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Electric field gradient in bixbyite rare-earth oxides R_2O_3 $(R = \mathrm{Tl}, \mathrm{Eu}, \mathrm{Lu}, \mathrm{Tm})$ measured by perturbed angular correlation *

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The electric field gradient (EFG) at ^{111}Cd nuclei dilutely substituting the cation site in bixbyite rare-earth oxides Tl_2O_3, Eu_2O_3, Lu_2O_3 and Tm_2O_3 has been measured using perturbed angular correlation technique. The ^{111}In(EC) ^{111}Cd probe nuclei were introduced into the samples by thermal diffusion. The experimental EFG values are compared with those calculated using the point charge model (PCM). The results are discussed in terms of a correlation between the electric field gradient and cation–oxygen bond length in metal oxides.

1. Introduction

All rare earth metals form, under suitable conditions, a sesquioxide RE_2O_3, and have been reported to belong to up to five crystallographic space groups [1]. The bixbyite structure (body centered cubic C-form) can be obtained for all rare earth metal oxides, and belongs to the Ia3 space group where the metal atoms present two forms of six coordinated first neighbor oxygen polyhedra. Up to 2000°C, two more polymorphous crystallographic structures have been found in some rare earth metal oxides: the A-form (hexagonal, where the metal atoms are seven coordinated) and the B-form (monoclinic, with the metal atoms either six or seven fold coordinated). Besides the rare earth oxides, other metal oxides like In_2O_3, Sc_2O_3, Tl_2O_3 are also found in the cubic C-form.

The PAC technique was already used in the past to measure the electric field gradient in some bixbyite oxides. These results are collected in [2], where the experimental values of the EFGs are compared with the point charge model calculations. The ionic character of the chemical bonding in the binary oxides is assumed to depend on the cation–oxygen bond length in each compound. More recently, this systematics was extended to ternary oxides ABO_2 with delafossite structure [3,4] through the measurement of EFGs at both A and B sites of these oxides. The aim of the present measurements is to further extend this systematics to other rare-earth sesquioxides.

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In this work we report PAC measurements of the sesquioxides Tl_2O_3, Eu_2O_3, Lu_2O_3 and Tm_2O_3 using the ^{111}In–^{111}Cd nuclear probe at the metal site.

2. Experimental

The compounds Eu_2O_3, Lu_2O_3 and Tm_2O_3 were obtained from Johnson Matthey (99.9%) while the Tl_2O_3 sample was produced from oxidation of metallic thalium (99.99%) in an oxygen flux at 473 K during 12 hours. The samples were analyzed by X-ray powder diffraction and the crystal lattice parameters were obtained by the Rietveld method. The oxide powders were pressed into small discs and carrier free solution of ^{111}In in the form of $InCl_3$ was deposited on each disc, dried under infra red lamp, and diffused into the samples, at 1073 K for Eu_2O_3, Lu_2O_3 and Tm_2O_3, and at 823 K for Tl_2O_3, in air during 18 hours.

The PAC measurements were performed with a conventional slow–fast coincidence setup using four BaF_2 detectors in 90° geometry. The time resolution of the detector system was of the order of 0.7 ns. The perturbation function $R(t)$ was calculated from four $W(90°, t)$ and four $W(180°, t)$ coincidence spectra as

$$R(t) = 2\frac{W(180°,t) - W(90°,t)}{W(180°,t) + 2W(90°,t)} = A_{22}\sum_i f_i G^i_{22}(t), \tag{1}$$

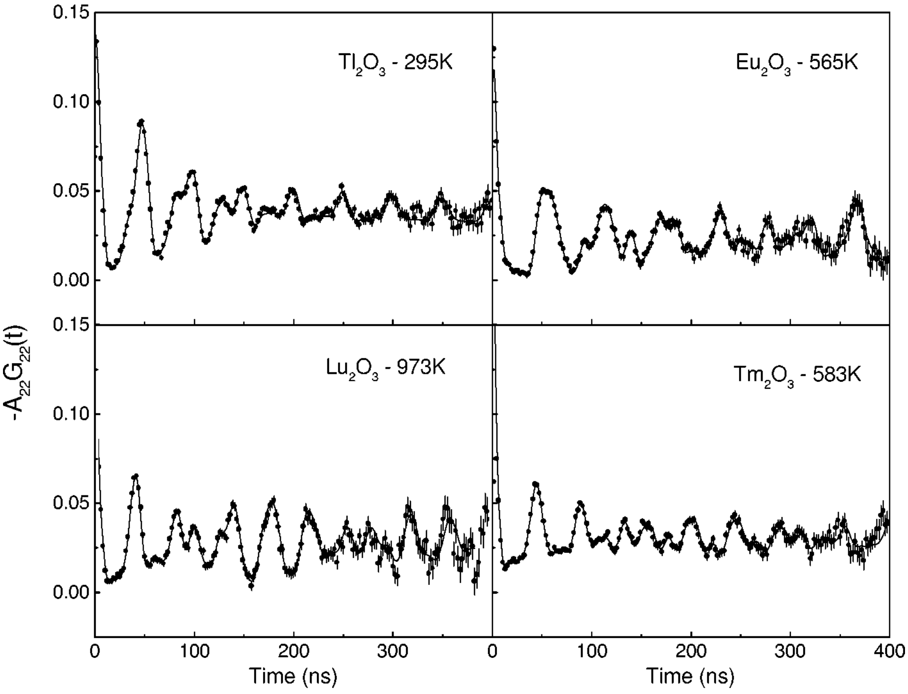

Figure 1. Perturbation functions $R(t)$ for ^{111}In–^{111}Cd in bixbyite oxides.

Table 1
Hyperfine parameters for the investigated bixbyite compounds.

Compound	A (Å)	d(cation-O) (Å)	V_{zz}(exp) · 10^{21} (V/m^2)	η (exp)	V_{zz} (PCM) · 10^{21} (V/m^2)	η (PCM)
Tl_2O_3	10.541	2.279	6.652	0	5.273	0
		2.272	6.489	0.21	5.573	0.57
Eu_2O_3	10.868	2.306	7.249	0	8.529	0
		2.353	2.154	0.87	−3.340	0.61
Lu_2O_3	10.391	2.243	7.482	0	7.850	0
		2.234	2.931	0.78	−3.418	0.68
Tm_2O_3	10.488	2.255	7.894	0	8.173	0
		2.260	3.475	0.72	−3.50	0.24

where f_i are the relative fractions of different EFGs contributing to the PAC spectrum and $G^i_{22}(t)$ are the corresponding perturbation factors for the static quadrupole interaction in polycrystalline materials.

The measurements were carried out at several temperatures. The results for Tm_2O_3 and Lu_2O_3 show strongly damped oscillations at temperatures below 600 K. This damping is believed to be due to a time-dependent interaction which is being investigated and will be reported in a future work.

The PAC spectra taken at 295 K for Tl_2O_3, 565 K for Eu_2O_3, 973 K for Lu_2O_3 and 600 K for Tm_2O_3 are shown in figure 1.

Two EFGs were found for each compound in an intensity ratio of 1 : 3 corresponding to the D and C sites for the cations in the bixbyite structure. The EFGs for the D-site show axial symmetry, while the EFGs for the site-C present an asymmetry parameter $\eta \neq 0$. The hyperfine parameters for the compounds investigated are shown in table 1 along with the calculated parameters with the point charge model.

3. Discussion

The EFGs due to the local oxygen configuration around the cation sites have been systematically investigated in the past with PAC using ^{111}Cd probes [2–4], in binary and ternary metal oxides. These studies revealed an interesting correlation between the electric field gradient at the ^{111}Cd probe and the cation–oxygen bond length. The results show that oxides with bond length exceeding 2.1 Å have predominantly ionic bonding, whereas those with bond lengths less than 2.1 Å have a partial covalent bonding with positive as well as negative contributions to the EFG. The results are summarized in figure 2. In this figure the ratio $R = |V_{zz}^{\mathrm{Exp}}/V_{zz}^{\mathrm{PCM}}|$ is plotted against the cation–oxygen bond length in the undoped oxides. The V_{zz}^{PCM} is the principal component of the EFG tensor calculated by a simple point charge model (PCM), whereas the V_{zz}^{Exp} is the corresponding experimental value. One can observe from the figure that for oxides with cation–oxygen bond lengths $\geqslant$ 2.1 Å the values of the ratio cluster around $R = 1$ whereas for those with cation–oxygen bond lengths

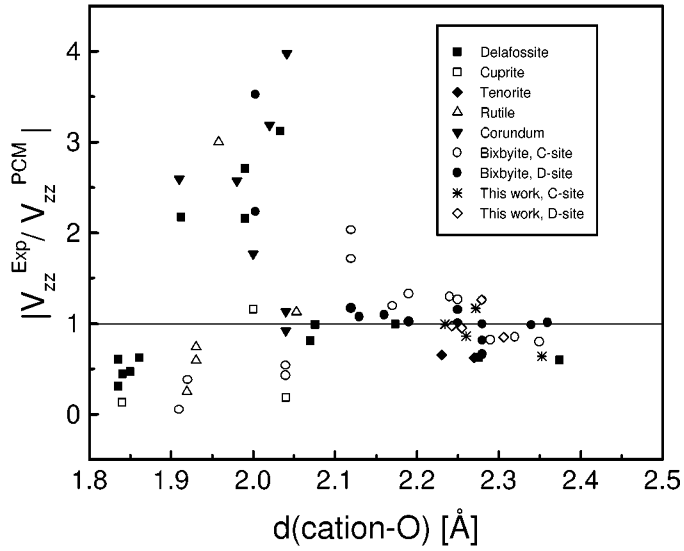

Figure 2. The ratio $R = |V_{zz}^{\mathrm{Exp}}/V_{zz}^{\mathrm{PCM}}|$ plotted versus d(cation-O) in oxides.

< 2.1 Å the ratio splits into two branches with values greater and smaller than $R = 1$ indicating positive and negative contributions to the EFGs most probably due to the partial covalent cation–oxygen bonding. The critical bond distance 2.1 Å is just the sum of the Shannon radii [5] of the O^{-2} and Cd^{+2} ions. In this work the systematic is extended to heavy rare-earth oxides which have cation–oxygen bond lengths larger than 2.1 Å. The values of the ratio, $R = |V_{zz}^{\mathrm{Exp}}/V_{zz}^{\mathrm{PCM}}|$ as can be seen in figure 2, are found around $R = 1$, and therefore confirm the general trend for binary and ternary oxides. This systematics should also be extended to other rare-earth bixbyite oxides, specifically the light rare-earth oxides. Some of the lighter rare-earth oxides are however quite difficult to obtain in the C-form structure.

References

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