

Eu³⁺ and Pb²⁺ Spectroscopy in Lead Germanate Glasses

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Íons Eu³⁺ adicionados como impurezas são utilizados como sondas estruturais no estudo de vidros no sistema binário PbO-GeO₂. As variações espectroscópicas observadas são relacionadas a variações estruturais para diferentes composições. Dependendo da quantidade relativa de PbO, aumento ou supressão da emissão característica dos íons Eu³⁺ podem ser observados. Estruturas vibrônicas observadas nos espectros de excitação de Eu³⁺ são relacionadas a modos de estiramento Ge-O de diferentes espécies germanato que compõem a estrutura vítrea.

Eu³⁺ ions added as impurities are utilized as structural probes in the study of glasses in the PbO-GeO₂ binary system. Spectroscopic variations are rationalized in terms of structural variations with different compositions. Sensitization or quenching is observed for Eu³⁺ emission depending on the PbO content. Vibronic structures observed in Eu³⁺ excitation spectra are related to Ge-O stretching modes of different molecular germanate species composing the vitreous structure.

Keywords: *lead germanate glasses, lanthanides spectroscopy, luminescent probes, glass structure*

Introduction

Lead germanate glasses are well known and may be easily prepared with compositions of up to 65% mol PbO¹. In a previous work we suggested, based on vibrational (IR absorption and Raman scattering) and X-rays absorption (EXAFS) data, that structures are composed mainly of [GeO₄] tetrahedra and [PbO₃] and/or [PbO₄] pyramidal groups². Interestingly enough, there is a controversy in the literature²⁻⁴ about the existence of [GeO₆] octahedral structures proposed for the explanation of the "germanate anomaly", more easily observed in alkali germanate glasses⁵. It has also been proposed for lead germanate glasses³, but we could not unequivocally identify these [GeO₆] structures².

Another spectroscopic technique for studying the vitreous structure is shown here. The utilization of rare earth spectroscopy, in particular Eu³⁺, as a tool for understanding the vitreous structure is well known⁶ and, in addition, rare

earths containing materials have an increasing potential for technological applications⁶.

We present some results for Eu³⁺ ions added as impurities for some glass compositions in the PbO-GeO₂ system. The spectroscopic variations are rationalized in terms of structural variations with different compositions. Also, complex Eu³⁺-Pb²⁺ energy transfer interactions are evidenced in these highly Pb²⁺ concentrated systems.

Experimental Details

Preparation of samples

Glasses were prepared by melting appropriate starting mixtures of oxides in a Pt crucible for 1 h at 1000 °C. The melted mixtures were then cast and poured into graphite molds at 200 °C for annealing purposes. The following compositions were studied (mole fraction): (1-x)GeO₂ .xPbO (x = 0.20, 0.29, 0.40 and 0.50) + 1% in wt. Eu₂O₃.

Spectroscopic measurements

Room temperature excitation and emission spectra (≈ 3 Å resolution) as well as excited state decay times were obtained with powdered samples in a SPEX Fluorolog F1211 fluorimeter equipped with both continuous (450 W) and pulsed (5J/pulse; 3 μ s bandwidth) Xe lamps. Spectra were all corrected for spectral variations for lamp intensity, optics and detection system.

Results and Discussion

Figure 1 shows emission spectra obtained under UV excitation. The Eu^{3+} emission spectrum (Fig. 1a) is composed of the characteristic f-f lines broadened by the statistical distribution of Eu^{3+} sites in the vitreous matrix (inhomogeneous broadening). Assignments could be easily made by comparison with the literature⁶. With an increase in PbO content is observed a variation in the relative intensities of the two bands centered at ≈ 590 and ≈ 615 nm. This feature will be discussed later. Qualitatively, it must be pointed out that the overall emission efficiency decreases with an increase in PbO content. The broad emission band with a maximum at around 430 nm (Fig. 1b) can be assigned to Pb^{2+} $^3\text{P}_0 \rightarrow ^1\text{S}_0$ transition⁷. There is no appreciable shift in the energy position with variation in composition.

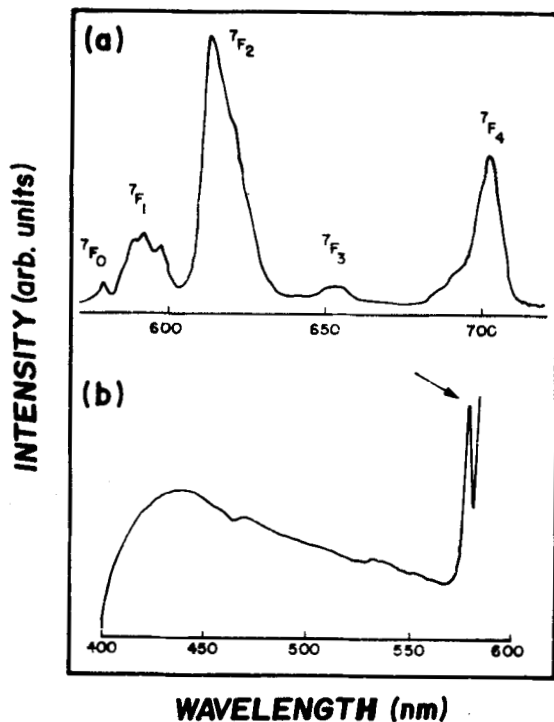


Figure 1. Room temperature emission spectra ($x = 0.29$). (a) Eu^{3+} ($\lambda_{\text{exc}} = 394$ nm). Terminal levels are indicated for the transitions arising from $^5\text{D}_0$ excited state. (b) Pb^{2+} ($\lambda_{\text{exc}} = 315$ nm). Arrow indicates $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition of Eu^{3+} .

Figure 2 shows Eu^{3+} $^5\text{D}_0$ excitation spectra ($\lambda_{\text{em}} = 615$ nm). As for the emission spectra, assignments could be made by comparison with the literature⁶. Besides the intra-configurational $4f^6$ characteristic lines, a broad band centered at 310 nm for the $x = 0.20$ sample is observed. With an increase in the PbO content this band decreases in intensity and is red shifted.

Figure 3 shows Pb^{2+} excitation spectra ($\lambda_{\text{em}} = 430$ nm). At least 4 components that do not shift may be identified in the broad band. Clearly the red shift for the maximum is due to the different contributions of the four components to the overall intensity. This band, as well as the broad band in Fig. 1, may be assigned to the $^1\text{S}_0 \rightarrow ^3\text{P}_{1,0}$ ($6s^2 \rightarrow 6s6p$) electronic transitions of Pb^{2+} configurations⁷. The observation of this band in the Eu^{3+} excitation spectra denote in this way $\text{Pb}^{2+} \rightarrow \text{Eu}^{3+}$ energy transfer processes. In fact $\text{Eu}^{3+} \rightarrow \text{Pb}^{2+}$ back transfer is also observed by the Eu^{3+} 394 nm line in the Pb^{2+} excitation spectra (Fig. 2), showing the complexity of the situation.

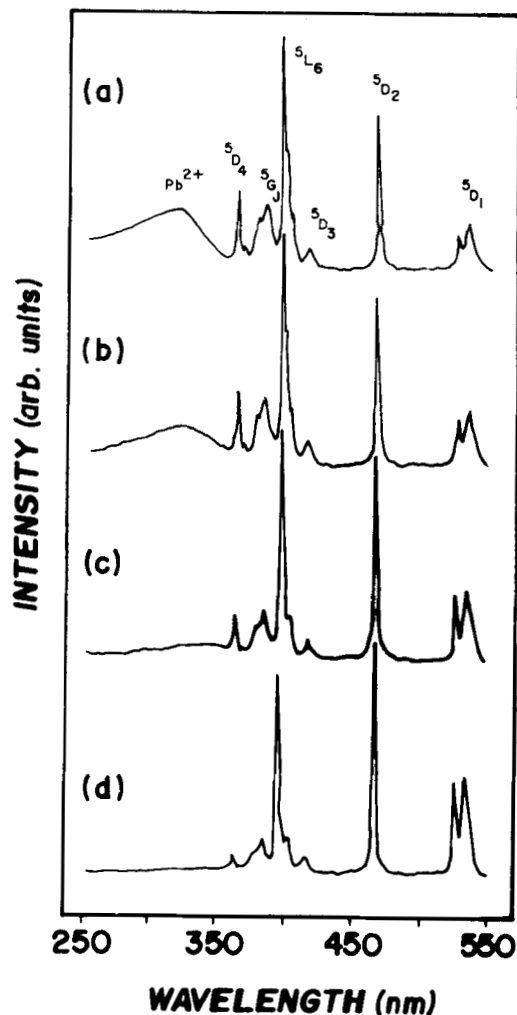


Figure 2. Room temperature Eu^{3+} emission excitation spectra ($\lambda_{\text{em}} = 615$ nm). (a) $x = 0.20$; (b) $x = 0.29$; (c) $x = 0.40$; (d) $x = 0.50$. Excited state levels are indicated for the transitions arising from $^7\text{F}_{0,1}$ levels.

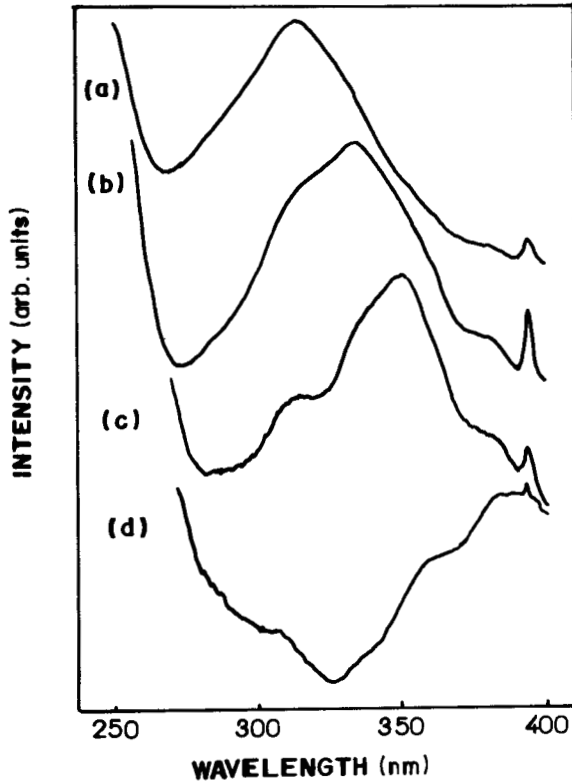


Figure 3. Room temperature Pb²⁺ emission excitation spectra ($\lambda_{em} = 430$ nm). (a) $x = 0.20$; (b) $x = 0.29$; (c) $x = 0.40$ and (d) $x = 0.50$.

Figure 4 shows a selected part of the Eu³⁺ excitation spectra (scale has been changed to cm⁻¹). It shows the weak vibronic structure observed with the ${}^7F_0 \rightarrow {}^5D_2$ (at ≈ 21510 cm⁻¹) electronic transition. These bands correspond on the high energy side of the electronic transition (0-phonon line) to transitions from the vibrationless level of 7F_0 to a one-phonon excited vibrational level of 5D_2 . On the low energy side (not shown in the figure) they correspond to transitions from thermally populated excited vibrational levels of 7F_0 .

As shown in the literature⁸, for oxide glasses these vibronic structures show vibrational modes of molecular anionic structures present in the glass. The bands shown in Fig. 4 could be compared with the high frequency part of the polarized (VV) Raman spectra studied in our previous work². The Raman bands could be deconvoluted in Gaussian components assigned to different anionic germanate species. The evolution of the relative concentrations of those species were then rationalized in terms of a depolymerization processes, with an increase in PbO content. Species with more non-bridging oxygens increase in concentration as x increases.

We show here that vibronics may be deconvoluted in the same way. Hall *et al.*⁹ demonstrated the similarities between vibronics and depolarized (VH) Raman spectra, but, as shown by recent publications⁸, selection rules are

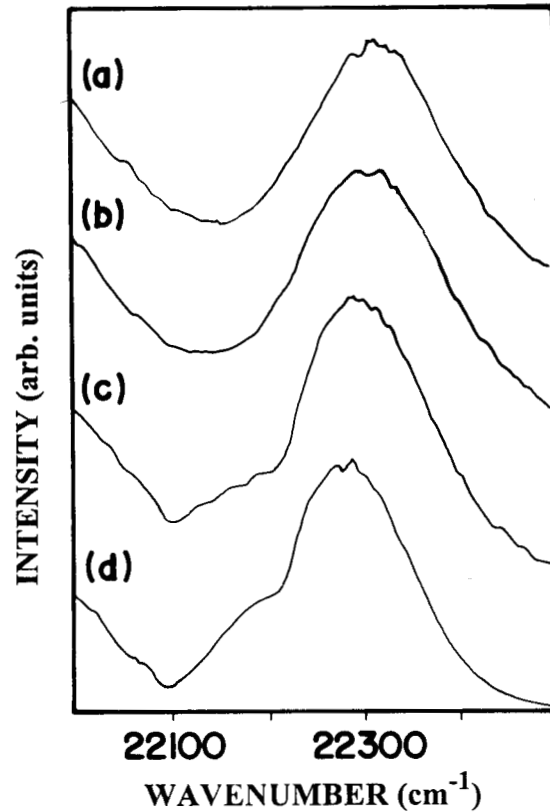


Figure 4. Selected region of Eu³⁺ emission excitation spectra showing vibronic structure for the ${}^7F_0 \rightarrow {}^5D_2$ transition (a) $x = 0.20$; (b) $x = 0.29$ (c) $x = 0.40$ and (d) $x = 0.50$.

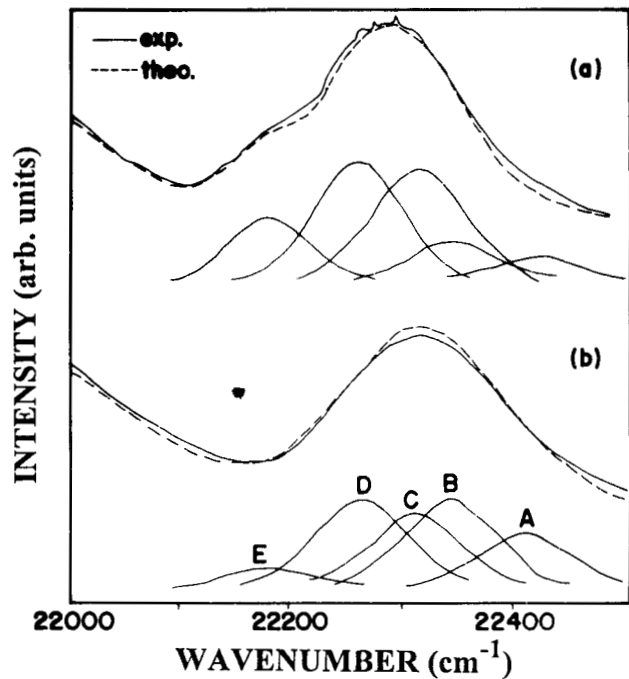


Figure 5. Gaussian decomposition for the vibronic spectra. (a) $x = 0.50$; (b) $x = 0.20$. See Table 1 for assignments of the components.

Table 1. Position, $\bar{\nu}$, and tentative assignments for the Gaussian components obtained from deconvolution of vibronic and Raman^a spectra.

Vibrational Mode	$\bar{\nu}$		Assignment
	Raman	Vibronic	
A	915	900	Q4
B	833	830	Q3
C	810	795	Q2,Q1
D	766	745	Q2,Q1
E	720	668	Q0

^a data from our previous work²

still not well understood for these transitions. In fact, we found poor fits when not considering polarized bands. Figures 5 and 6 show the results obtained from Raman spectra and from vibronic spectra, denoting the "probe" utilization of Eu³⁺ spectroscopy.

In Table 1 we show the mean wavenumber position observed for each component in Raman and in the vibronic spectra. We also add tentative assignments based on our previous work². It must be noted that in the same way observed for Raman data, we could not identify the contribution from octahedral [GeO₆] species to the vibronics. Different basic germanate structures containing 4, 3, 2, 1 and 0 bridging oxygens for the tetrahedral [GeO₄] unit, are labelled Q⁴ to Q⁰

Table 2. Results for electron-phonon coupling strength parameter (g), intensity parameter (η_{21}), maximum position and bandwidth ($\Delta\nu$) for the ⁵D₀ → ⁷F₀ transition and ⁵D₀ observed lifetime (τ).

x	g (.10 ⁻²)	η_{21}	⁵ D ₀ → ⁷ F ₀		τ (ms)
			peak (nm)	$\Delta\bar{\nu}$ (cm ⁻¹)	
0.20	0.95	4.72	578.6	68	1.58
0.29	1.2	4.34	578.8	62	1.47
0.40	1.9	4.36	579.1	57	1.31
0.50	2.6	4.1	579.3	53	1.18

as is usual in NMR notation. In fact, a red shift is observed for the bands observed in the vibronic spectra. For the vibrational mode E (assigned to Q⁰) this shift is more important (≈ 52 cm⁻¹), and in addition this mode could be identified even in the samples with lower PbO content. In Raman spectra we could easily identify this component only for the higher PbO contents. These features could reflect some additional effect of the utilization of Eu³⁺ modifiers, and the localized scale of the vibrational modes probed.

The electron-phonon coupling strength parameter, g , could be evaluated from the intensity ratios between the vibronics and respective electronic (0-phonon) transition¹⁰. Table 2 shows that g increases with increasing x . Then, we may say that non-radioactive decay paths become more important in the depopulation of excited states for the samples with higher PbO content.

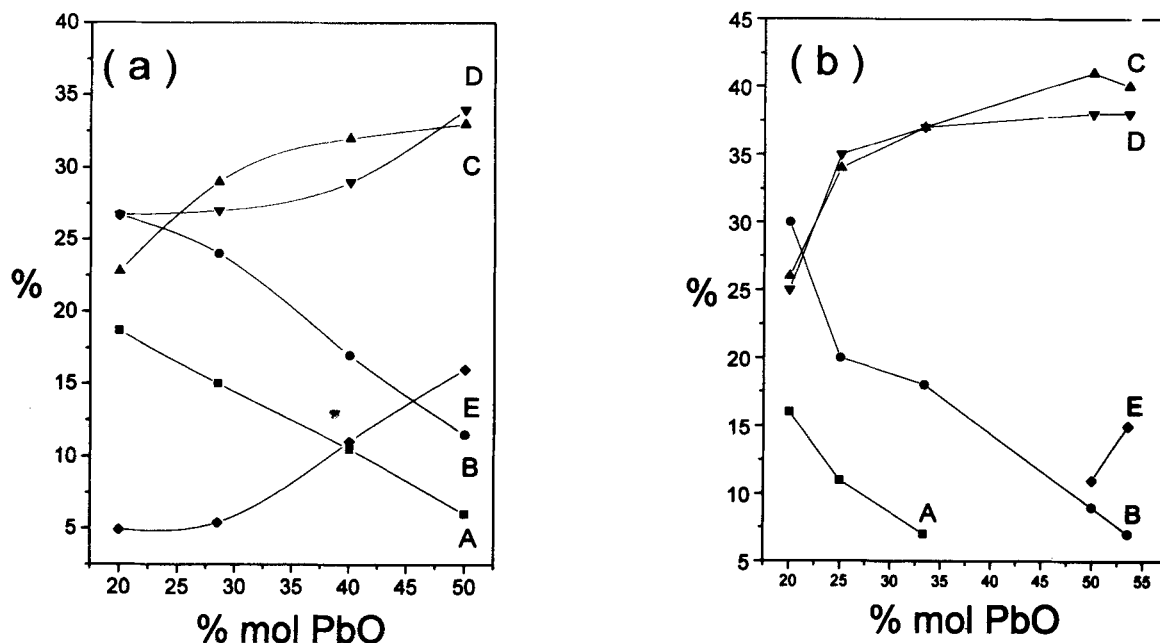


Figure 6. Evolution of the contribution (in %) to the overall band intensity for the five Gaussian components. (a) vibronic spectra (this work); (b) Raman spectra (our previous work²).

Intensities for the electronic transitions were studied in light of Judd-Ofelt formalism⁶. Absolute values for intensities are difficult to obtain experimentally and the Judd-Ofelt intensity parameter, Ω_2 , was taken as the intensity ratio, η_2 , between the hypersensitive $^5D_0 \rightarrow ^7F_2$ transition and the magnetic dipolar $^5D_0 \rightarrow ^7F_1$ transition. This last transition does not depend on ligand field effects and so may be taken as an internal reference. In general, the lower the values for η_{21} , the lower the intensity for the hypersensitive transition and the closer the point symmetry is to an inversion center¹¹. Table 2 gathers the results for the intensities ratios, 5D_0 lifetimes, and also the maxima and the bandwidths ($\Delta\bar{\nu}$) for the $^5D_0 \rightarrow ^7F_0$ electronic transition.

With an increase in PbO content one observes a decrease for the η_{21} , a decrease for the $^5D_0 \rightarrow ^7F_0$ bandwidths and also for the 5D_0 lifetimes, and a red shift for the $^5D_0 \rightarrow ^7F_0$ transition.

Eu³⁺ must play the role of the modifier in the vitreous structure. As previously shown from X-rays and vibrational spectroscopies, and as shown here from vibronic spectra, we concluded for the depolymerization of the structure with an increase in PbO content. One may suppose that in a more polymerized medium steric constraints cause more distorted sites to be disposable for Eu³⁺ modifiers. Decrease in the intensities ratios and also in $\Delta\bar{\nu}$ ($^5D_0 \rightarrow ^7F_0$) must reflect the broader site distribution for Eu³⁺ in the more polymerized structures. A high energy position for the 5D_0 level, together with higher intensity ratios, agree with the idea of less symmetric Eu³⁺ sites for lower PbO contents. This relationship between lower symmetries and higher energy values for the $^5D_0 \rightarrow ^7F_0$ transition have been previously considered¹².

5D_0 lifetime variation seems more difficult to rationalize. It should be observed that the closer the point symmetry is to an inversion center the higher are the lifetimes due to the forbidden character of the electric dipolar transitions. By the variation observed in η_{21} , it can be said that the symmetry is higher for the higher PbO contents, and so lifetimes should increase in this way. The variation observed for τ in Table 2 is exactly contrary to this. Lifetimes also decrease with decreasing η_{21} . Two mechanisms must be evoked to account for this behavior. Firstly, non-radioactive decay paths become more important for the higher PbO concentrations as evidenced by g values in Table 2. Secondly, quenching due to Eu³⁺ \rightarrow Pb²⁺ energy transfer may be considered. In fact, in Fig. 1 it is observed that with an increase in PbO content, the red shift for the broad Pb²⁺ band is accompanied by a relative decrease in intensity for all Eu³⁺ excitation lines situated around 400 nm. It seems that the population or depopulation mechanisms of 5D_0 state depends on the energy position of the Pb²⁺ electronic levels. The higher these levels, the more efficient is the sensitization of Eu³⁺ emission.

Conclusions

We have demonstrated the utilization of Eu³⁺ ions as structural probes in the study of lead germanate glasses. Eu³⁺ and Pb²⁺ excitation and emission bands could be easily assigned to intraconfigurational 4f⁶ and 6s² \rightarrow 6s6p electronic transitions respectively.

For lower PbO contents, Eu³⁺ emission is sensitized by Pb²⁺ \rightarrow Eu³⁺ energy transfer. However, for higher PbO contents a red shift is observed for the maximum of the Pb²⁺ absorption band, and this effect is followed by the quenching processes of Eu³⁺ 5D_0 emission.

Eu³⁺ emission excitation spectra shows vibronic structures that could be deconvoluted in Gaussian components assigned to stretching modes of molecular germanate species present in the vitreous structure. With an increase in PbO content depolymerization processes are observed an increase in the concentration of tetrahedral germanate structures with more non-bridging oxygens.

Acknowledgments

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