Hyperfine Interactions at Lanthanide Sites in Europium Doped Oxide Glasses

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A series of europium doped Na_2O-B_2O_3-SiO_2, PbO-GeO_2 and ZnO-TeO_2 glasses was investigated by means of ^{151}Eu Mössbauer spectroscopy. The distortion of the Eu sites has been evaluated in the Na_2O-B_2O_3-SiO_2 glasses by means of the quadrupolar interaction parameter and the asymmetry parameter; the disorder has been estimated by the line width. The occupancy of the sites in the borosilicate glasses is discussed. The correlation of the isomer shift with the optical basicity of the glass is discussed in terms of the degree of covalence of the Eu-O bond.

Key words: Europium; Oxide Glasses; Borosilicates; Germanates; ^{151}Eu Mössbauer Spectroscopy.

1. Introduction

Glass materials containing lanthanide ions exhibit interesting technological properties for applications in the development of optical devices, for example, glass lasers, fibre amplifiers, and upconversion materials. It is well known that the optical properties of these materials are influenced by the local structure of the sites accommodating the lanthanide ions [1]. Several techniques have been employed in order to obtain information on this local structure, such as X-ray diffraction [2], extended X-ray absorption fine structure [3], and molecular dynamics simulations [4]. In this field, the europium ion can be considered as a very useful structural probe for the lanthanide sites in glasses, as it is possible to employ in a simple way informative experimental techniques such as Fluorescence Line Narrowing (FLN) and Mössbauer spectroscopy. FLN is a powerful optical technique which has widely been used to obtain a precise insight in the distribution and symmetry of the sites occupied by the dopant [5 - 7]. On the other hand, it has been shown that ^{151}Eu Mössbauer spectroscopy represents a sensitive and relatively unexploited tool to investigate the local structure of the lanthanide sites in europium doped glasses.

Some previous Mössbauer investigations of trivalent europium in glasses did not determine the contribution of the quadrupolar interaction to the observed spectra [8 - 11]. This problem has been investigated for Eu^{2+} in amorphous $EuFe_2Si_2$ by Hodges et al., who fitted the spectrum using a convolution of Lorentzian multiplets [12]. The quadrupolar interaction (QI) in oxide glasses containing trivalent europium has been studied by Concas et al. [13, 14]; the spectra have been analysed using a quadrupole multiplet. The disorder of the lanthanide sites in a glass has been estimated, by comparing the glass to the corresponding crystalline material, in trivalent europium metaphosphate [15]; the distribution of the parameters in the glass, due to the structural disorder, has been determined. The isomer shift was found to be correlated with the optical basicity of the oxide glasses [13, 14].

In this work the investigation of the symmetry and disorder of the Eu^{3+} sites is extended to a series of glasses belonging to the Na_2O-B_2O_3-SiO_2, PbO-GeO_2 and ZnO-TeO_2 systems. The covalent admixture of the Eu-O bond in various glasses is discussed. Some of the glasses under investigation have been the object of previous optical investigations [16 - 19], and the present results are compared with the infor-

Table 1. Molar compositions of the investigated glasses.

Composition	Label
$0.99[25Na_2O{\cdot}75SiO_2]{\cdot}0.01Eu_2O_3$	ENSO
$0.99[33Na_2O{\cdot}67B_2O_3]{\cdot}0.01Eu_2O_3$	ENBO
$0.99[25Na_2O{\cdot}50B_2O_3{\cdot}25SiO_2]{\cdot}0.01Eu_2O_3$	ENBSO
$29PbO{\cdot}70GeO_2{\cdot}1Eu_2O_3$	EPGO7
$39PbO{\cdot}60GeO_2{\cdot}1Eu_2O_3$	EPGO6
$49PbO{\cdot}50GeO_2{\cdot}1Eu_2O_3$	EPGO5
$19ZnO{\cdot}80TeO_2{\cdot}1Eu_2O_3$	EZTO

mation obtained from absorption and luminescence spectroscopy.

2. Experimental Procedure

The glasses under investigation are listed in Table 1. The silicate, borate and borosilicate glasses ENSO, ENBO, and ENBSO [17], and the lead germanate glasses EPGO7, EPGO6, and EPGO5 [18] were prepared as previously described. The glass EZTO was prepared by melting appropriate quantities of ZnO and TeO_2 (Aldrich Analytical Grade) at 800 °C for 30 minutes and quenching the melt on a stainless steel plate. The samples were then annealed for 12 hours at 250 °C.

The Mössbauer measurements were carried out using a source of $^{151}SmF_3$ with activity 3.7 GBq, in transmission geometry. The spectrometer was calibrated using a source of ^{57}Co in rhodium and a natural α-Fe foil with thickness 25 µm. The width of the emission peak of our ^{151}Sm source was measured on $Cs_2NaEuCl_6$, which contains Eu^{3+} in a cubic site [20], using absorbers of different effective thickness (t). The effective thickness is evaluated using the recoilless fraction of the source $f = 0.6$; $t = 1$ corresponds to a surface density of europium equal to 3.8 mg/cm^2. The full width at half maximum (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 the usual EuF_3, as suggested by Cohen et al. [21], because EuS gives a single line (europium in cubic site). The isomer shift of the anhydrous fluoride, referred to the sulphide, is (11.54 ± 0.01) mm/s; for the sake of comparison with literature data, the isomer shifts have been referred to EuF_3 by subtracting 11.54 mm/s [21].

The measurements were carried out at room temperature on powder samples contained in a Plexiglas holder. The effective thickness of the absorber is $t = 1$ for the ENSO, ENBO and ENBSO samples. It has been reduced for the samples containing heavy atoms (Pb, Te) in order to optimize the signal to noise ratio with respect to the time of measurement; we have $t = 0.25$ for the EPGO7 and EPGO6 samples, $t = 0.16$ for the EPGO5 sample and $t = 0.5$ for the EZTO sample.

An effective thickness equal or less than 1, as chosen here, allows the use of the thin absorber approximation in the analysis of the experimental data [22, 23].

The spectra were tentatively fitted with a single line of Lorentzian shape, corresponding to the absence of quadrupolar interaction. This is a good fit for the spectra of the samples containing Pb or Te, which have a low signal to noise ratio.

The absorption peak of the spectra of the three glasses from the Na_2O-B_2O_3-SiO_2 system must be fitted taking the quadrupole interaction into account; in the most general case it splits the nuclear transition into twelve allowed transitions, which give twelve non-resolved absorption lines. The position and intensity of these lines depend on two parameters, the quadrupolar interaction parameter (eQV_{zz}) and the asymmetry parameter (η). These absorption spectra were then fitted using twelve lines of Lorentzian shape; we used the method for the analysis of pure quadrupole spectra proposed by Shenoy and Dunlap [24], with a value of the quadrupole ratio R = 1.312 [25].

The use of a quadrupole multiplet of twelve lines with Lorentzian shape is the usual procedure for crystalline materials in the thin absorber approximation [13]. It has been demonstrated by Concas et al. that it is possible to use the same procedure in Eu^{3+} containing glasses because the line broadening due to the structural disorder is small compared to the line width (about 5%) [13 - 15]; this broadening does not change the line shape.

The quality of the fit was tested using the usual χ^2 test and a weighted form of the Durbin-Watson d statistics; this statistics has been used in the Rietveld analysis of X-ray diffraction data and has been recently introduced in the analysis of Mössbauer data [13, 26]. The magnitude of the d parameter quantifies the serial correlation between adjacent least-squares residuals and is defined as

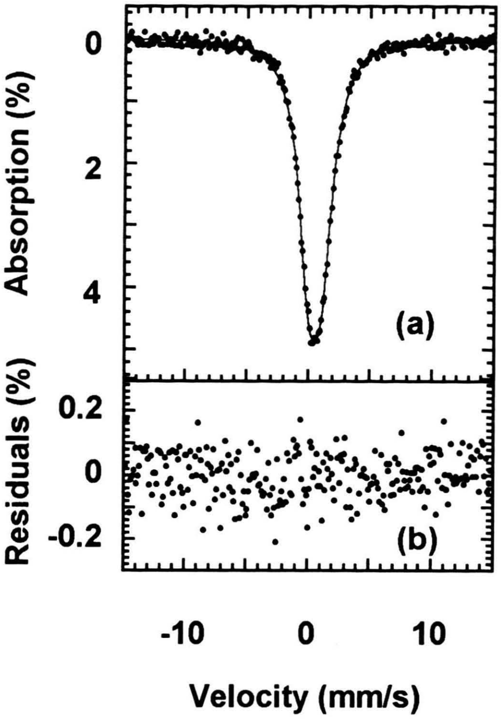

Fig. 1. (a) Absorption spectrum of the sample ENSO. As in Figs. 2, 3, and 4, the experimental data (dots) and the fit curve (full line) are shown. (b) Difference between experimental and calculated data.

$$d = \sum_i \left[(\Delta_i/\sigma_i) - (\Delta_{i-1}/\sigma_{i-1}\right]^2 / \sum_i (\Delta_i/\sigma_i)^2, \quad (1)$$

where the sums are from 1 to N (the number of data points), Δ_i is the ith residual and σ_i indicates the standard deviation. The d parameter must be tested against the Q_d parameter, defined as

$$Q_d = 2[(N-1)/(N-P) - 3.0902/(N+2)1/2], \quad (2)$$

where P is the number of least-squares parameters. If consecutive residuals are not correlated, $|d-2|$ is smaller than $|Q_d-2|$ [26].

Table 2. Mössbauer parameters as obtained by fitting the spectra. δ is the isomer shift with respect to EuF_3, γ_p is the FWHM of the absorption peak, Γ the FWHM of the Lorentzian components, eQV_{zz} 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 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
ENSO	0.83(2)	2.61(2)	1.80(3)	−6.0(1)	0.90(4)	1.8	1.7	1.1
ENBO	0.63(2)	2.71(2)	1.78(3)	−6.4(1)	0.92(4)	1.8	1.7	1.2
ENBSO	0.63(2)	2.86(2)	1.89(3)	−6.7(1)	0.91(3)	1.8	1.7	1.2
EPGO7	0.59(4)	2.9(1)				2.0	1.6	0.9
EPGO6	0.61(4)	2.5(1)				2.0	1.6	1.1
EPGO5	0.71(6)	2.7(1)				1.9	1.6	1.0
EZTO	0.49(3)	2.53(7)				1.9	1.6	1.0

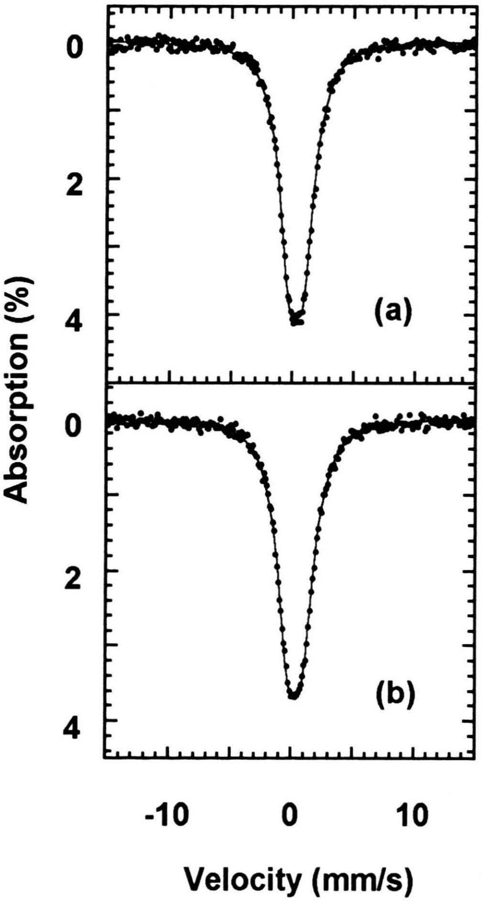

Fig. 2. Absorption spectra of the samples ENBO (a) and ENBSO (b).

3. Results

The spectrum of the glass ENSO, shown in Fig. 1a, can be well fitted allowing for the quadrupolar interaction parameter (eQV_{zz}) and the asymmetry parameter (η); the fitting procedure uses free parameters, without any constraint. Figure 1a shows the experimental data and the resulting calculated curve; Fig. 1b shows the difference between the experimental and the cal-

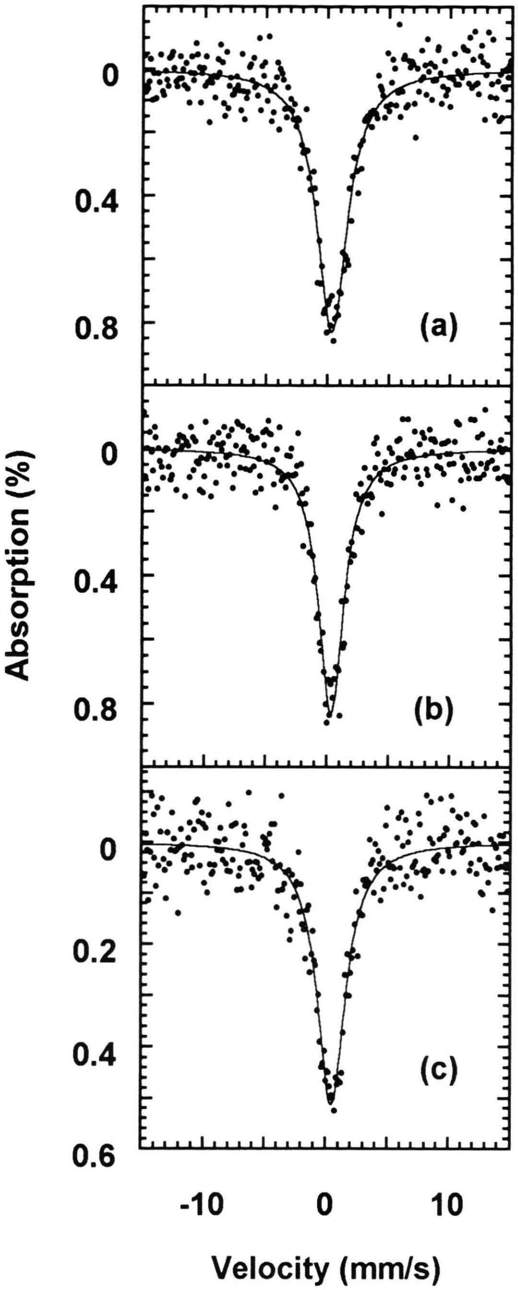

Fig. 3. Absorption spectra of the samples EPGO7 (a), EPGO6 (b) and EPGO5 (c).

culated data. The plot of the residuals gives visual evidence of a random distribution around zero; the values of the control parameters reported in Table 2 confirm the absence of correlation of the consecutive residuals.

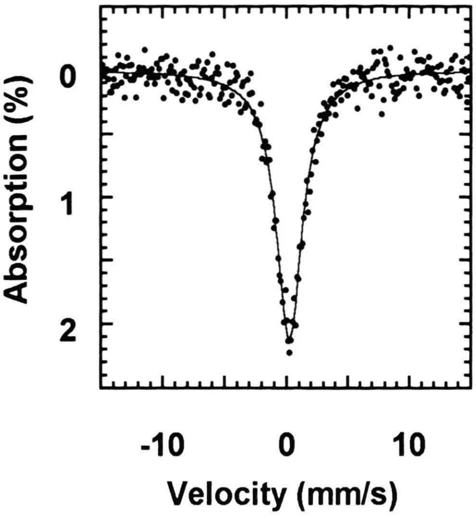

Fig. 4. Absorption spectrum of the sample EZTO.

The values of 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 (1.80 mm/s) is larger than the value measured in crystalline $Cs_2NaEuCl_6$ with the effective thickness $t = 1$. The full width at half maximum of the absorption peak ($\gamma_p = 2.61$ mm/s) can be interpreted as the result of the unresolved splitting of the quadrupole interaction ($eQV_{zz} = -6.0$ mm/s, $\eta = 0.90$) and of the width of the Lorentzian component.

Figure 2 shows the experimental absorption spectra of the glasses ENBO and ENBSO, along with the calculated data resulting from the fitting procedure. The physical parameters obtained by the data analysis are reported in Table 2. Note the striking similarity of the isomer shift and the FWHM of the absorption peaks of these two glasses. In all three samples from the Na_2O-B_2O_3-SiO_2 system the spectra can be fitted satisfactorily only by accounting for the quadrupolar interaction with the asymmetry parameter η not fixed to zero, as shown in Table 2.

Figure 3 shows the experimental absorption spectra of the germanate glasses EPGO7, EPGO6 and EPGO5. The signal to noise ratio is rather low compared to the other spectra; it is due to the large content of lead with respect to the amount of europium in these glasses. This low quality of the spectra allows only a simple data analysis using a single Lorentzian line; the resulting parameters of the fit are given in Table 2.

The spectrum of the glass EZTO is shown in Figure 4. The signal to noise ratio is lower than in the spectra of the borosilicate glasses because of the high content of tellurium. It was not possible to calculate the size of the quadrupolar interaction in this glass; it is due also to the rather smallness of this interaction, as pointed out by the value of the width of the absorption peak. The spectrum has been fitted by a single Lorentzian curve, as reported in Table 2.

4. Discussion

The isomer shifts of trivalent europium compounds range between the IS of EuF_3 (zero mm/s) and the IS of cubic Eu_2O_3 (1.04 mm/s) [27]; they range from the most ionic compound (EuF_3) toward the more covalent compounds [28]. The compounds of divalent and metallic europium have values of IS outside this range. The IS of the glasses investigated in this work are between 0.49 mm/s and 0.83 mm/s; therefore the europium ion has an oxidation number equal to +3.

The tendency of the oxygen anions to donate electrons to the cations in the glass can be estimated by using the optical basicity (Λ) [29 - 31], defined as

$$\Lambda = \sum_i (z_i r_i)/(2\gamma_i). \quad (3)$$

In this definition z_i is the oxidation number of the ith cation, γ_i is its basicity moderating parameter, r_i is the atomic ratio of the ith cation and of the oxygen, and the sum is extended over the number of cation species.

The optical basicity of the glass is a measure of the electron donation by the oxygen anions to the cation used as probe; it can be measured using the optical transitions of the Pb^{2+} ion in lead doped glasses [32] or calculated on the basis of published data [29 - 31]. In the glasses investigated, the europium ion can be considered as a probe; the charge transfer from the oxygen anions to the probe cation can be detected from the isomer shift of the europium.

The experimental relation between isomer shift and optical basicity is shown in Fig. 5; the glass EZTO is not considered because of the lack of a value of Λ for TeO_2. The optical basicity of the undoped borate and silicate glasses was calculated using the basicity moderating parameters given by Duffy [31]; the basicity of the lead germanate glasses was calculated using the values $\Lambda = 0.35$ for GeO_2 (value when the germanium is octahedral) and $\Lambda = 0.8$ for PbO. It is apparent that the isomer shift increases with the optical basicity of the glass.

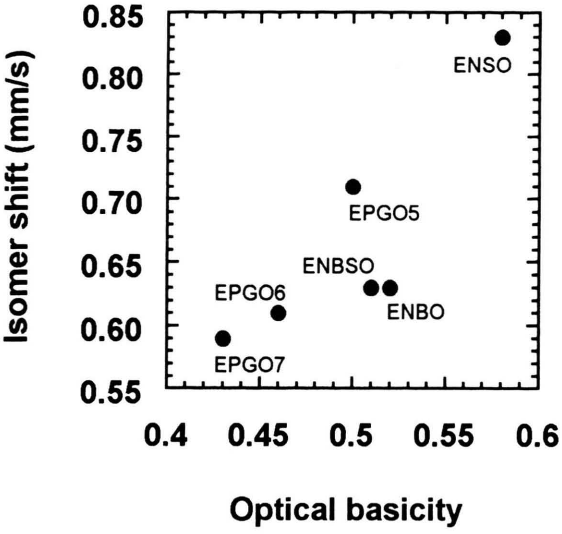

Fig. 5. Isomer shift versus calculated optical basicity.

This behaviour can be discussed on theoretical and experimental grounds. Theoretical calculations show that the electron density at the nucleus and the isomer shift increase by adding 6s electrons and decreases by adding 5d and 4f electrons, because of the screening effect; the addition of 6p electrons has no effect [33]. If it is considered that the optical basicity measures the entire electron donation to the Eu^{3+} ion, the experimental relation between IS and optical basicity points out that the charge transfer to the Eu^{3+} ion is mainly towards the 6s orbitals.

A similar relation between the isomer shift (IS) and optical basicity has been found in other series of Eu^{3+} doped glasses [9, 13, 14]. Therefore the IS represents a measure of the degree of covalence of the Eu-O bond in trivalent europium doped glasses. For the three glasses from the Na_2O-B_2O_3-SiO_2 system, ENBO and ENBSO have a very similar calculated optical basicity and IS's, while the higher optical basicity of ENSO is reflected in a higher IS. These results agree nicely with optical investigations performed on these glasses [17], where the peak position of the $^7F_0 \rightarrow {}^5D_0$ transition was used as a measure of the Eu-O covalence. In the case of the lead germanate glasses, the present results indicate that the Eu-O bond shows about the same covalence for the glasses EPGO7 and EPGO6, whilst EPGO5 is characterised by a stronger covalent character. This is in fair agreement with the results of the optical investigation of the same materials [18]. It is interesting to note that the IS of the three lead germanate glasses shows the expected dependence on the optical basicity if the Λ value for GeO_2 containing octahedral germanium atoms ($\Lambda = 0.35$) is employed. This agrees with the neutron scattering results, which show that a prevailing amount of octahedral germanium atoms is present in high PbO content germanate glasses [34].

The quadrupolar interaction is described by two parameters, the QI parameter and the asymmetry parameter η [35]; the QI parameter is proportional to the axial component of the electric field gradient V_{zz} and is expressed as eQV_{zz}, where e is the proton charge and Q is the quadrupole moment of the nucleus in the ground state. The asymmetry parameter, which ranges between 0 and 1, is defined as

$$\eta = (V_{xx} - V_{yy})/V_{zz}, \qquad (4)$$

where V_{xx} and V_{yy} are the EFG components along the x and y axes.

The QI parameter and the asymmetry parameter are given by a lattice contribution and a contribution of the valence electrons. In a large class of crystalline oxides of trivalent europium, the lattice contribution to the QI parameter is negative with size about two times the valence contribution, which is positive [36, 37]. It results that $eQV_{zz} = 0$ in a system with cubic symmetry of the europium site; η is zero in a system with one threefold or higher symmetry axis passing through the Eu nucleus [34].

The spectra of the three glasses belonging to the Na_2O-B_2O_3-SiO_2 system were fully resolved into the components generated by the quadrupole splitting; the negative value of the QI parameter suggests a larger contribution of the lattice component than in crystalline oxides.

The broadening of the absorption line due to the structural disorder of the glass is given by the FWHM of the Lorentzian components of the multiplet (Γ) compared with the FWHM measured in $Cs_2NaEuCl_6$, with the same source and the same absorber effective thickness.

The glasses ENBO, ENBSO, and ENSO have values of the FWHM of the Lorentzian components between 1.78 mm/s and 1.89 mm/s; these values must be compared with the crystalline width, which is 1.76 mm/s. Therefore the broadening is between 1% and 7% of the line width. Similar values of the broadening have been found in other Eu^{3+} doped amorphous oxides [13, 14]; the largest broadening was found in the amorphous trivalent europium phosphate (11%) [15].

The spectra of the lead germanates EPGO7, EPGO6, and EPGO5 and the spectrum of the zinc tellurite have a rather low signal to noise ratio; only a fit with a single Lorentzian curve is possible. The width of the peak ranges from 2.53 mm/s to 2.9 mm/s in these samples; these values cannot be justified by the broadening due to the structural disorder. Therefore in these samples also the apparent width of the absorption peak is due to the quadrupole splitting; its size cannot be determined in these spectra. The values of the peak width, similar to the width in the sodium borate and silicate glasses, point out that the size of the QI parameter is similar.

The sample ENBSO deserves some further comment. This sample has an intermediate composition between the sodium borate and the sodium silicate sample. The Mössbauer parameters of the Eu^{3+} ion in the borate network and in the silicate network has been determined in the samples ENBO and ENSO; the difference between the two isomer shifts is about 10% of the line width. According to the Bray structural model of sodium borosilicate glasses [38], in a glass with the composition of the ENBSO sample a sodium borate and a silicate network coexist. The europium ions could occupy sites in one of the networks or in both at the same time. Using the very sensitive FLN technique, the co-existence of Eu^{3+} ions in a sodium borate and in a silicate environment has been established for the ENBSO composition in an earlier investigation [16]. These results, however, do not provide a quantitative measure for the distribution of Eu^{3+} onto the two networks. A method for estimating the relative amounts of rare-earth ions in the two networks of ternary sodium borosilicate glasses has more recently been introduced using Nd^{3+} as the structural probe [39, 40]. For the present investigation we therefore also prepared a reference sample with the same glass host composition as ENBSO but with Nd^{3+} instead of Eu^{3+}. The amount of Nd^{3+} ions in the silicate environment of this glass, using the above mentioned method, was found to be less than 6%, i. e. at least 94% of the Nd^{3+} ions are located in a sodium borate environment. Assuming a similar distribution of the Eu^{3+} ions in ENBSO, the agreement of the Mössbauer parameters of the ENBSO and the ENBO sample is no longer surprising.

The IS and the QI parameter of the sample ENBSO are identical to the parameters of the ENBO glass within the experimental error; the larger value of the line width reflects a bigger structural disorder of the europium sites, which is reasonable in a ternary glass. These results of course do not exclude the presence of two europium sites, as indicated by optical measurements [16]; but given the small relative amount of silicate sites, these sites can cannot be resolved in the Mössbauer spectrum. In any case, a strong preferential occupation of sites in the sodium borate network in the glass ENBSO is established in the present investigation and agrees perfectly with the behaviour of Nd^{3+} ions in the same glass.

5. Conclusions

In the glasses we investigated, the europium ions have oxidation number +3. The Eu-O bond is ionic with a covalent admixture with 6s character. The main transfer charge is into the 6s orbitals of the Eu, but the other p, d, and f orbitals play also a role.

In the sodium borate and silicate glasses, the europium ion is accommodated in sites distorted with respect to a cubic symmetry, with no threefold symmetry axis or higher symmetry. In the sodium borosilicate glass, the europium ion occupies preferentially sites in the sodium borate network. In the lead germanate glasses and in the zinc tellurite glass, the structure of the spectrum is not resolved, but the width of the peak points out a distortion of the sites.

The isomer shift was found to be correlated with the optical basicity of the glass.

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