = 570$ nm) of Dy^{3+} in (a) $19La_2O_3–20Nb_2O_5–60B_2O_3$:$1Dy_2O_3$ and (b) $4CaO–2Na_2O–18La_2O_3–75B_2O_3$:$1Dy_2O_3$ glasses.

Table 2
Decay times for the Eu^{3+} ($^5D_0$) and Dy^{3+} ($^4F_{9/2}$) emissions at room temperature

Sample	Decay time (ms)
25BLANB1:0.1–3Eu	1.20
25BLACN:0.1Eu	1.50
25BLANB:0.1Dy	0.42
19BLANB:0.5Dy	0.33
25BLANB:5Dy	0.10
25BLACN:0.1Dy	0.69

not seem to be very efficient, since the band is only slightly more intense than the f–f lines.

In contrast, the excitation spectra of the Dy^{3+} emission, presented in Fig. 4, consist of only 4f lines, and are identical in BLACN and BLANB glasses. It should also be noted that the excitation spectrum of the niobate emission in $19La_2O_3$–$20Nb_2O_5$–$60B_2O_3$:$1Dy_2O_3$ glass is, as expected, identical to that of Fig. 3c ($24La_2O_3$–$10Nb_2O_5$–$65B_2O_3$:$1Eu_2O_3$ glass). These results rule out the possibility of energy transfer from the niobate groups to the Dy^{3+} ion.

The differences in the behavior of the Eu^{3+} and Dy^{3+} ions can be assigned to the presence of a charge-transfer state for the Eu^{3+} in this region of the spectrum. Assuming that the energy transfer from the niobate excited states to the Ln^{3+} ions occurred by electric dipole interaction, it would be active over much longer distances (up to ca. 3 nm) for the Eu^{3+} ion if charge-transfer states were involved [5]. In contrast, if the accepting states were 4f states, then the energy transfer would be active only up to ca. 0.5–0.7 nm [5].

The room temperature decay times for the emissions of the excited Eu^{3+} ($^5D_0$) and Dy^{3+} ($^4F_{9/2}$) ions in some selected glass samples are presented in Table 2. For the Eu^{3+} emission in BLANB glasses the decay times are independent of the lanthanide concentration (up to 3 mol%). This

implies that inter-Eu^{3+} energy transfer processes are negligible in the samples investigated, as expected due to the low concentrations and the energy mismatch imposed by the glass disorder [5].

In contrast, the decay times for the emission of the Dy^{3+} ion in BLANB glasses are strongly dependent upon the lanthanide concentration, decreasing as the concentration increases. This effect is ascribed to cross-relaxation between Dy^{3+} pairs, for instance, the $(^6H_{15/2}, {}^4F_{9/2}) \rightarrow (^6H_{9/2}, {}^6F_{1/2})$ process [5] and is also observed for Dy^{3+} in BLACN glasses. These cross-relaxation processes are already noticed at rather low concentrations, for instance, 19BLANB:0.5Dy, suggesting that either the Dy^{3+} ions have a tendency to pair or there are Ln^{3+}-rich domains in these glasses.

The decay times of Eu^{3+} and Dy^{3+} in BLACN glasses are longer than those observed in BLANB glasses, indicating that the niobate groups increased the covalent contribution to the ligand-field at the Ln^{3+} sites. This can be ascribed to larger average oxygen polarizabilities, consistent with the higher refractive indices of BLANB glasses in comparison with BLA and BLACN glasses [4].

We have reported before [4] that the introduction of Bi^{3+} in 19BLANB20 glasses gives rise to a broad band emission ($\lambda_{em(max)} = 570$ nm, $\lambda_{exc(max)} = 340$ nm). Based on the strong temperature dependence of the decay times [4] and on the absence of such an emission in BLACN:Bi^{3+} glasses, this band was tentatively assigned to the so-called "D-level", that is, a $Bi^{3+} \rightarrow Nb(V)$ charge-transfer state [4,5]. However, this assignment is not consistent with the emission of Bi^{3+} in $LaNbO_4$ ($\lambda_{em(max)} = 450$ nm), although an
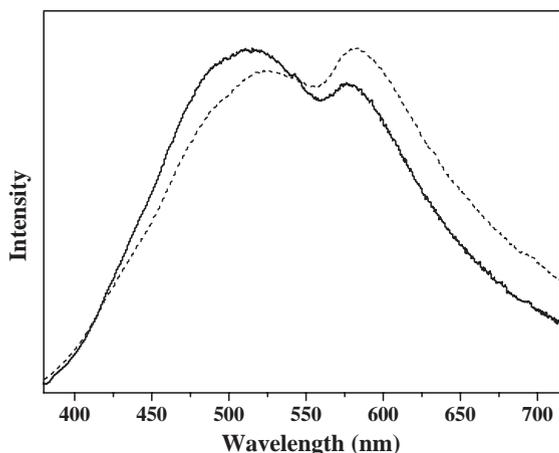
Fig. 5. Emission spectra at 4.2 K of BLANB10:Bi^{3+} upon excitation at 300 nm (dashed line) and 260 nm (solid line).

Fig. 6. Excitation spectra at 4.2 K of BLANB18:Bi^{3+} (dashed line) and BLANB10:Bi^{3+} (solid line) at 520 nm.

absorption maximum at 340 nm is in fact observed and ascribed to Bi–O groups [11]. Therefore, in order to achieve a better understanding of the Bi^{3+} emission in BLANB glasses we have investigated samples with lower Nb(V) concentrations.

The emission spectra of BLANB10:Bi^{3+} and BLANB18:Bi^{3+} upon UV excitation are presented in Fig. 5. They are very similar and can be described as two overlapping broad bands with maxima at 520 and 580 nm, with maxima at 580 nm being more intense for the BLANB18:Bi^{3+} sample.

The excitation spectra of BLANB10:Bi^{3+} and BLANB18:Bi^{3+} for the emissions at 520 nm are presented in Fig. 6. They can be characterized as two overlapping bands with maxima at 270 and 300 nm for BLANB10:Bi^{3+} and an even broader band for BLANB18:Bi^{3+}, with an intense tail extending up to 360 nm.

Excitation at wavelengths longer than 300 nm enhances the 580 nm emission band, whereas excitation at wavelengths shorter than 270 nm enhances the 520 nm emission. The emission band at 300 nm for BLANB10:Bi^{3+} is similar to the excitation of Bi^{3+} observed [10] in BLACN glasses ($\lambda_{em(max)} = 420$ nm, $\lambda_{exc(max)} = 300$ nm). Both bands in the excitation spectra presented a strong temperature dependence, namely, they decreased by a factor 40 for BLANB10:Bi^{3+} and 100 for BLANB18:Bi^{3+} when the temperature increased
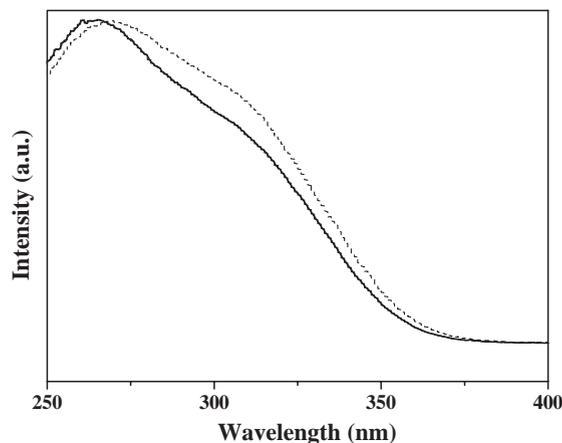
from 4.2 to 300 K. It is important to notice that both emission bands were already observed in the undoped samples (Fig. 1), although the 520 nm was clearly dominant. Furthermore, only the excitation band at 270 nm can be distinguished in the undoped sample (Fig. 1). These results showed that the Bi^{3+} ions transfer their excitation energy preferentially to extrinsic niobate groups, thus suggesting that the Bi^{3+} ions favor sites closer to extrinsic niobate groups, that is, niobates lacking oxygen. It is known that ions with $6s^2$ configuration, such as Bi^{3+}, favor asymmetrical sites and tend to strengthen the asymmetry (pseudo-Jahn–Teller effect) [5]. At higher Nb(V) concentrations (ca. 20 mol% Nb_2O_5) the interaction between the Bi^{3+} ions and the extrinsic niobate groups becomes stronger, favoring the formation of a $Bi^{3+} \rightarrow$ extrinsic niobate charge-transfer state (band at 340 nm).

4. Conclusion

The Nb(V) ions are incorporated into the glass network as NbO_6 octahedra, substituting BO_4 groups and giving rise to non-bridging oxygens. As the Nb(V) concentration increases, the NbO_6 groups condense into a subnetwork by edge-sharing and later by corner sharing, giving rise to energy migration and luminescence quenching.

Energy transfer from the niobate groups to the lanthanide ions was observed for Eu^{3+}, probably due to the presence of charge-transfer states, but not for Dy^{3+}, which has no charge-transfer state in the investigated spectral region. The existence of energy transfer between the Ln^{3+} ions can be ruled out for Eu^{3+} up to concentrations of 3 mol%, but is very important for Dy^{3+}, due to the cross-relaxation processes. The niobate groups increased the covalent contribution to the ligand-field at the Ln^{3+} sites, probably due to the enhancement of the average oxygen polarizability. The Bi^{3+} ions in BLANB glasses transfer their excitation energy preferentially to oxygen deficient (extrinsic) niobate groups.

Acknowledgements

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