

Magnetic susceptibility and ordering of Yb and Er in phosphors Yb,Er:Lu₂O₃

J. Blanusa^{*}, N. Jovic, T. Dzomic, B. Antic, A. Kremenovic, M. Mitric, V. Spasojevic

Condensed Matter Physics Laboratory, The “Vinca” Institute, POB 522, 11001 Belgrade, Serbia

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Abstract

Mixed sesquioxides (Lu_{0.9}Er_{0.1})₂O₃ and (Lu_{0.9}Yb_{0.1})₂O₃ were prepared and analyzed by the XRD and magnetic susceptibility measurements. The samples crystallize in the space group $Ia\bar{3}$ with a bixbyite structure type. The structure refinement have shown that Er³⁺ exclusively occupy C₂ sites in (Lu_{0.9}Er_{0.1})₂O₃, while Yb³⁺ are preferentially distributed in C_{3i} sites in (Lu_{0.9}Yb_{0.1})₂O₃. Magnetic susceptibility data in the whole 2–300 K temperature region was analyzed by the model based on perturbation theory. The mean energy gap between ground and some of the excited crystal field levels (E_i), and their effective magnetic numbers M_{eff} were determined. The obtained energy levels are compared with theoretical values, and discussed in relation to the cation distribution. An analysis of paramagnetic temperature has shown absence of magnetic ion clustering.

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1. Introduction

The rare earth doped materials are widely used as phosphors, catalysts, fuel cells, solid electrolytes, additive for the iron and steel industry and biological applications [1–7]. Particularly, rare earth doped sesquioxides Y₂O₃, Lu₂O₃ and Sc₂O₃ are subject of intensive investigation as materials suitable for optical applications [4,6]. As well as Y₂O₃ and Sc₂O₃, Lu₂O₃ has higher thermal conductivity than YAG, so it could be a promising laser host crystal. Particularly, the conductivity of Yb doped Lu₂O₃ is found to be twice of that for Yb doped YAG [4]. Both experimental and theoretical investigations show the lowest drop in thermal conductivity of Lu₂O₃ when doped with ytterbium ion [4].

Ternary sesquioxides obtained by mixing of two C-type binary sesquioxides (one magnetic and the other diamagnetic) belong to the class of diluted magnetics [8–10], so

Yb and Er doped Lu₂O₃ belongs to that class. The C-type (bixbyite) structure of sesquioxides (RE₂O₃) is cubic (space group $Ia\bar{3}$). The cations are distributed over two nonequivalent crystallographic sites: 8b with local symmetry C_{3i} and 24d with local symmetry C₂, while oxygen ions are in the general 48e positions [11]. Cation site occupancy is very important structural parameter that determine optical, magnetic and the other physical properties. RE³⁺ ions in host sesquioxide matrices are preferable to be at C₂ site from optical point of view [5]. We used X-ray powder diffraction (XRPD) to determine C_{3i}/C₂ site occupancies in phosphors Yb,Er:Lu₂O₃.

Both Er³⁺ and Yb³⁺ ions have a large splitting between ground and the first excited manifold level, so the latter do not significantly contribute to the magnetic properties at room temperature. In the case of Yb³⁺, that gap is about 10,000 cm⁻¹ which is the largest splitting among all rare earth elements. Because of the simple energy level diagram of Yb³⁺ ion in crystal field and its pronounced optical activity, it is considered as a good candidate to replace Nd³⁺ in laser materials [3,12].

^{*} Corresponding author. Tel.: +381 11 8065828; fax: +381 11 8065829.
E-mail address: blanusa@vin.bg.ac.yu (J. Blanusa).

Griebner et al. [4] demonstrated that Yb: Lu₂O₃ are promising isotropic crystals for high-power lasers in 1 μm range. Polizzi et al. have shown that Er doped Lu₂O₃ is suitable for a number of application in the field of optical materials [6]. Following these results we have synthesized Yb and Er doped Lu₂O₃, to determine structure properties (especially site occupancies) and to analyze their magnetic behavior in respect to the crystal field influence, which in turn result in determination of the mean energy gap between ground and some of the excited crystal field levels (E_i) of Yb³⁺ and Er³⁺, and their effective magnetic numbers M_{ieff} .

2. Experimental

The ceramic procedure is used to prepare (Lu_{0.9}Er_{0.1})₂O₃ mixed sesquioxide. Starting oxides Lu₂O₃ and Er₂O₃ were mixed in appropriate stoichiometric ratio, pressed in pellets, pre-sintered at 950 °C for 24 h and sintered at 1350 °C for 12 h. (Lu_{0.9}Yb_{0.1})₂O₃ was prepared as follow: mixture of Yb₂O₃ and Lu₂O₃ was dissolved in HNO₃. Precipitation of the appropriate hydroxide was achieved by the addition of NH₄OH. The precipitates were washed in distilled water, dried and milled. The powder was pressed and fired at 1000 °C for 24 h. Crystal structures of prepared samples were analyzed by XRPD.

To refined crystal structure of prepared samples, X-ray diffraction data collected at Philips PW1010 diffractometer (CuK_{α1,2}) were used. Data were collected at every 0.02° in angle range 15–120° in 2θ . The counting time was fixed at 15 s per step for both samples.

Zero-field-cooled (ZFC) magnetization was measured in the temperature region of 1.8–300 K, and in an applied field of 300 Oe using an MPMS XL-5 SQUID magnetometer.

3. Results and discussion

3.1. Crystal structure refinement by the Rietveld method

Diffraction patterns have shown single-phase formation, with reflections corresponding to space group $Ia\bar{3}$ and bixbyite structure type. The crystal structures of the samples were refined by the Rietveld method using the Fullprof computer program [13]. The following structure and atomic parameters were refined: lattice parameters (a), occupation numbers (N) (coupled in order to keep the stoichiometric ratio constant), isotropic temperature vibration factors (B) and atomic coordinates. Fig. 1 shows a comparison between observed and calculated intensities of samples. The results of Rietveld refinement procedure, given in Table 1 and Fig. 1, confirm good agreement between the structural model and the observed data. The final R-factors (Bragg's, weighting profile and the profile) are listed in Table 1.

The values of lattice parameter a , obtained by the crystal structure refinement, are given in Table 1. Tacking literature values for lattice parameters of pure sesquioxides [14]: a (Lu₂O₃) = 10.3907 Å, a (Er₂O₃) = 10.5473 Å and a

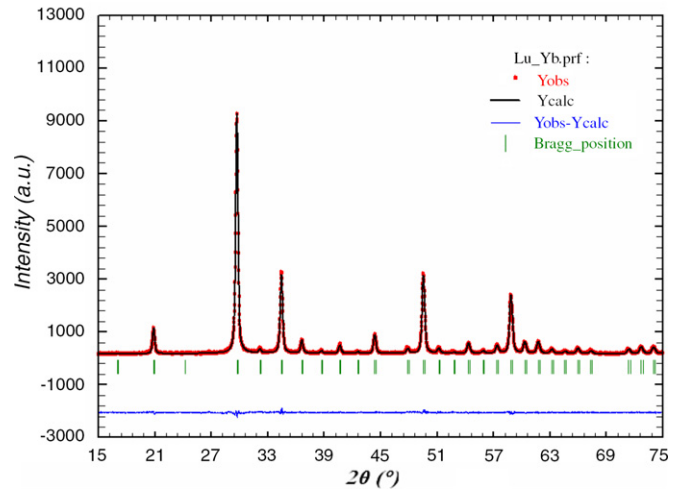


Fig. 1. Comparison of observed (circles) and calculated (solid line) intensities for (Lu_{0.9}Yb_{0.1})₂O₃. The difference pattern appears below. The vertical bars, at the bottom, indicate reflection position.

Table 1

Refined atomic and crystal parameters and corresponding R-factors

	(Lu _{0.9} Er _{0.1}) ₂ O ₃	(Lu _{0.9} Yb _{0.1}) ₂ O ₃
a (Å)	10.4044 (2)	10.3996 (1)
Lu, Er (Yb) C ₂		
x	−0.03318 (7)	−0.03278 (5)
O		
x	0.3904 (8)	0.3905 (7)
y	0.1501 (8)	0.1528 (6)
z	0.381 (1)	0.3801 (8)
$d(C_{3i}-O)$ (Å)	2.251 (9)	2.239 (7)
$\langle d \rangle(C_{2}-O)$ (Å)	2.234 (9)	2.240 (7)
$N(\text{Lu})$ C ₂	2.63 (2)	2.85 (2)
$N(\text{Er, Yb})$ C ₂	0.37 (2)	0.15 (2)
$N(\text{Lu})$ C _{3i}	0.97 (2)	0.75 (2)
$N(\text{Er, Yb})$ C _{3i}	0.03 (2)	0.25 (2)
B (Å ²) C _{3i}	0.72 (1)	0.43 (1)
B (Å ²) C ₂	0.659 (1)	0.33 (1)
B (Å ²) 48e	2.0 (1)	1.0 (1)
R_B (%)	3.85	2.15
R_{wp} (%)	15.1	10.5
R_p (%)	14.1	10.2

(Yb₂O₃) = 10.4334 Å, it was found that Vegard's rule was obeyed: $a(x) = a_0 + bx$ with $a_0 = 10.3897$ and $b = 0.0787$ for (Lu_{0.9}Er_{0.1})₂O₃. The coefficient b reflects the difference in ionic radii of Er³⁺ and Lu³⁺. In the bixbyite type of structure the relationship between lattice parameters and cationic radii is [15]: $\delta r = r(\text{Er}^{3+}) - r(\text{Lu}^{3+}) = 2b/4 = 0.039$ Å. For comparison, the difference in ionic radii for Er³⁺ and Lu³⁺ coordinated by six anions is $\delta r = 0.033$ Å [16]. Similarly, the parameters found for the sample (Lu_{0.9}Yb_{0.1})₂O₃ were: $a_0 = 10.3907$ and $b = 0.0783$.

Isotropic temperature factors (B) are refined for each crystallographic position, Table 1. We point to the influence of diffusion scattering on B-factors because of substitution of Lu³⁺ by Er³⁺ / Yb³⁺.

Refined values of the occupation number N show that Er³⁺ ions are distributed exclusively at C₂ site in

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