

Local Structure of Europium Sites in Oxide Glasses by Nuclear Gamma Resonance

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The symmetry and disorder of the Eu^{3+} site was investigated in some phosphate and borate glasses by means of ^{151}Eu Mössbauer spectroscopy. The quadrupole interaction parameter, which is due to the distortion of the Eu site compared to a cubic symmetry, has been measured together with the asymmetry parameter, which points out the absence of a threefold or fourfold axis of symmetry at the rare earth site. The correlation of the isomer shift with the optical basicity of the glass indicates a covalent component with 6s character in the Eu-O bond. The axial component of the electric field gradient at the Eu site is also correlated with the optical basicity.

Key words: Europium; Oxide Glasses; Phosphates; Borates; ^{151}Eu Mössbauer Spectroscopy.

1. Introduction

Glasses containing rare-earth ions are presently extensively investigated by means of optical spectroscopy, because they are of interest for applications in optical devices, for example laser glasses, fibre amplifiers, upconversion materials. ^{151}Eu Mössbauer spectroscopy provides information about the symmetry and disorder of the rare earth site, allows to evaluate the ionicity of the Eu-O bond, and thus helps to investigate the local structure around rare earth ions in glasses, which in turn affects the optical spectra of these materials.

In some measurements on trivalent Eu in oxide glasses broader absorption lines than expected for Eu^{3+} in a site with cubic symmetry were found [1 - 4]. The separation of the contribution of the true broadening from the contribution of the quadrupole splitting in glasses containing Eu^{3+} has been discussed in [5, 6].

In the present work, the symmetry and degree of disorder of the Eu sites in phosphate glasses, which are of special interest for optical devices [7], is studied. A borate glass with the same cation (zinc) is also considered for comparison. To this end, we have determined the quadrupole interaction (QI) and the full width at half maximum (FWHM) of the absorption

lines in glasses containing trivalent europium. The parameters are discussed in terms of the electronic properties and bonding of the lanthanide ion.

2. Experimental Procedure

Glasses of the molar composition $90\text{M}(\text{PO}_3)_2 \cdot 10 \text{Eu}(\text{PO}_3)_3$, with $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Zn}, \text{Cd}$ or Pb , were prepared by mixing appropriate quantities of reagent grade CaCO_3 , SrCO_3 , BaCO_3 , ZnO , CdO or PbO , $(\text{NH}_4)_2\text{HPO}_4$ or $\text{NH}_4\text{H}_2\text{PO}_4$ and Eu_2O_3 . In the following these samples will be indicated as ECAPO, ESPO, EBPO, EZPO, ECDPO and EPPO, respectively. $\text{Cd}(\text{PO}_3)_2$ was melted at 1050°C for 2 hours in a platinum crucible. $\text{Ca}(\text{PO}_3)_2$, $\text{Sr}(\text{PO}_3)_2$, $\text{Ba}(\text{PO}_3)_2$ and $\text{Zn}(\text{PO}_3)_2$ were melted at 1250°C for 2 hours in an alumina crucible. $\text{Pb}(\text{PO}_3)_2$ was melted at 900°C for 1.5 hours in a ceramic crucible. Each melt was then cast in a brass mould and annealed for 12 h at 200°C ($\text{M} = \text{Pb}$), 350°C ($\text{M} = \text{Zn}$ and Cd) or 450°C ($\text{M} = \text{Ca}, \text{Sr}$ and Ba).

A zinc borate glass of composition $4\text{ZnO} \cdot 3\text{B}_2\text{O}_3$ doped with 2.5 mol% of Eu^{3+} (substituting for Zn^{2+}) (EZBO) was prepared by mixing appropriate quantities of ZnO , H_3BO_3 and Eu_2O_3 in a platinum crucible and melting the batch at 1250°C for 4 hours. The melt

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was cast in a brass mould, and the obtained glass was annealed at 500 °C for 12 hours.

The Mössbauer measurements were performed in transmission geometry, using a source of $^{151}\text{SmF}_3$ with activity 3.7 GBq. The spectrometer was calibrated using a source of ^{57}Co in rhodium and a natural iron foil as absorber. The width of the emission peak of our ^{151}Sm source was measured on $\text{Cs}_2\text{NaEuCl}_6$, which contains Eu^{3+} in a cubic site [8], using absorbers of different effective thickness (t). The effective thicknesses were evaluated using the recoilless fraction of the source $f = 0.6$; $t = 1$ corresponds to a surface density of europium of 3.8 mg/cm². The FWHM found is (1.76 ± 0.01) mm/s with an absorber of thickness $t = 1$, (1.73 ± 0.01) mm/s with $t = 0.5$ and (1.81 ± 0.01) mm/s with $t = 2$. Hence, the expected FWHM is 1.70 mm/s for zero thickness of the absorber.

The isomer shift (IS) of the samples was measured using EuS as reference material; this compound is a better standard than EuF_3 because EuS gives a single line (europium in cubic site). For sake of comparison with the data of literature, the isomer shifts have been referred to EuF_3 by subtracting the shift of the anhydrous fluoride with respect to the sulphide (11.54 mm/s) [9].

The measurements on the phosphate and borate glasses were carried out at room temperature on powder samples with effective thickness $t = 1$, except for the glass EPPO; the thickness t was 0.5 for EPPO in order to optimise the signal to noise ratio. The samples were contained in a Plexiglas holder. In our experimental conditions we can use the thin absorber approximation in the analysis of the experimental data because t is equal or less than 1 [10, 11].

Some trial fits of the spectra showed that it was necessary to take the quadrupole interaction into account. The absorption spectra were then fitted using lines of Lorentzian shape, allowing for the full quadrupole interaction; we used the method for the analysis of pure quadrupole spectra proposed by Shenoy and Dunlap [12], with a value of the quadrupole ratio $R = 1.312$ [13].

The use of a quadrupole multiplet of twelve lines with Lorentzian shape, corresponding to the twelve allowed transitions, is the usual procedure for crystalline materials in the thin absorber approximation [11]. For Eu^{3+} containing glasses it has been demonstrated by Concas *et al.* that it is possible to use this procedure, as we did in this work,

Table 1. Mössbauer parameters as obtained by fitting the spectra. δ is the isomer shift with respect to EuF_3 , γ_p the FWHM of the absorption peak, Γ the FWHM of the Lorentzian components, eQV_{zz} is the quadrupole interaction parameter, η the asymmetry parameter, d , Q_d and χ^2 are the Durbin-Watson and the reduced chi-squared parameters. Errors in the last digit are given in parenthesis.

Sample	δ mm/s	γ_p mm/s	Γ mm/s	eQV_{zz} mm/s	η	d	Q_d	χ^2
EZBO	0.45(2)	2.76(2)	1.85(5)	-6.6(1)	0.83(6)	1.8	1.7	1.1
EZPO	0.37(2)	2.48(2)	1.83(2)	-5.3(1)	0.83(6)	1.8	1.7	1.1
ECDPO	0.32(2)	2.44(2)	1.82(2)	-5.2(1)	0.83(6)	1.9	1.7	0.9
ECAPO	0.37(2)	2.59(2)	1.81(2)	-6.0(1)	0.82(5)	1.3	1.7	1.3
ESPO	0.36(2)	2.67(2)	1.88(2)	-6.1(1)	0.80(5)	1.7	1.7	1.1
EBPO	0.37(2)	2.57(2)	1.86(2)	-5.7(1)	0.81(5)	1.7	1.7	1.2
EPPO	0.29(2)	2.26(5)	1.74(7)	-4.2(3)	1.0(1)	1.7	1.7	1.0

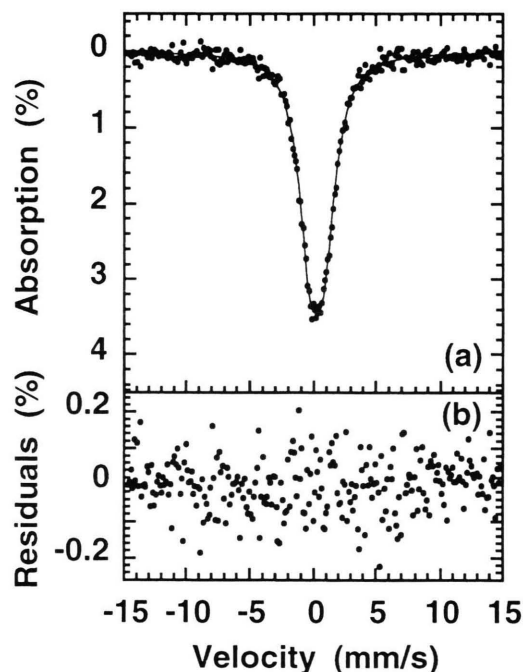


Fig. 1. (a) Absorption spectrum of the sample EZBO: the experimental points and the fitted curve are shown. (b) Difference between experimental and calculated data.

or a convolution of quadrupole multiplets [5, 6, 14, 15].

The quality of the fits must be adequately tested because the component lines of the multiplet are not resolved; it was tested using the usual χ^2 test and a weighted form of the Durbin-Watson d statistics, that was used in the Rietveld analysis of powder diffraction data [16]. The d parameter quantifies the serial

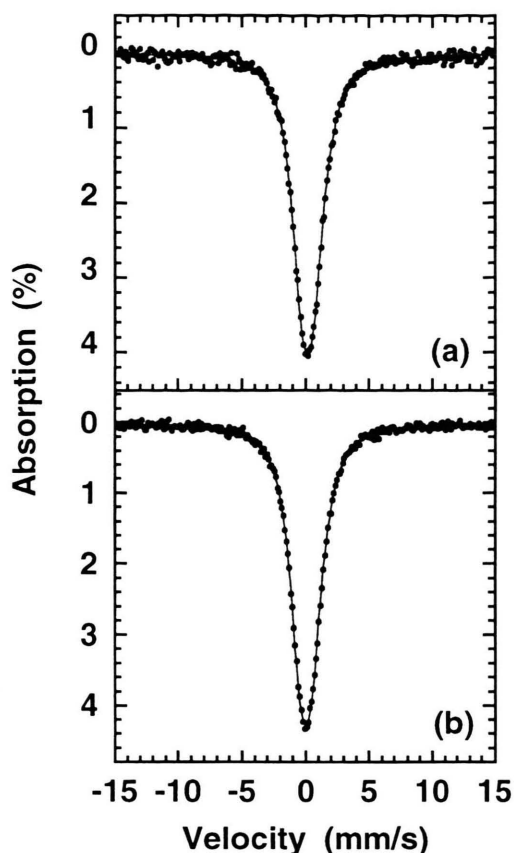


Fig. 2. Absorption spectra of the samples EZPO (a) and ECDPO (b): the experimental points and the fitted curve are shown.

correlation between adjacent least-squares residuals and must be tested against the Q_d parameter; if $|d - 2|$ is smaller than $|Q_d - 2|$, the consecutive residuals are not correlated [16].

3. Results

The experimental spectrum of the EZBO sample can only be fitted satisfactorily allowing for the quadrupolar interaction parameter (eQV_{zz}) and the asymmetry parameter (η); in this procedure all the parameters reported in Table 1 and the background were free parameters of the fit, without any constraint. Figure 1(a) shows the experimental data and the resulting calculated curve; Figure 1(b) shows the difference between the experimental and the calculated data. The lack of structure in the residuals points out that this is the correct peak shape; the values of the control

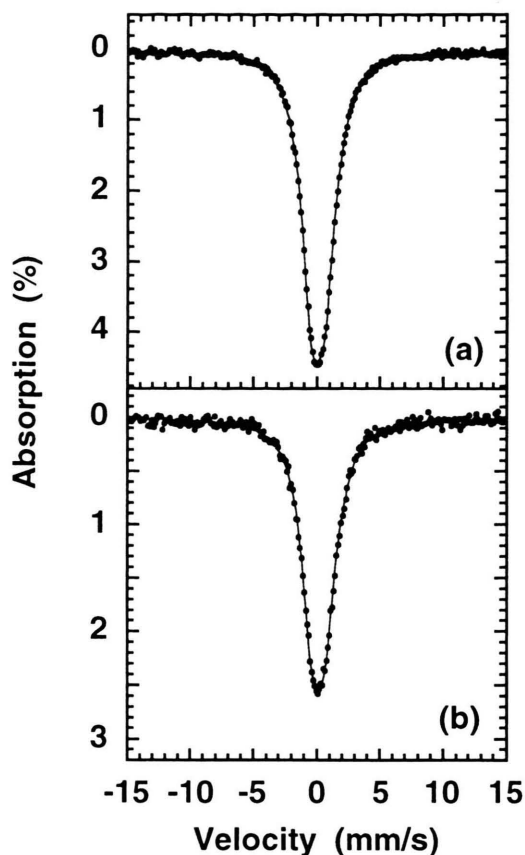


Fig. 3. Absorption spectra of the samples ECAPO (a) and ESPO (b): the experimental points and the fitted curve are shown.

parameters reported in Table 1 confirm that this fit is fully satisfactory.

All the Mössbauer parameters found in this analysis are physically acceptable; the value of η lies between 0 and 1. The value of the FWHM of the components of the multiplet is 1.85 mm/s and is larger than the value measured for trivalent Eu in a cubic site, with the same effective thickness. Therefore the experimental absorption components which come from the splitting due to the quadrupole interaction with $eQV_{zz} = -6.6$ mm/s; these components are overlapped in the spectrum.

The absorption spectra of the phosphate glasses are shown in Figs. 2, 3 and 4; the best fits are also shown for each sample. The physical parameters obtained by the fitting procedure are reported in Table 1 along with the control parameters of the fit.

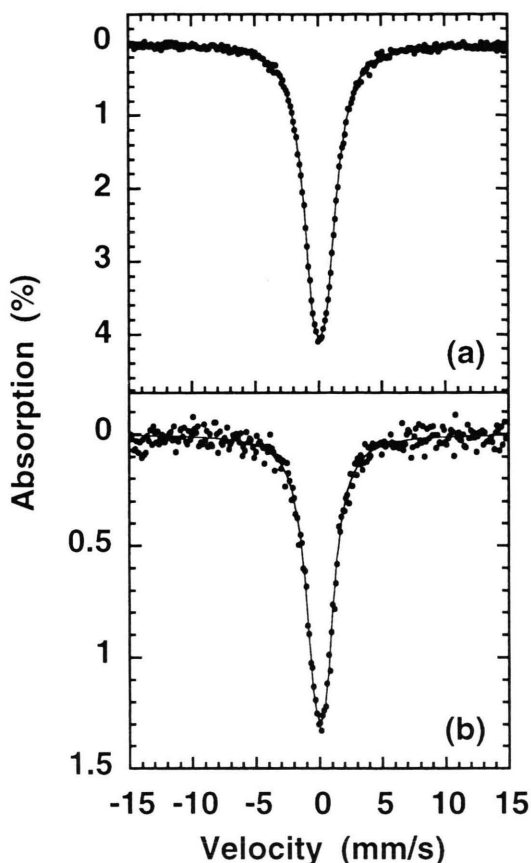


Fig. 4. Absorption spectra of the samples EBAPO (a) and EPPO (b): the experimental points and the fitted curve are shown.

The spectra of the other glasses are also fitted satisfactorily only by accounting for the quadrupolar interaction with asymmetry parameter η different from zero. In the glass EPPO it is also possible to obtain a good fit without the use of the quadrupolar interaction, because of the small magnitude of the quadrupole splitting. However in a study of the optical spectroscopy of a Eu-doped lead metaphosphate glass it was shown by Bettinelli *et al.* that the symmetry of the Eu sites is similar to that of the other metaphosphate glasses [17]; therefore we prefer to fit the spectrum allowing for the effect of the quadrupolar interaction due to the low symmetry of the Eu sites.

4. Discussion

The glasses investigated show only one resonance peak with values of the isomer shift between 0.29 and

0.45 mm/s, corresponding to an oxidation number +3 of the europium atom; there is no detectable presence of Eu^{2+} . The lead metaphosphate shows the smallest value of isomer shift.

The IS of most non-conducting europium compounds in the trivalent charge state deviates from the shift of the fluoride towards a higher electron density at the nucleus [18]; this applies also to the present oxide glasses. This fact is a consequence of covalent admixtures to the bond, since the fluoride compound is considered to be the most ionic species [18].

The electron density of Eu^{3+} at the nucleus, and therefore the isomer shift, increases by adding 6s electrons, while it decreases by adding 5d and particularly 4f electrons because of the screening; the 6p electron has a very small effect [19]. It is possible to estimate the charge transfer to the Eu^{3+} ion by using the optical basicity (A) concept proposed by Duffy and Ingram [20, 21], which measures the electron donation by the oxygen anions. It is defined as

$$A = \sum_i \frac{z_i r_i}{2\gamma_i}, \quad (1)$$

where z_i is the oxidation number of the i th cation, γ_i is its basicity moderating parameter, r_i the atomic ratio of the i th cation and of the oxygen, and the sum is extended over the number of cation species. The optical basicity of the undoped glass measures the electron donation by the oxygen anions to the metal ion used as probe, i.e. the europium.

Figure 5(a) shows the isomer shift of the phosphate and borate glasses versus the optical basicity, calculated using the parameters given by Duffy [20 - 22]; there is an increasing trend of the IS with the optical basicity. This result agrees with the correlation found by Tanabe *et al.* in silicate and aluminate glasses [2]. The correlation that we found indicates that the charge transfer to the Eu^{3+} ion is mainly towards the 6s orbitals. However the irregular tendency of the IS shows that the f, d, and p orbitals play a role in the charge transfer.

The QI parameter is proportional to the axial component (V_{zz}) of the electric field gradient (EFG) by a factor eQ , where e is the proton charge and Q is the quadrupole moment of the nucleus in the ground state; V_{zz} is given by the relation

$$V_{zz} = V_{zz}^{\text{latt}} + V_{zz}^{\text{val}}, \quad (2)$$

where V_{zz}^{latt} is the lattice contribution and V_{zz}^{val} the valence contribution. In Eu^{3+} , V_{zz}^{val} is due to a second

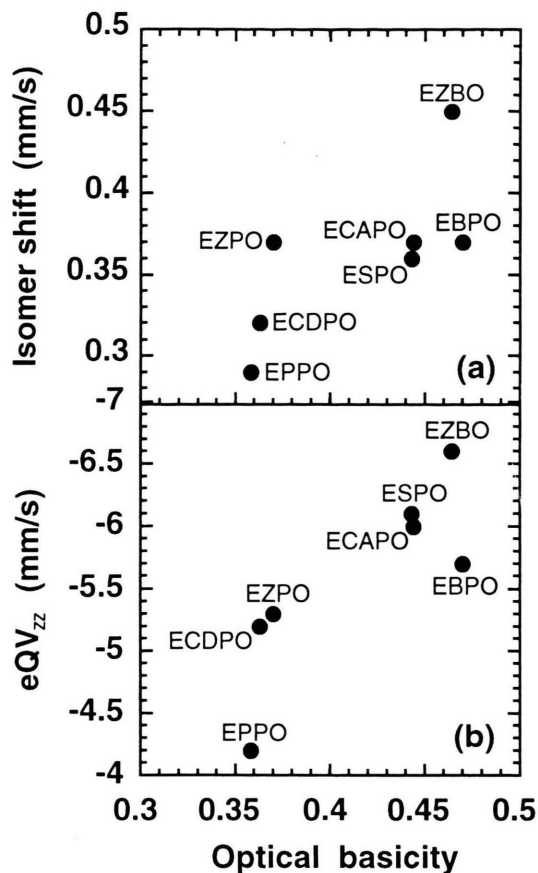


Fig. 5. (a) Isomer shift versus calculated optical basicity. (b) Quadrupole interaction parameter versus calculated optical basicity.

order 4f contribution [23]; in a large class of crystalline oxides it is positive and equal, in absolute value, to about half V_{zz}^{latt} , which is negative [23, 24]. Therefore the QI parameter is usually negative in the trivalent europium oxides, with values ranging from -5 to -8 mm/s [23–25]. Values of the asymmetry parameter around 0.8 are frequently found [24, 25].

In the glasses investigated here, the values of the parameter eQV_{zz} are similar to those found in crystals; this fact suggests that the relative contribution of the two components to V_{zz} is not very different from that found in crystals.

A nonzero QI parameter indicates a deviation of the Eu sites from the cubic symmetry and is therefore related to the distortion of the sites. Moreover, the fact that the asymmetry parameter η is different from zero indicates also a lower symmetry; there is no fourfold or threefold axis of symmetry at the Eu sites.

Figure 5(b) shows that the QI parameter tends to increase, in absolute value, along with the optical basicity. This empirical correlation can be due to an influence of a different degree of covalency of the Eu–O bond on the axial component of the EFG; it is consistent with the observation of an increase of V_{zz} on decreasing the minimum Eu–O distance in an isostructural series of oxides (pyrochlores) [23].

The true broadening of the Lorentzian component of the multiplets results from local inhomogeneities of the hyperfine fields [26]; these can be due to stoichiometric inhomogeneities, impurities and defects, also found in crystals [27] or, more importantly, to the disordered structure of the glass [15, 28, 29]. The main effect of broadening is due to the distribution of the quadrupole interaction parameters, as it happens in the ^{57}Fe spectroscopy [15]. The FWHM measured in our glasses must be compared with the FWHM measured in crystalline trivalent cubic Eu (in $\text{Cs}_2\text{NaEuCl}_6$) with the same effective absorber thickness, which is $t = 0.5$ for EPPO and $t = 1$ for the other samples; the broadening ranges from 0.01 mm/s in the glass EPPO to 0.12 mm/s in the glass ESPO.

The widths of the Lorentzian components are not directly comparable with those reported in literature because of the different linewidths of the various $^{151}\text{SmF}_3$ sources [25]. Nevertheless, it is possible to say that the linewidths of the components that we found are not very different from those found in crystals. Our results agree with the results found by Coey *et al.* [30] in fluorozirconate glasses, where the FWHM of the absorption peak of Eu^{3+} , which includes an unresolved quadrupole splitting, was found to be 2.10 mm/s.

The larger broadening in our glasses (0.12 mm/s in the glass ESPO) results to be about 7% of the crystalline line width measured in the same conditions (1.76 mm/s); this fact indicates that the disorder of the glass structure has no dramatic effect on the width in glasses containing Eu^{3+} .

The behaviour of the EPPO glass deserves some further comments. In fact, the glass EPPO shows the lowest values of the IS and QI parameters, and the smallest linewidth. In this regard, we note that a lead metaphosphate glass doped with Nd^{3+} was found to be characterised by the lowest values of the Judd–Ofelt intensity parameter Ω_2 found in oxide glasses. This behaviour was related to the strong and directional nature of the Pb–O bond [31]. We suggest that this explanation can also be invoked in the case of the IS

and QI parameters of the EPPO glass. As far as the linewidth is concerned, it has been shown recently by some of us that the presence of large amounts of PbO in the glass host induces a small degree of disorder at the sites of the lanthanide ion [32].

6. Conclusions

In the phosphate and borate glasses that we examined, the europium atom was found to have the oxidation number +3. The bond is mainly ionic with a small covalent admixture. The main transfer charge is into the 6s orbitals of Eu, but the other p, d and f orbitals play also a role.

In all of the glasses investigated the europium ion is accommodated in sites distorted with respect to a cubic symmetry, with no threefold or fourfold symmetry axis. The maximal broadening of the Lorentzian component of the peak amounts to seven per cent of the crystalline width.

The isomer shift and the axial component of the electric field gradient were found to be correlated with the optical basicity of the glass.

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