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Nano- and microcrystalline Lu_2O_3:Eu phosphors: variations in occupancy of C_2 and S_6 sites by Eu^{3+} ions

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Abstract
The occupancy of C_2 and S_6 sites by Eu^{3+} ions in nanocrystalline powders and microcrystalline ceramics of Lu_2O_3 prepared from these powders was studied by Mössbauer spectroscopy. It was proved that in nanopowders prepared by vigorous combustion syntheses the occupancy of the C_2 and S_6 sites by Eu^{3+} is almost random, with only a very limited preference for the former. For ceramic specimens formed at $1750\,°C$ within a few hours, it was found that Eu^{3+} ions strongly prefer to enter the Lu_2O_3 host at the C_2 site. We concluded that thermodynamically the non-centrosymmetric site C_2 is preferred to the S_6 site by Eu^{3+}. However, if the formation of crystallites is very fast, like in combustion syntheses, the Eu^{3+} ions are entrapped into the two sites nearly randomly.

1. Introduction

Lutetium oxide, Lu_2O_3, has been attracting ever-growing attention from researchers for the last fifteen years. This simple oxide doped with various lanthanides was fabricated and investigated in different forms such as nanocrystalline powders [1–3], thin films [4, 5], sintered ceramics [6–10], single crystals [11, 12] or nanoparticles embedded into a glass host [13]. In most cases the driving force of the research was that Lu_2O_3 is a very attractive host for scintillators or x-ray phosphors. This is due to an exceptionally high density of lutetia ($9.42\ \mathrm{g\,cm^{-3}}$), which ensures that any kind of ionizing radiation is very efficiently absorbed in relatively thin layers of lutetia-based phosphors. This is of a great importance for some applications, for example in medical diagnosis [6, 14]. It was proved that Lu_2O_3 activated with Eu^{3+} ions is an efficient x-ray phosphor and it can be commercially attractive [1, 6]. We also proved that nanocrystalline powder of Lu_2O_3:Eu shows red emission whose quantum efficiency reaches 90% [15]. However, since the interest in lutetia-based phosphors is relatively new, we still lack knowledge about many important properties of the material.

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Lu_2O_3, which crystallizes in a cubic C-type structure [7, 16, 17], offers two different sites for the metal cations. One of them possesses C_2 symmetry. Since it is non-centrosymmetric, the f–f electric dipole induced transitions of lanthanides are partially allowed. The other crystallographic site possesses S_6 (C_{3i}) symmetry. Due to its centrosymmetric surroundings, essentially only the magnetic dipole induced transitions can be recorded both in absorption and emission [7, 18] for ions occupying this site. However, the magnetic dipole transitions are significantly less probable than electric dipole ones, and this makes them less intense. Therefore, it is preferred to have the optically active ions placed in the C_2 site. Fortunately, there are as many as 75% of sites of the C_2 type and only 25% of sites of the S_6 type offered by the Lu_2O_3 host. Since most of the lanthanide ions are larger than the substituted Lu^{3+} ions it may well be that the activators do not distribute statistically within the two host sites but prefer to enter either the C_2 or the S_6 site.

The problem of the occupancy of the different sites in Lu_2O_3 by the ions of activators was almost completely omitted in the research published so far. There is only scant information presented in [19], where the statistical occupancy of both sites by Eu^{3+} ions in one nanocrystalline specimen of Lu_2O_3:Eu was reported. However, there was such a work performed for Y_2O_3, which is a structural analogue of lutetia. The conclusions derived by various authors are not consistent, unfortunately. While Grill and Schieber deduced from magnetic susceptibility measurements that Eu^{3+} ions prefer to enter the C_2 site [20], Antic *et al* stated that the distribution is random [21]. Recently, Mössbauer spectroscopy was successfully employed to determine the distribution of Eu^{3+} ions in bulk and nanocrystalline yttria, giving evidence that about 75% of the dopant locates in the C_2 site and 25% in the S_6 site of yttria [19]. Thus both in the bulk and nanocrystalline yttria there is observed a random occupation of the S_6 symmetry site. What is important is that the Mössbauer spectroscopy seemed to produce highly reliable and straightforward results.

[151]Eu Mössbauer spectroscopy is a useful tool to examine structural questions in crystals and glasses [22, 23]; it can 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 equal to 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. For compounds with the cubic C-type structure of Y_2O_3, the question can be dealt with by a suitable procedure of fitting, as shown in our previous work [19].

In this paper we use the Mössbauer spectroscopy to determine the occupancy by Eu^{3+} ions of the two metal sites in four different specimens of Lu_2O_3:Eu^{3+}. Two of the samples were prepared as nanocrystalline powders using combustion synthesis and two other samples were fabricated as sintered ceramics derived from the nanocrystalline powders. We believed that applying the same technique for investigation of the occupancy problem would give us the possibility to observe how various synthesis procedures influence the dopant distribution between the symmetry sites.

2. Material fabrication and experimental details

Two samples of $Lu_{1.8}Eu_{0.2}O_3$ were prepared using the combustion technique, whose details we described in previous papers [1, 3]. The combustion was performed between metal nitrates

Table 1. Details of investigated samples.

	Nanocrystalline powders		Ceramics	
Sample number	S1	S2	S3	S4
Preparation	Combustion with urea	Combustion with glycine	Sintered from S1	Sintered from S2
Crystallite size	10–15 nm	~35 nm	5–10 μm	5–10 μm
Formation time	Seconds	Seconds	5 h	5 h

and an organic fuel. For the first powder the fuel was urea, $CO(NH_2)_2$, (sample S1) and for the other it was glycine, NH_2CH_2COOH (S2). In each case an ultimate mixture of the starting materials was put in a furnace preheated up to 650 °C, at which temperature a vigorous reaction occurred, producing nanocrystalline powders of $Lu_{1.8}Eu_{0.2}O_3$.

Two next samples (S3 and S4) were prepared in the form of sintered ceramics. To fabricate the ceramics, the powders produced as described above were cold-pressed under 9 tons of load and such pellets were sintered in vacuum for 5 h at 1750 °C. Before any measurements the sintered pellets were polished to remove the surface material. Some additional details about the samples are given in table 1.

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 [24]; the measured FWHM is 1.76 ± 0.1 mm s^{-1} with an effective thickness of the absorber $t = 1$. The measurements were carried out at room temperature on powders with an absorber thickness of 3.8 mg cm^{-2} of Eu for samples S1, S2 and S3 and 1.3 mg cm^{-2} for S4; these values correspond to an effective thickness $t = 1$ and 0.33 respectively, when calculated using the recoilless fraction of the source, $f = 0.6$ [25]. The powders were contained in a Plexiglas holder.

The absorption spectra were analysed 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]; when the QI is present, we used a quadrupole multiplet of Lorentzian curves.

The fitting procedure uses a least squares method with some constraint on the parameters established in our previous work for compounds with the bixbyite-type structure [19]; the procedure has been tested with the cubic Eu$_2$O$_3$, which enables control of the results as it concerns the occupation of the sites by Eu atoms (ratio 75:25). Two components corresponding to the two crystallographic sites of europium were used; in this procedure the asymmetry parameter of the S$_6$ site has been fixed to zero, because of the threefold axis of symmetry, and the FWHM of the quadrupole multiplets has been fixed to the crystalline width (1.76 mm s^{-1}). Trial fits of Eu$_2$O$_3$ showed that the value of the IS of the two sites is about the same, and the QI of the S$_6$ site is very small. Therefore, in order to reduce the number of free parameters, the value of the 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 fit with these constraints gives the right occupancy ratio in Eu$_2$O$_3$ [19]. 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 S$_6$ site can be explained by an equal value of the six Eu–O distances [29]. In order to bear out the validity of such an approach we performed some trial fits of the spectra presented in this work,
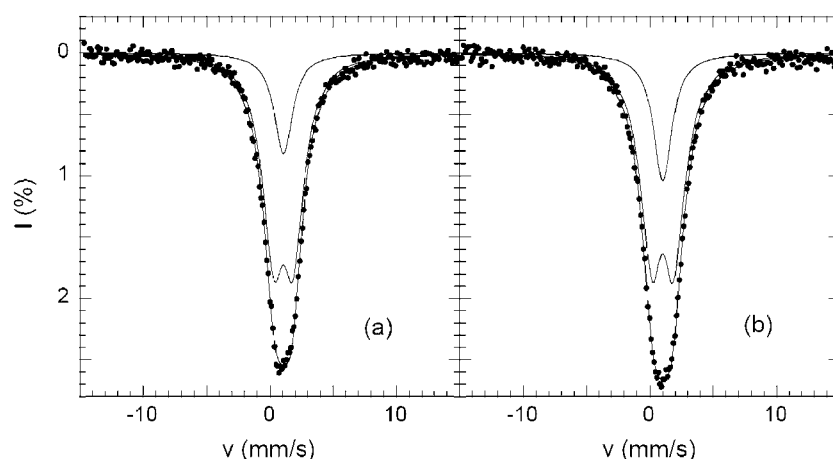
Figure 1. Mössbauer spectra of the $Lu_{1.8}Eu_{0.2}O_3$ nanocrystalline powders: (a) sample S1 and (b) sample S2. Relative absorption intensity (I) versus velocity (v): the experimental data (dots) and the fit with the two components separately (full line) are shown.

allowing for a free variation of the fitting parameters. These fits gave no significant reduction of the chi-squared parameter (a few per cent); moreover the value of the QI parameter for the S_6 site and the difference of IS of the two sites were smaller than or about equal to the error.

The quality of the fits was tested using the usual chi-squared test and a weighted form of the Durbin–Watson d statistics [30]. The d and Q_d values quantify the serial correlation between adjacent least squares residuals; if consecutive residuals are insignificantly correlated, d has a value nearer to 2 than Q_d.

3. Results

Both the fabricated powder materials are white. The ceramics have a gently pink hue. X-ray powder diffraction patterns and TEM images presented in already published papers [1, 8, 9, 13, 31] show that the investigated materials are made up of crystallites of very different sizes. The powders are nanocrystalline, while the sintered ceramics consist of crystallites whose diameters are in the range of micrometres. Details of the important properties of the investigated materials are given in table 1.

Figure 1(a) presents a measured Mössbauer spectrum for $Lu_{1.8}Eu_{0.2}O_3$ nanocrystalline powder S1 prepared through combustion with urea fuel, together with the line representing the fit of the experimental data using two components, as well as the lines for each of the separate constituents. The detailed parameters for each of the component for this and all other investigated samples are collected in table 2; the asymmetry parameter has been fixed to the value found in $Eu_2O_3(\eta = 1)$. First, we should note that the chi-squared parameter, χ^2, is much higher than 1. This means that the fit is burdened with a relatively high error and, consequently, that the conclusions concerning this specific sample have to be drawn with caution. We shall comment on this in detail in the following section. In table 2 we see that the ratio of areas under the components for C_2 and S_6 site is 80:20. Both numbers are laden with ± 2 statistical error. Thus from the results for the urea-made nanocrystalline powder S1 we can state that Eu^{3+} ions seem to have a slight tendency to preferentially occupy the C_2 site. However, both the relatively high error of the fits and rather small deviation from the 75:25 ratio suggest seeing this effect as minor only.

Table 2. Mössbauer parameters obtained by fitting the spectra. eQV_{zz} is the quadrupole interaction parameter, η is the asymmetry parameter and area is the relative area of the components. The d and Q_d Durbin–Watson parameters and the chi-squared parameter χ^2 are also reported. Statistical errors are given in parentheses as errors on the last digit.

Sample	eQV_{zz} (mm s^{-1})	η	Area (%)	d	Q_d	χ^2
S1				1.71	1.64	1.59
Site S_6			20(2)			
Site C_2	$-8.9(2)$	1.0	80(2)			
S2				1.90	1.64	1.18
Site S_6			23(2)			
Site C_2	$-10.0(2)$	1.0	77(2)			
S3				1.62	1.64	1.12
Site S_6			16(1)			
Site C_2	$-8.9(2)$	1.0	84(2)			
S4				1.73	1.64	1.04
Site S_6			15(2)			
Site C_2	$-8.8(1)$	1.0	85(2)			

Figure 1(b) shows a Mössbauer spectrum for $Lu_{1.8}Eu_{0.2}O_3$ nanocrystalline powder S2 prepared using again combustion procedure but with glycine fuel. The figure shows the experimental points and the curves representing the fit with two components and each of the separate constituents. Detailed data for the fitting curves are summarized in table 2; the isomer shift, referred to anhydrous fluoride (EuF_3), is 1.25 ± 0.01 mm s^{-1}. It is striking that the fit quality is now much better than it was for the above-discussed urea-made powder S1. Thus the data derived from the Mössbauer spectrum for the glycine-prepared nanocrystalline powder S2 are much more reliable. The ratio of the occupation of the two sites by Eu^{3+} ions in this material found is 77:23, with the statistical error being ±2. Thus for this material we can state that the occupational probability is very close to the 75:25. Accordingly, Eu^{3+} tends to occupy the two sites almost randomly in this nanopowder, with only a slight indication of preference given to the C_2 site.

The situation is different in the case of both ceramic samples prepared from the powders just discussed above. Figure 2(a) shows the Mössbauer spectrum for the ceramic S3 sintered using the urea-prepared powder and figure 2(b) presents the spectrum for the ceramic S4 made using glycine-prepared powder. In addition to the experimental points there are lines in the figures representing the fits obtained using two components of Lorentzian shape as well as the lines for each of the separate constituents. Table 2 summarizes data for the components for each sample. The chi-squared parameters, χ^2, are very close to 1 for each sample, proving that both fits are very reliable. It is striking that for both ceramic specimens the probability of both sites being occupied by Eu^{3+} ions is practically the same and is close to 85:15; see the details in table 2. Thus during the sintering there occurs a significant change in the population of the two metal sites by Eu^{3+} towards a preferential occupation of the C_2 site compared to the starting powders.

4. Discussion

We applied the same technique, Mössbauer spectroscopy, to investigate the distribution of Eu^{3+} ions between the C_2 and S_6 sites in Lu_2O_3 prepared in various ways as nanocrystalline powders and microcrystalline ceramics. This gives us the possibility not only to observe the
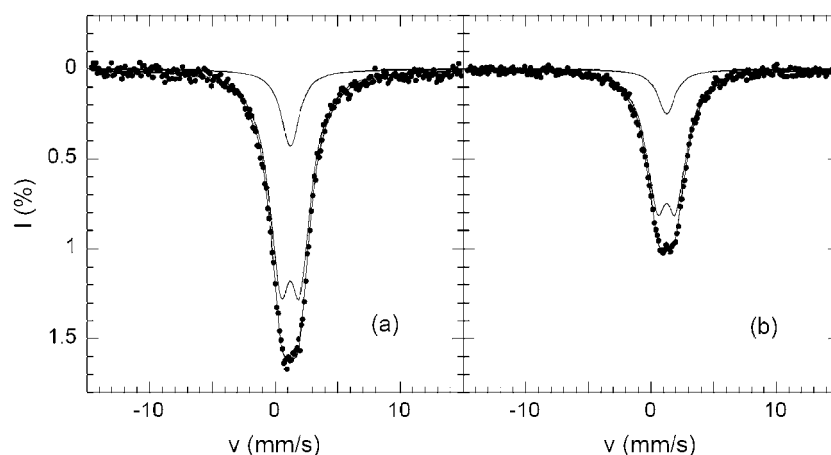
Figure 2. Mössbauer spectra of the $Lu_{1.8}Eu_{0.2}O_3$ ceramic samples: (a) sample S3 and (b) sample S4. Relative absorption intensity (I) versus velocity (v): the experimental data (dots) and the fit with the two components separately (full line) are shown.

distribution of the Eu^{3+} between the two sites for a specific specimen but also to analyse the variations of the occupancy of both sites depending on the fabrication conditions.

Comparing the results for all specimens and the derived parameters summarized in table 2 we see two important points:

- In the nanocrystalline powders there is observed only a small preferential occupation of the C_2 site over the S_6 one by Eu^{3+} ions.
- Sintered ceramics derived at high temperatures within a few hours from two different powders clearly exhibit a significant tendency to incorporate the Eu^{3+} ions into the non-centrosymmetric site, C_2.

Seeking the possible reasons of the variation in the site occupancy for nanocrystalline powders and ceramics we should note two important differences between the two types of materials. The size of the crystallites in powders is at least 100–300 times smaller in diameter than in ceramics. This means that the *volume* of crystallites in ceramics is roughly 6–7 orders of magnitude larger than in nanocrystalline powders. Thus during the sintering at elevated temperatures there takes place a very profound mass transfer occurring over a relatively long period of time. The fabrication of sintered ceramics taking place at 1750 °C for times as long as a few hours leads to a deep rearrangement of atoms making up the material. Consequently, we can think about the grains in ceramics as built up from scratch during the high-temperature sintering. What is more is that the grains in ceramics are being formed relatively slowly, systematically enlarging from nano-sized particles up to micron-sized ones. Thus during the sintering the material is not far from equilibrium state, and it systematically approaches equilibrium as the sintering proceeds. In contrast, the nano-sized crystals in powders are formed within seconds during the very vigorous combustion—the formation of the nanocrystals that appear is very rapid. Consequently, this process may be considered as occurring in the lack of equilibrium conditions. We think that the extremely different kinetics of the formation of the crystallites in both types of materials is the crucial parameter behind the different occupational probability of the C_2 and S_6 sites in Lu_2O_3 by Eu^{3+} ions. Hence, we think that the situation observed in ceramics validates that thermodynamically it is preferred to incorporate the Eu^{3+} ions into the C_2 site. In the case of the nanocrystalline powders, however, the very fast formation of the grains

and crystallites precludes the Eu^{3+} ions from the possibility to migrate to the positions they would otherwise favour. We can imagine the situation in the quickly formed nanocrystalline powders as if the Eu^{3+} ions were randomly entrapped rather than freely incorporated into the various sites offered by the host. Upon high-temperature synthesis the Eu^{3+} ions gain the possibility to diffuse within relatively large distances and then they choose to preferentially enter the C$_2$ site in the Lu$_2$O$_3$ host.

The preferential occupancy of the non-centrosymmetric site C$_2$ may be considered as a positive effect. Eu^{3+} is being introduced into the Lu$_2$O$_3$ host as an optically active ion, which is expected to produce red emission of high efficiency and relatively fast kinetics. This may be achieved if the emitting ion occupies the non-centrosymmetric site C$_2$, since in this case the faster (more probable) and more efficient electric dipole induced transitions occur.

We wish to comment now on the relatively high error of the fitting for the urea-made powder S1. We have recently reported [31] that in the powders prepared using the combustion technique and urea fuel the Eu^{3+} ions do not distribute uniformly over the whole volume of crystallites but they tend to gather mostly in their outer parts. Consequently, the concentration of Eu^{3+} in the interior part of these nanocrystallites is lower than in the outer shell. This inhomogeneous distribution of europium within a crystallite volume may easily increase the error of the fit, since the varying concentration of Eu leads to some variations of the size of the unit cell [2]. This in turn causes some variations in the crystal field felt by Eu^{3+} ions located in the outer part of crystallites compared to those which happened to locate in the core of crystallites. In fact the high error of the χ^2 parameter for this specimen (S1) additionally supports the conclusions drawn in [31]. Such a non-uniform distribution of Eu^{3+} within the crystallites does not occur for samples S2, S3 and S4, however. Therefore the results obtained here for these three materials are more appropriate for direct comparison.

Our research demonstrated that the synthesis technique and processing parameters may influence the occupancy of the two sites in Lu$_2$O$_3$ by dopant ions. Thus we should be very cautious in transforming the knowledge acquired in our research onto materials prepared using considerably different synthesis procedures. On the other hand, it is apparent that crystalline grains slowly formed at high temperatures conspicuously prefer incorporation of Eu^{3+} into the C$_2$ site of Lu$_2$O$_3$ host at the expense of the centrosymmetric site S$_6$. These results differ from those found for Y$_2$O$_3$, which we cited in introduction. This indicates that the formal similarity between Y$_2$O$_3$ and Lu$_2$O$_3$ hosts does not indeed mean that they always behave in the same or even a similar manner. Knowledge about yttria-based phosphors cannot be routinely transferred onto phosphors with a lutetia host lattice.

Acknowledgments

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