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ScienceDirect

Ceramics International 42 (2016) 3899–3906

CERAMICS INTERNATIONAL

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Photoluminescence of europium(III)-doped $(Y_xSc_{1-x})_2O_3$ nanoparticles: Linear relationship between structural and emission properties

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Received 23 June 2015; received in revised form 5 November 2015; accepted 11 November 2015
Available online 27 November 2015

Abstract

Europium (III)-doped $(Y_xSc_{1-x})_2O_3$ nanocrystalline powders of different compositions ($x=0$, 0.25, 0.5, 0.75 and 1) are synthesized using a polymer complex solution method. Comparative structural and optical characterization is carried out with powder X-ray diffraction and photoluminescence excitation, emission and emission decay measurements. Detailed information about unit cell parameter and energy levels of europium (III) ions are presented for all powder compositions. The second rank crystal field parameters $\left(B_0^2\right)$ and $\left(B_2^2\right)$ and crystal field strength (N_v) are calculated from the energies of Stark components of the $^7F_1$ manifold of the europium (III) emissions. It has been shown that the crystal field parameter changes with the powder composition and shows a linear relationship with the average ionic radii of cations in the solid solutions. A similar dependence is also found for the magnitude of splitting of $^7F_1$ manifold vs. unit cell parameter values. Moreover, this linear relationship is demonstrated for the whole family of europium (III)-doped mixed rare-earth sesquioxide hosts ($RR'O_3$; R, R′ = rare earth ions) by taking into consideration results published in the literature so far. A simple, semi-empirical equation which relates structural properties (unit cell parameters, ionic radii) of the sesquioxide host material and the emission properties of europium (III) ions (energy splitting of the $^7F_1$ manifold, crystal field parameters and crystal field strength) are presented.

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Keywords: A. Powders: chemical preparation; C. Optical properties; D. Y_2O_3; Crystal field

1. Introduction

The rare earth elements and their compounds have unique spectroscopic properties that make them attractive to both scientists, who probe the fundamental properties of these systems, and engineers, who develop these systems into photonic devices. Knowledge of an almost complete electronic energy level scheme of rare earth ions and the possibility of reproducing through effective operators numerous free ion and crystal field interactions in the 4*f* configuration gained many fundamental studies of magneto-optical effects. These studies, and the fact that much of luminescent and laser materials include rare earths as active ions, have had a profound impact on rare earth compound development in terms of practical opto-electronic devices. The number of functional materials based on rare earth compounds has been developed for various fields of application. The intense emissions and almost monochromatic colors obtained by diluting rare-earths activators in appropriate hosts were the primary reason for this development. In this way, a great variety of emissions can be obtained, depending on the type of activator and on the respective positions of the excited and ground energy levels [1–8].

The luminescence of ions in crystals are influenced by the crystal field (electric field) created by the neighboring ions at a site occupied by the luminescent ion. Among rare-earths, the well-known emission of the trivalent europium ion provides valuable information about the structure and the symmetry of the host materials. When the europium (III) ion is incorporated into a host material, the crystal field splits the *J*-multiplets of energy levels into sublevels (Stark splitting) depending on the

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http://dx.doi.org/10.1016/j.ceramint.2015.11.056

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symmetry [9,10]. Even though the interaction between the 4*f* electrons and the crystal field is weak and only a small Stark splitting of a few hundred cm^{-1} occurs, europium (III) emissions can be recognized as the fingerprints of structure and symmetry of the host materials, making europium (III) a structural probe ion [11,12].

To date, several studies have reported on the relationship between the structure and the luminescence of europium (III)-doped rare earth sesquioxides and mixed sesquioxides [13–17] where experimental results have been related to the crystal field theory [18–21]. In this paper, we investigated in detail the emission properties of a europium (III)-doped mixed Y_2O_3-Sc_2O_3 nanocrystalline host. Moreover, we aimed to analyze the structure-luminescence relationship in the mixed sesquioxide host with the large difference between ionic radii of the constituting cations ($Y^{3+}_{VI}=0.9$ Å; $Sc^{3+}_{VI}=0.745$ Å, [22]), and sought to find a semi-empirical formula which describes this relationship. For these reasons, the detailed structural and photoluminescent characterization of the samples is performed by X-ray diffraction (XRD) and photoluminescence (PL) excitation, emission and emission decay measurements. The energy levels of the europium (III) ions in Y_2O_3–Sc_2O_3 hosts of different compositions were derived from the excitation and emission spectra, and second rank crystal field parameters $\left(B^2_0\right)$ and $\left(B^2_2\right)$ and the crystal field strength (N_v) was calculated from the experimental data.

2. Materials and methods

A set of 5 samples $(Y_xSc_{1-x})_2O_3$ ($x=1$, 0.75, 0.5, 0.25, 0) doped with 3 at% europium (III) ions (with respect to all constituent atoms) were synthesized with a polymer complex solution, the basic principles of which are given in more detail in our previous manuscripts [13–17].

X-ray diffraction measurements were performed on a SmartLab (Rigaku) instrument, using Cu $K_{\alpha1,2}$ radiation at 30 mA and 40 kV. Diffraction data were recorded in a 2θ range from 10° to 80° in 0.02° steps. Relevant results of structural analysis (crystal coherence size, unit cell parameter, microstrain values and data fit parameters) were obtained using built-in package software. Excitation and emission measurements were performed at room temperature on a Fluorolog-3 Model FL3–221 spectrofluorometer system (Horiba JobinYvon), using a 450 W Xenon lamp as an excitation source for steady state measurements and a Xenon–Mercury pulsed lamp for lifetime measurements. A TBX-04-D (Horiba JovinYvon) detector was used for both lifetime and steady state acquisition. The photoluminescence measurements were performed on 12 mm pellets prepared by compacting powders under a load of 5000 kg, without any additives.

3. Results and discussion

3.1. Structural characterization

Binary systems of the rare-earth sesquioxides, R_2O_3–R'_2O_3 (R, R′= rare earth ions) can form solid solutions. The solubility of one oxide into another is determined by the difference in the ionic radii, the structural compatibility and the temperature [23]. It is well known that at atmospheric pressure rare-earth sesquioxides crystallize into five polymorphic forms: low temperature (< 2000 °C) cubic (C), monoclinic (B) and hexagonal (A) as well as high temperature (> 2000 °C) hexagonal (H) and high temperature cubic (X) forms [23]. Among them, the low-temperature cubic (C) phase takes the broadest range.

The C-type R_2O_3 sesquioxides (space group $Ia3^-$, No 206, $Z=16$) crystallize isomorphic to the mineral bixbyite $(Mn, Fe)_2O_3$. The R_2O_3 bixbyite unit cell is conveniently presented as eight fluorite cells obtained by a doubling of the fluorite lattice constant, while the simple fluorite cell has two vacancies paired along the body (or face) diagonally to the anion cube. In this manner, crystallographic positions of R^{3+} ions are usually presented as cubes with oxygens and vacancies in their corners. Nevertheless, the structure topologically differs from the fluorite structure, since it is heavily cation disordered oxygen-deficient to the fluorite structure. As can be seen in Fig. 1a, the R^{3+} ions form two types of cation layers in the crystal lattice. One of them consists of R^{3+} with C_2 point symmetry ions exclusively, while the other contains equal numbers of R^{3+} with C_2 and C_{3i} (S_6) point symmetries. These are two distinct six-fold coordinations of the R^{3+} ion, 24d (x, 0, 1/4) with point symmetry C_2 and the other, three times less abundant, position 8b (1/4, 1/4, 1/4) with point symmetry C_{3i} (S_6). The corresponding coordinaton polyhedra are presented in Fig. 1b and compared to the simplified interpretation of the vacancy pairs in fluorite subcells oriented along body or face diagonals in the cube.

According to our previous results all samples were calcinated at 800 °C for 2 h. However, in this case, the applied thermal treatment was not long enough. The diffraction pattern of the $(Y_{0.5}Sc_{0.5})_2O_3$ sample shown as Supplementary Fig. S1 clearly indicates barely crystalline material. The reason is the marked difference in ionic radii of constituting atoms, $Y^{3+}_{VI}=0.9$ Å; $Sc^{3+}_{VI}=0.745$ Å [22]. Therefore, calcination time was prolonged at 18 h and X-ray diffraction patterns of all five samples are presented in Fig. 2a.

The XRD analysis confirms that all samples crystallize in a cubic bixbyite structure same as pure Y_2O_3 and Sc_2O_3. The main diffraction peaks are indexed according to the yttrium-oxide, ICDD01-074-7392 and scandium-oxide, ICDD01-073-1691 cards. No other phase peaks or traces of impurities were detected, verifying the complete dissolution of the two oxides in the final product and the formation of a solid solution of cubic structure. The increase of the unit cell parameter with the decrease in content of bigger in size yttrium(III) ion, $Y^{3+}_{VI}=0.9$ Å $>$ $Sc^{3+}_{VI}=0.745$ Å, is manifested through a notable shift of the reflection peaks towards higher angles (see Fig. 2b). The graphic interpretation of the (222) diffraction peak shift (Fig. 2c) shows the XRD spectra are shifted uniformly with a change in composition of the solid solutions (with reference to the Y_2O_3 sample), following a linear trend.

The results of the structural analysis (crystallite size (CS), unit cell parameter, microstrain values and data fit parameters) are presented in Table 1. The average crystallite size is in the ~7–21 nm range, while the unit cell parameter, *a*, almost linearly

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