Investigation of Eu$^{3+}$ Site Occupancy in Cubic Y$_2$O$_3$ and Lu$_2$O$_3$ Nanocrystals

Giorgio Concas, Giorgio Spano, Marco Bettinelli, and Adolfo Speghini

Dipartimento di Fisica, Università di Cagliari and Istituto Nazionale per la Fisica della Materia, S. P. Monserrato-Sestu km 0.700, I-09042 Monserrato (Cagliari), Italy

a Dipartimento Scientifico e Tecnologico, Università di Verona and INSTM, UdR Verona, Ca’ Vignal, Strada le Grazie 15, I-37134 Verona, Italy

Reprint requests to Dr. G.C.; Fax: +39070510171; E-mail: giorgio.concas@dsf.unica.it

Z. Naturforsch. 58a, 551 – 557 (2003); received July 24, 2003

The distribution of luminescent Eu$^{3+}$ ions in crystals with the cubic bixbyite-type structure is subject of debate. In this work, the actual occupancy of the two cation sites available for europium in yttria and lutetia nanocrystals with sizes of 10 – 20 nm has been evaluated by means of $^{151}$Eu Mössbauer spectroscopy. The spectral contribution of the ion at different crystalline sites has been resolved, allowing for the quadrupole splitting. The spectra of the nanocrystalline Y$_{1.8}$Eu$_{0.2}$O$_3$ and Lu$_{1.8}$Eu$_{0.2}$O$_3$ compounds have been analyzed in detail; the C$_3i$ and C$_2$ sites are occupied by the europium ion in a statistical way. The hyperfine parameters have been discussed in terms of symmetry and bonding. An increase of the covalence of the Eu-O bond has been found in the series of compounds Gd$_2$O$_3$, Eu$_2$O$_3$, Y$_2$O$_3$ and Lu$_2$O$_3$.

Key words: Europium; Oxides; Nanocrystals; Mössbauer Spectroscopy; Structural Properties.

1. Introduction

Yttrium, gadolinium and lutetium sesquioxides doped with lanthanide ions are important materials with many applications in different fields. In particular, Eu$^{3+}$ doped cubic Y$_2$O$_3$ and monoclinic Y$_2$O$_3$ are well-known luminescent materials [1, 2], whilst cubic Y$_2$O$_3$:Ln (Ln = lanthanide) systems form an interesting class of diluted magnetic semiconductors [3]. On the other hand, Lu$_2$O$_3$ has recently been studied for its interesting luminescent properties when doped with Er$^{3+}$ [4, 5] and for its possible application as scintillator when doped with Eu$^{3+}$ [6, 7]. Moreover, yttria and rare earth oxide based catalysts find applications in the selective oxidation of ethane to ethene [8, 9]. In the case of cubic Y$_2$O$_3$, the Y$^{3+}$ ions are located in the two non-equivalent positions 24d (site symmetry C$_3$) and 8b (site symmetry C$_3h$) [10]. In principle, the luminescent and magnetic ion Eu$^{3+}$ may replace Y$^{3+}$ in a random or preferential way. The location of Eu$^{3+}$ in these two sites in bulk cubic Eu$^{3+}$ doped Y$_2$O$_3$ was investigated by Grill and Schieber [11] by means of magnetic susceptibility measurements. The authors concluded that the Eu$^{3+}$ ions occupy preferentially the C$_2$ sites. On the other hand, more recently Antic et al. [12], on the basis of X-ray powder diffraction and magnetic susceptibility data, reported that in bulk cubic Y$_2$O$_3$:Eu, the Eu$^{3+}$ ions are randomly distributed between the two possible substitutional sites. In any case, these investigations have been limited to bulk cubic yttria materials. It is interesting to investigate the distribution of the luminescent Eu$^{3+}$ dopant ion in nanocrystalline cubic Y$_2$O$_3$ and Lu$_2$O$_3$, which are characterized by interesting spectroscopic properties [13].

$^{151}$Eu Mössbauer spectroscopy represents a useful and sensitive tool to investigate structural questions about the lanthanide ion in europium containing materials [14 – 16]. In particular, this spectroscopy can give direct information about the site symmetry of the lanthanide atom. In fact, the gamma ray from $^{151}$Eu is emitted during a transition from an excited state with spin 7/2 to the ground state with spin 5/2 [14]. If there is no threefold or fourfold symmetry axis passing through the nucleus, the components of the electric field tensor along the principal axes are different and the asymmetry parameter $\eta$ is non-zero [17]. There are 12 allowed transitions which give 12 emission or absorption lines if we consider the source or the absorber. If a threefold or fourfold axis is present, the
asymmetry parameter is zero and 8 transitions are allowed. In a compound with two mutually perpendicular axes of threefold or higher symmetry (e.g., a site with cubic symmetry), the electric field gradient (and the quadrupole interaction) is zero and a single emission or absorption line is observed [14].

The resolution of the absorption spectrum in a multiplet of lines split by the quadrupolar interaction is limited by different experimental factors. First of all, the best kind of source available (\(^{151}\)SmF\(_3\)) gives a line width much larger than the natural width of 1.33 mm/s [14]. The quadrupole splitting is usually smaller than the line width; therefore the multiplet lines are not resolved and must be identified by the fitting procedure. The resolution of the absorption peaks requires that multiplet lines have a Lorentzian shape; in some cases the knowledge of the line width is also required.

Mössbauer spectroscopy can also determine the relative abundance of europium atoms in different crystallographic sites, because the probability of resonant absorption by a single \(^{151}\)Eu nucleus is approximately equal for trivalent ions in different sites of the same compound. The contribution of sites with higher or lower symmetry can be identified by the fact that the quadrupolar interaction (QI) parameter and the asymmetry parameter are zero or not. The discrimination of the contribution of different sites occupied by Eu\(^{3+}\) is limited by experimental factors: the difference of isomer shift (IS) is usually smaller than the line width and comparable with the quadrupolar splitting. Therefore in the spectrum only a single absorption peak appears which must be resolved into two contributions of the sites split by the quadrupolar interaction separately; in some simple cases the question can be dealt with a suitable procedure of fitting, as shown in the present study.

Cubic Eu\(_2\)O\(_3\), which has the same structure of cubic yttrium and lutetium oxides, is one of the most investigated compounds by \(^{151}\)Eu Mössbauer spectroscopy, but the spectrum is usually fitted with a single peak [14, 18], or by using one quadrupole multiplet [19]. Europium doped bulk Gd\(_2\)O\(_3\), Y\(_2\)O\(_3\) and Lu\(_2\)O\(_3\) has also been investigated by Mössbauer spectroscopy [20, 21]. In particular for cubic bulk europia, yttria and lutetia a resolution of the contribution of the two different sites is proposed, which uses a fitting of the spectra with two single Lorentzian curves [21], i.e., without quadrupole splitting.

The aim of this study is to evaluate the actual occupancy of the two available cation sites by the Eu\(^{3+}\) ions, in the cubic structure of nanocrystalline Y\(_2\)O\(_3\) and Lu\(_2\)O\(_3\). To this end we resolved in the absorption spectrum the contribution of different crystalline sites which can be occupied by trivalent europium, allowing for the quadrupole splitting. The hyperfine parameters will be discussed in terms of symmetry and bonding of the lanthanide ion. We studied the Mössbauer absorption spectra of Eu\(^{3+}\) in the bulk cubic Eu\(_2\)O\(_3\) and Y\(_{1.8}\)Eu\(_{0.2}\)O\(_3\) compounds and in the nanocrystalline cubic Y\(_{1.8}\)Eu\(_{0.2}\)O\(_3\) and Lu\(_{1.8}\)Eu\(_{0.2}\)O\(_3\) and monoclinic Gd\(_{1.8}\)Eu\(_{0.2}\)O\(_3\) compounds.

2. Experimental Details

Bulk cubic Eu\(_2\)O\(_3\) was prepared by heating commercial Eu\(_2\)O\(_3\) (Aldrich, 99.99%) at 1000 °C for 6 h [22]. The cubic structure of the material was confirmed by powder X-ray diffraction. Bulk Y\(_{1.8}\)Eu\(_{0.2}\)O\(_3\) was prepared by heating two times Eu\(_2\)O\(_3\) and Y\(_2\)O\(_3\) (Aldrich, 99.99%) at 1500 °C for 24 h with intermediate regrinding.

Nanocrystalline Y\(_2\)O\(_3\), Gd\(_2\)O\(_3\) and Lu\(_2\)O\(_3\) powders doped with 10% Eu\(_2\)O\(_3\) (Ln\(_{1.8}\)Eu\(_{0.2}\)O\(_3\); Ln=Y, Gd or Lu) were prepared by a propellant synthesis procedure [13, 23, 24], using an aqueous solution containing glycine NH\(_2\)CH\(_2\)COOH (Sigma, 99%), \(M'(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}\) (\(M' =\) Y, Gd or Lu) and Eu(\(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}\) (Aldrich, 99.9%). The reaction is

\[
6M(\text{NO}_3)_3 + 10\text{NH}_2\text{CH}_2\text{COOH} + 18\text{O}_2 \\
\rightarrow 3M_2\text{O}_3 + 5\text{N}_2 + 18\text{NO}_2 + 20\text{CO}_2 + 25\text{H}_2\text{O},
\]

where M=Y, Gd, Lu or Eu.

A glycine-to-metal nitrate molar ratio of 1.2:1 was employed to prepare the precursor solution. After the synthesis, the powders were fired for 1 hour at 500 °C in order to decompose the residual nitrate ions. Raman and FTIR spectra were measured on all the samples. Nitrate ions were found to be absent, but traces of OH and carbonate groups were detected.

The Mössbauer absorption spectra were obtained in a standard transmission geometry, using a source of \(^{151}\)SmF\(_3\) with activity 3.7 GBq. A calibration was performed using a source of \(^{57}\)Co in rhodium and a metallic iron foil (25 μm thick) as the absorber. The full width at half maximum (FWHM) of the crystalline absorption peak, determined with our source, was measured using Cs\(_2\)NaEuCl\(_6\) which contains Eu\(^{3+}\) in a site with cubic symmetry [25]; the measured FWHM is (1.76±0.1) mm/s with an effective thickness of the absorber \(t = 1\). The isomer shift of the samples was mea-
sured using the anhydrous fluoride EuF₃ as reference material.

The measurements on the compounds were carried out at room temperature on a powder sample with an absorber thickness of 3.8 mg/cm² of Eu; this value corresponds to an effective thickness \( t = 1 \), when calculated using the recoilless fraction of the source, \( f = 0.6 \) [14]. The powders were contained in a Plexiglas holder. Only the Eu₂O₃ powder was mixed with graphite in order to spread it uniformly over the bottom of the sample holder.

The absorption spectra were analyzed by fitting the data with curves of Lorentzian shape, allowing for the quadrupole interaction when present. We used the method for the analysis of pure quadrupole spectra proposed by Shenoy and Dunlap [26], with a value of the quadrupole ratio \( R = 1.312 \) [27]. The thickness of the absorbers permits the use of a Lorentzian line shape, because the thin absorber approximation can be used (thickness less than 6 mg/cm² of Eu) [28, 29]; when QI is present, we used a quadrupole multiplet of Lorentzian curves.

The quality of the fits was tested using the usual chisquared test and a weighted form of the Durbin-Watson d statistics that was used in the Rietveld analysis of powder diffraction data [30]. The \( d \) value quantifies the serial correlation between adjacent least-squares residuals and is defined as

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

where \( N \) is the number of experimental data, \( \Delta_i \) is the \( i \)-th residual and \( \sigma_i \) indicates the standard deviation. It is useful to test \( d \) against the parameter \( Q_d \) 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 insignificantly correlated, \( d \) has a value nearer to 2 than \( Q_d \).

3. Results

The crystal structures of the samples investigated were checked by powder X-ray diffraction. The patterns confirmed that all the samples were single phase with the cubic C structure, with the exception of Gd₁₈Eu₀₂O₃, which had been obtained as monoclinic B polymorph. In particular Wide Angle X-Ray Scattering (WAXS) measurements show that nanocrystalline yttria samples prepared by propellant synthesis have a cubic crystalline structure and particle sizes in the 10–20 nm range [24]. Moreover, Small Angle X-Ray Scattering results show that the yttria nanopowders have a mass-fractal behaviour, with fractal dimension, \( D_f \), in the 1.6–2.0 range and particle sizes similar to those found with the WAXS technique [23]. Similar particle sizes are observed for nanocrystalline yttria from images obtained using transmission electron microscopy [24]. The particle surface is “fuzzy” because of lattice disorder and/or adsorbed CO₂. The nanocrystalline lutetia prepared by propellant synthesis shows similar structural properties [31].

Figure 1 shows the Mössbauer absorption spectrum of the Gd₁₈Eu₀₂O₃ nanocrystalline sample. Table 1 shows the parameters given by a single line fit, while the calculated data are shown in Fig. 2 as solid curve. The isomer shift value can be considered an average value for the three cation sites of the monoclinic structure of Gd₂O₃. The measured FWHM is 2.87(1) mm/s (to be compared with a crystalline line width of 1.76 mm/s), and is due to unresolved quadrupole splitting and to the three contributions of the sites; it also explains the high value of the \( \chi^2 \) parameter. Some trial fits of the spectrum of the Gd₁₈Eu₀₂O₃ sample using 3 contributions, each of them with its quadrupole splitting, gave no result because there are too many parameters to determine. Attempts to fit the spectrum with 3 single Lorentzian lines gave a misleading result with unreasonable values of isomer shift, because the quadrupole splitting of the components is likely to be larger than the difference in the isomer shift for...
Table 1. Mössbauer parameters obtained by fitting the spectra. \( \delta \) is the isomer shift with respect to EuF3, \( \Gamma \) the FWHM, \( eQV_{zz} \) the quadrupole interaction parameter, \( \eta \) the asymmetry parameter and Area the relative area of the components. The \( d \) and \( Q_d \) Durbin-Watson parameter and the chi-squared parameter \( \chi^2 \) are also reported. Statistical errors are given in parenthesis as errors in the last digit. The trial fit was performed with a single Lorentzian curve.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \delta ) mm/s</th>
<th>( eQV_{zz} ) mm/s</th>
<th>( \eta )</th>
<th>Area %</th>
<th>( d )</th>
<th>( Q_d )</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>nanocr. Gd(<em>{1.8})Eu(</em>{0.2})O(_3)</td>
<td>0.9(1)</td>
<td>-8.6(1)</td>
<td>24(1)</td>
<td>0.80</td>
<td>1.64</td>
<td>3.00</td>
<td></td>
</tr>
<tr>
<td>Eu(_2)O(_3) (trial fit)</td>
<td>1.04(1)</td>
<td>1.00(1)</td>
<td>76(1)</td>
<td>0.54</td>
<td>1.64</td>
<td>4.15</td>
<td></td>
</tr>
<tr>
<td>Eu(_2)O(_3)</td>
<td>1.67</td>
<td>1.26</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Site C(_3i)</td>
<td>1.03(1)</td>
<td>-8.6(1)</td>
<td>24(1)</td>
<td>1.04</td>
<td>1.54</td>
<td>2.18</td>
<td></td>
</tr>
<tr>
<td>Site C(_2)</td>
<td>1.03(1)</td>
<td>1.00(1)</td>
<td>76(1)</td>
<td>1.67</td>
<td>1.65</td>
<td>1.26</td>
<td></td>
</tr>
<tr>
<td>Y(<em>{1.8})Eu(</em>{0.2})O(_3)</td>
<td>1.14(1)</td>
<td>-9.4(4)</td>
<td>27(3)</td>
<td>1.70</td>
<td>1.65</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>Site C(_3i)</td>
<td>1.14(1)</td>
<td>-9.4(4)</td>
<td>73(3)</td>
<td>1.79</td>
<td>1.65</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>Site C(_2)</td>
<td>1.14(1)</td>
<td>1.00(1)</td>
<td>78(3)</td>
<td>1.78</td>
<td>1.65</td>
<td>1.02</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. Mössbauer spectrum of the Eu\(_2\)O\(_3\) sample. (a) Relative absorption intensity \( (I) \) vs. velocity \( (\nu) \): the experimental data (dots) and the fit by two quadrupole multiplets with the separate components (full lines) are shown. (b) Differences \( (\Delta I) \) between the experimental and calculated data.

The Mössbauer spectrum of the cubic Eu\(_2\)O\(_3\) sample is shown in Fig. 2(a). This compound has a known occupation of the sites by europium and can be used in order to find a fitting procedure which discriminates, in the spectrum, the contribution of the C\(_{3i}\) and of the C\(_2\) sites; a good procedure will give, as result of the fitting, two components with a ratio of the areas equal to the actual occupancy of the sites, i.e. 1:3. Then the tested method can be used in order to find the unknown occupancy of sites by Eu ions in the isostructural Y\(_2\)O\(_3\) and Lu\(_2\)O\(_3\) crystals. The simple use of two quadrupole multiplets with free parameters is difficult because the big number of parameters makes the fitting unstable.

The experimental data of Eu\(_2\)O\(_3\) were first analyzed with a single Lorentzian curve and the results are given in Table 1; the measured FWHM is 2.93(1) mm/s. Also in this case the effect of the two sites and of the quadrupole splitting gives a high value of the \( \chi^2 \) parameter. The data were also tentatively analyzed with the fitting procedures proposed in [19] and [21], but a satisfactory result was not obtained. The experimental spectrum was then well fitted using two components corresponding to the two crystallographic sites of europium; in this procedure the asymmetry parameter of the C\(_{3i}\) site has been fixed to zero because of the threefold axis of symmetry, and the FWHM of the multiplets has been fixed to the crystalline width (1.76 mm/s). Some trial fits showed that the value of IS of the two sites is about the same and the QI of the C\(_{3i}\) site is very small. Therefore, in order to reduce the number of free parameters, the value of IS of the sites has been forced to take the same variable value and the QI parameter of the more symmetric site has been fixed to zero. The fact that the average Eu-O distance of the two sites is equal justifies the equality of the IS, while
the smallness of the QI in the C3i site can be explained by an equal value of the six Eu-O distances [10]. The resulting calculated curve is shown in Fig. 2(a) with the components separately; the residuals are shown in Fig. 2(b). The lack of structure in the plot of the residuals demonstrates that this is the correct peak shape; the values of the control parameters \(d\) and \(Q_d\) reported in Table 1 confirm that this fit is fully satisfactory.

All the physical parameters resulting from this last fit are physically acceptable. The relative areas of the components, which are 24% and 76% for the C3i and C2 sites, respectively, can be taken to be equal to the relative number of europium atoms in the these sites with good approximation, and give the right number of sites (25% and 75%) within the experimental error.

The fitting procedure developed and tested in the Eu2O3 sample has been applied to the spectra of the cubic yttria and lutetia samples, which have the same bixbyte-type structure; the asymmetry parameter has been fixed to the value found in Eu2O3 in order to reduce the number of free parameters. The absorption spectrum of the cubic bulk Y1.8Eu0.2O3 sample is shown in Fig. 3(a) along with the best fit; the parameters obtained by the fitting procedure are reported in Table 1. It results that the europium ion occupies the C3i and the C2 sites with a probability 22% and 78%, respectively, which is equal to the relative number of sites within the experimental error.

The spectrum of the cubic nanocrystalline Y1.8Eu0.2O3 sample is shown in Fig. 3(b). The data have been fitted with the described procedure and the resulting parameters are reported in Table 1. The occupational probability of the C3i and C2 sites results as 27% and 73%, respectively, which agrees with the relative number of sites.

Figure 4 shows the spectrum of the nanocrystalline Lu1.8Eu0.2O3 sample. The fit of the data has been performed with the described procedure; the parameters are given in Table 1. It results that the occupational probability of the C3i and C2 sites is 25% and 75%, respectively, according to a random distribution.

4. Discussion

The spectra of the crystalline samples here investigated have values of the isomer shift corresponding to an oxidation number +3; the values near to 1 mm/s point towards a strong covalency of the Eu-O bond for the crystalline hosts [14]. In particular the value of IS increases in the sequence Gd2O3, Eu2O3, Y2O3 and
Lu₂O₃, while the value of the mean A-O distance (A = Gd, Eu, Y, Lu) decreases in the same sequence (2.42, 2.34, 2.28 and 2.24 Å) [21]. This behaviour suggests that the covalence of the Eu-O bond increases along the above mentioned sequence.

On the basis of the analysis of the Mössbauer spectrum, the europium dopant ion in cubic bulk Y₂O₃ is distributed between the C₃i and the C₂ site nearly in a random way, without preferential occupancy. In several studies carried out in the '60s, based on paramagnetic resonance spectroscopy, it has been claimed that trivalent lanthanide ions occupy in cubic Y₂O₃ both the C₂ and C₃i sites with nearly equal probability [32, 33, 34]. However, it has been shown more recently, using powder X-ray diffraction and magnetic susceptibility measurements [35], that several Ln³⁺ ions, such as Gd³⁺ [36] and Yb³⁺ [37], tend to occupy preferentially one of the two sites in bulk Y₂O₃. In the case under investigation for 6-fold co-ordination the dopant ion (Eu³⁺) is characterised by an ionic radius (0.950 Å) significantly different from that of Y³⁺ (0.892 Å) [38]. It is therefore conceivable that the substitution of Y³⁺ with Eu³⁺ can occur with some difficulty, and that one of the two sites, which are characterized by different Ln-O distances, is preferentially occupied. However, in a recent study it has been found that in bulk Y₂O₃:Eu, on the basis of magnetic susceptibility data and X-ray diffraction, the two C₂ and C₃i sites are randomly occupied by Eu³⁺ ions. The present Mössbauer investigation gives a direct confirmation of this result.

As far as the nanocrystalline Y₁₈Eu₀₂O₃ compound is concerned, we point out that the sample under investigation is nanosized and obtained by a propellant synthesis and that occurring in the bulk sample obtained by conventional ceramic techniques [12]. On the other hand it has already been found that the optical spectra of nanocrystalline (prepared by propellant synthesis) and bulk Y₂O₃:Nd show several differences due to a different average local structure around the Nd³⁺ ions in the two materials [39]. However, we point out that a Rietveld analysis of Y₁₈Er₀₂O₃ and Y₁₈Nd₀₂O₃ samples obtained by propellant synthesis gave no indication of a significant preferential occupation of different crystallographic positions, i.e., the lanthanide ions seem to be statistically distributed over both cationic sites, within the limit of the sensitivity of the X-ray diffraction [31]. The analysis of the Mössbauer spectrum of the nanocrystalline Y₂O₃:Eu doped with 10% of Eu, presented in this work, shows that the europium ion also is statistically distributed over the cationic sites available in this cubic bixbyite-type structure.

On the basis of the analysis of the Mössbauer spectrum, we found also that the Eu³⁺ ion in cubic nanocrystalline Lu₂O₃ is distributed between the C₃i and the C₂ site in a random way.

5. Conclusions

The isomer shift of europium increases in the sequence Gd₂O₃, Eu₂O₃, Y₂O₃, and Lu₂O₃; it points out that the covalence of the Eu-O bond increases along the same sequence. The relative area of the 2 contributions due to the Eu³⁺ ion in the C₃i and C₂ sites, in the spectra of Y₁₈Eu₀₂O₃ and Lu₁₈Eu₀₂O₃ samples, show that about one fourth of the lanthanide ions is in the more symmetric site and three fourth in the less symmetric, in agreement with the ratio 1:3 of the number of available sites.

Acknowledgements

We thank C. Muntoni for helpful discussions and E. Viviani for expert technical assistance. This work was carried out within the MURST PRIN project 9903222581_005.

[31] S. Polizzi et al., unpublished results.