Investigation of Eu^{3+} Site Occupancy in Cubic Y_2O_3 and Lu_2O_3 Nanocrystals

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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_2O_3, Eu_2O_3, Y_2O_3 and Lu_2O_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_2O_3 and monoclinic Y_2O_3 are well-known luminescent materials [1, 2], whilst cubic Y_2O_3:Ln (Ln = lanthanide) systems form an interesting class of diluted magnetic semiconductors [3]. On the other hand, Lu_2O_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_2O_3, the Y^{3+} ions are located in the two non-equivalent positions 24d (site symmetry C_2) and 8b (site symmetry C_{3i}) [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_2O_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_2O_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_2O_3 and Lu_2O_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 η 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

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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_2O_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 multipet [19]. Europium doped bulk Gd_2O_3,Y_2O_3 and Lu_2O_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_2O_3 and Lu_2O_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_2O_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_2O_3 was prepared by heating commercial Eu_2O_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_2O_3 and Y_2O_3 (Aldrich, 99.99%) at 1500 °C for 24 h with intermediate regrinding.

Nanocrystalline Y_2O_3, Gd_2O_3 and Lu_2O_3 powders doped with 10% Eu_2O_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_2CH_2COOH (Sigma, 99%), $M'(NO_3)_3\cdot 6H_2O$ (M'=Y, Gd or Lu) and $Eu(NO_3)_3\cdot 6H_2O$ (Aldrich, 99.9%). The reaction is

$$\begin{aligned}&6M(NO_3)_3 + 10NH_2CH_2COOH + 18O_2\\&\quad\rightarrow 3M_2O_3 + 5N_2 + 18NO_2 + 20CO_2 + 25H_2O,\end{aligned}$$

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 $Cs_2NaEuCl_6$ 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 measured using the anhydrous fluoride EuF_3 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/cm^2 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 Eu_2O_3 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/cm^2 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 chi-squared 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

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

where N is the number of experimental data, Δ_i is the i-th residual and σ_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 $Gd_{1.8}Eu_{0.2}O_3$, which had been obtained as monoclinic B polimorph. 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 CO_2. The nanocrystalline lutetia prepared by propellant synthesis shows similar structural properties [31].

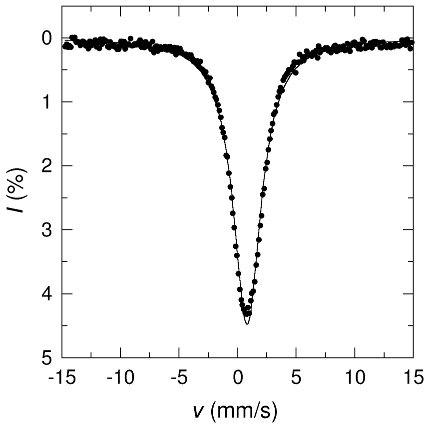

Fig. 1. Mössbauer spectrum of the nanocrystalline $Gd_{1.8}$-$Eu_{0.2}O_3$ sample. Relative absorption intensity (I) vs. velocity (v): the experimental data (dots) and the fit by a single Lorentzian curve (full line) are shown.

Figure 1 shows the Mössbauer absorption spectrum of the $Gd_{1.8}Eu_{0.2}O_3$ 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 Gd_2O_3. 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 χ^2 parameter. Some trial fits of the spectrum of the $Gd_{1.8}Eu_{0.2}O_3$ 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

Sample	δ mm/s	eQV_{zz} mm/s	η	Area %	d	Q_d	χ^2
nanocr. $Gd_{1.8}Eu_{0.2}O_3$	0.97(1)				0.80	1.64	3.00
Eu_2O_3 (trial fit)	1.04(1)				0.54	1.64	4.15
Eu_2O_3					1.67	1.65	1.26
Site C_{3i}	1.03(1)			24(1)			
Site C_2	1.03(1)	−8.6(1)	1.0(1)	76(1)			
$Y_{1.8}Eu_{0.2}O_3$					1.46	1.65	1.23
Site C_{3i}	1.14(1)			22(3)			
Site C_2	1.14(1)	−8.8(2)	1.0	78(3)			
nanocr. $Y_{1.8}Eu_{0.2}O_3$					1.79	1.65	1.18
Site C_{3i}	1.14(1)			27(3)			
Site C_2	1.14(1)	−9.4(4)	1.0	73(3)			
nanocr. $Lu_{1.8}Eu_{0.2}O_3$					1.78	1.65	1.02
Site C_{3i}	1.23(1)			25(1)			
Site C_2	1.23(1)	−10.4(2)	1.0	75(1)			

Table 1. Mössbauer parameters obtained by fitting the spectra. δ is the isomer shift with respect to EuF_3, Γ the FWHM, eQV_{zz} the quadrupole interaction parameter, η the asymmetry parameter and *Area* the relative area of the components. The d and Q_d Durbin-Watson parameter and the chi-squared parameter χ^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.

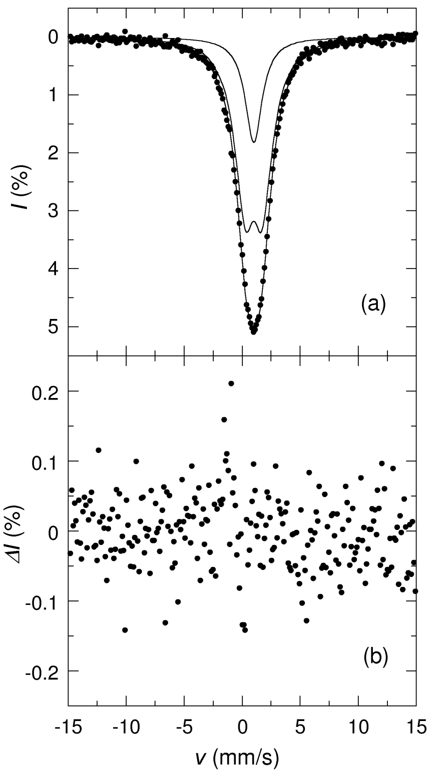

Fig. 2. Mössbauer spectrum of the Eu_2O_3 sample. (a) Relative absorption intensity (I) vs. velocity (v): the experimental data (dots) and the fit by two quadrupole multiplets with the separate components (full lines) are shown. (b) Differences (ΔI) between the experimental and calculated data.

the 3 sites. Therefore the fit reported in Table 1 must be considered as the most meaningful procedure for the analysis of the $Gd_{1.8}Eu_{0.2}O_3$ spectrum presented here.

The Mössbauer spectrum of the cubic Eu_2O_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_2O_3 and Lu_2O_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_2O_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 χ^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

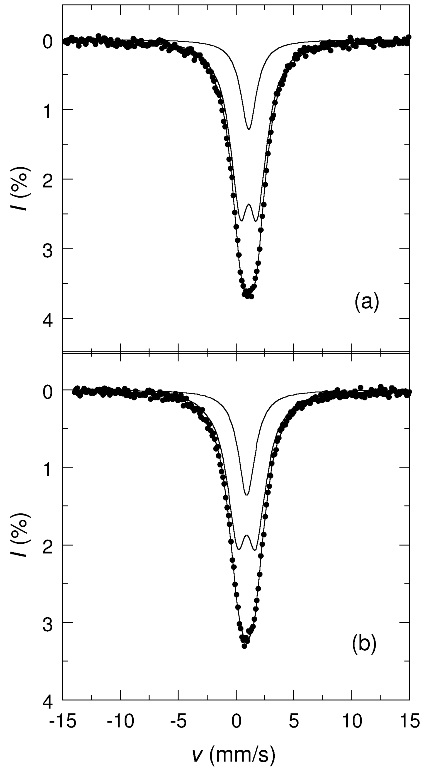

Fig. 3. Mössbauer spectra of: (a) the bulk $Y_{1.8}Eu_{0.2}O_3$ sample and (b) the nanocrystalline $Y_{1.8}Eu_{0.2}O_3$ sample. Relative absorption intensity (I) vs. velocity (v); the experimental data (dots) and the fit with two separate components (full lines) are shown.

the smallness of the QI in the C_{3i} 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 C_{3i} and C_2 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 Eu_2O_3 sample has been applied to the spectra of the cubic yttria and lutetia samples, which have the same bixbyite-type structure; the asymmetry parameter has been fixed to the value found in Eu_2O_3 in order to reduce the number of free parameters. The absorption spectrum of the cubic bulk $Y_{1.8}Eu_{0.2}O_3$ 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 C_{3i} and the C_2 sites with a probability 22% and 78%, respectively, which is equal to the relative number of sites within the experimental error.

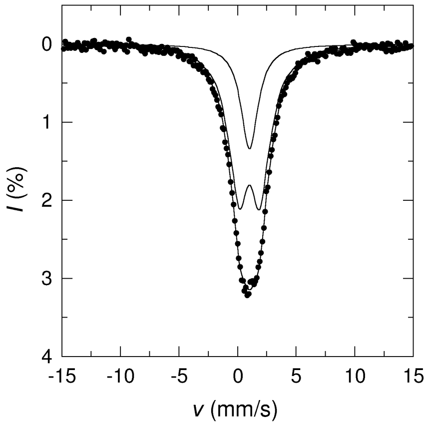

Fig. 4. Mössbauer spectrum of the nanocrystalline $Lu_{1.8}$-$Eu_{0.2}O_3$ sample. Relative absorption intensity (I) vs. velocity (v): the experimental data (dots) and the fit with two separate components (full lines) are shown.

The spectrum of the cubic nanocrystalline $Y_{1.8}Eu_{0.2}O_3$ 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 C_{3i} and C_2 sites results as 27% and 73%, respectively, which agrees with the relative number of sites.

Figure 4 shows the spectrum of the nanocrystalline $Lu_{1.8}Eu_{0.2}O_3$ 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 C_{3i} and C_2 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 Gd_2O_3, Eu_2O_3, Y_2O_3 and

Lu_2O_3, 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 Y_2O_3 is distributed between the C_{3i} and the C_2 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 Y_2O_3 both the C_2 and C_{3i} 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 Ln^{3+} ions, such as Gd^{3+} [36] and Yb^{3+} [37], tend to occupy preferentially one of the two sites in bulk Y_2O_3. In the case under investigation for 6-fold co-ordination the dopant ion (Eu^{3+}) is characterised by an ionic radius (0.950 Å) significantly different from that of Y^{3+} (0.892 Å) [38]. It is therefore conceivable that the substitution of Y^{3+} with Eu^{3+} 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 Y_2O_3:Eu, on the basis of magnetic susceptibility data and X-ray diffraction, the two C_2 and C_{3i} sites are randomly occupied by Eu^{3+} ions. The present Mössbauer investigation gives a direct confirmation of this result.

As far as the nanocrystalline $Y_{1.8}Eu_{0.2}O_3$ compound is concerned, we point out that the sample under investigation is nanosized and obtained by a propellant synthesis, which is intrinsically a non-equilibrium technique. It is therefore possible that the distribution of the Eu^{3+} ions in the this sample is different from 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 Y_2O_3:Nd show several differences due to a different average local structure around the Nd^{3+} ions in the two materials [39]. However, we point out that a Rietveld analysis of $Y_{1.8}Er_{0.2}O_3$ and $Y_{1.8}Nd_{0.2}O_3$ 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 Y_2O_3 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 Eu^{3+} ion in cubic nanocrystalline Lu_2O_3 is distributed between the C_{3i} and the C_2 site in a random way.

5. Conclusions

The isomer shift of europium increases in the sequence Gd_2O_3, Eu_2O_3, Y_2O_3, and Lu_2O_3; 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 Eu^{3+} ion in the C_{3i} and C_2 sites, in the spectra of $Y_{1.8}Eu_{0.2}O_3$ and $Lu_{1.8}Eu_{0.2}O_3$ 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.

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