SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Preparation, Morphology, and Luminescent Properties of Europium-Doped Nanodispersed Scandium Sesquioxide

I. V. Baklanova, V. N. Krasil'nikov, L. A. Perelyaeva, and O. I. Gyrdasova

Institute of Solid-State Chemistry, Ural Branch, Russian Academy of Sciences, ul. Pervomaiskaya 91, Yekaterinburg, 620990 Russia Received July 22, 2012

Abstract—Scandium sesquioxide-based solid solutions of composition $Sc_{2-2x}Eu_{2x}O_3$ (0.005 $\leq x \leq 0.05$) were prepared by thermolysis of $Sc_{1-x}Eu_x(CH_3COO)_3$ and by reacting mixtures of scandium and europium nitrates with ethylene glycol. Thermal decomposition of $Sc_{1-x}Eu_x(CH_3COO)_3$ was found to yield $Sc_{2-2x}Eu_{2x}O_3$ with the shapes of aggregates atypical of the cubic structure of this oxide, and the reaction products of scandium and europium nitrates were found to have a loose spongelike structure. A spectroscopic study showed that $Sc_{2-2x}Eu_{2x}O_3$ and $Sc_{1-x}Eu_x(CH_3COO)_3$ are potential luminescent materials active in the visible spectral region. The tervalent europium in the $Sc_{2-2x}Eu_{2x}O_3$ structure is the source of strong red emission (${}^5D_0 \rightarrow {}^7F_2$) and can be used in fluorescent lamps, colored lightning, and optoelectronic devices.

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Scandium sesquioxide (Sc_2O_3) , which has high thermal conductivity, mechanical strength, and radiation stability, is a promising material for manufacturing high-power solid laser matrices, laser displays, optical amplifiers, cathode ray tubes, and other devices [1-15]. A special advantage of Sc₂O₃ over Y_2O_3 (which is widely used in the manufacture of optically active materials, in particular, luminescent materials [16]) consists in the chemical inertness toward the natural components of air, namely, carbon dioxide and water vapor. Inasmuch as it is difficult to prepare Sc_2O_3 and $Sc_{2-2x}Ln_{2x}O_3$ solid solutions (where Ln stands for a lanthanide) in single crystals because of their very high melting temperatures (~2500°C), in the last years efforts have been made to prepare these oxides as nanosized samples, ceramics, and films. It is assumed that, thanks to quantum, dimensional, and surface effects, the manufacture of nanosized, specifically, quasi-one-dimensional (1D) structures would endow the material with unique optical properties. At the same time, nanosized $Sc_{2-2x}Ln_{2x}O_3$ oxides can serve as precursors for manufacturing transparent highdensity ceramics.

Of the simplest and productive methods for preparing highly dispersed oxide materials with a tailored aggregate morphology, the precursor method should be mentioned; the underlying idea of this method is the pseudomorphic transformation of the precursor to the oxide under heating. The most frequently used precursors are salts of carboxylic acids. For example, nanodispersed sesquioxides Y_2O_3 and Sc_2O_3 with extended particle shapes, which are atypical of their cubic (isotropic) structure, were prepared as a result of thermolysis of yttrium and scandium acetates (which crystallize in fibrous or acicular crystals) [17, 18]. A glycine nitrate method is very attractive for preparing nanostructured sesquioxide $Sc_{2-2x}Ln_{2x}O_3$; the underlying idea of this method is the reaction of mixtures of scandium and lanthanide nitrates with glycine at relatively low temperatures [2]. An interesting variant of this method is where the combustible agent is ethylene glycol; this method was employed to prepare nanodispersed oxides, namely, CeO₂ [19], Lu_{2-x}Eu_xO₃ [20] La₂O₃, Ga₂O₃, and MgO; a solid electrolyte of composition $La_{0.88}Sr_{0.12}Ga_{0.82}Mg_{0.18}O_{2.85}$ [21, 22]; and ytterbium-doped yttrium aluminum garnet [23]. Here, we used two original methods to prepare quasi-1D and nanostructured europium-doped scandium sesquioxide. One method involves thermolysis of Sc_{1 - x}Eu_x(CH₃COO)₃ precursors; the other involves the reaction of scandium and europium nitrates with ethylene glycol.

EXPERIMENTAL

The $Sc_{1-x}Eu_x(CH_3COO)_3$ precursor with extended crystal shapes was prepared by dissolving mixtures of Sc(OH)₃ and Eu(OH)₃ with a certain ratio Sc/Eu in 20% acetic acid at 60°C and subsequently concentrating the solution to dry residue on a water bath. The required hydroxide mixtures were prepared by coprecipitating the nitrates from solutions by adding aqueous ammonia. The nitrate solutions were prepared from Sc₂O₃ and Eu₂O₃ (99.95%), which were precalcined at 800°C for 2 h, and concentrated HNO₃ (high purity grade). The alternative method used to prepare $Sc_{1-x}Eu_x(CH_3COO)_3$ involved boiling Sc_2O_3 and Eu₂O₃ mixtures in 20% acetic acid followed by separation of acetate crystals from the mother solution by vacuum filtration and drying at 40°C.



Fig. 1. TG and DTA curves for $Sc_{0.95}Eu_{0.05}(CH_3COO)_3$.

The method used to prepare $Sc_{2-2x}Eu_{2x}O_3$ as a nanodispersed powder involved a reaction in the redox system where the oxidizer was a mixture of scandium and europium nitrates and the reducer (combustible material) was ethylene glycol. Ethylene glycol (unlike glycine) can dissolve scandium and yttrium nitrates under mild heating $(40-50^{\circ}C)$ to form a transparent gel. Upon further rise in temperature, the gel is dehydrated with elimination of water vapor. The presence of water in the gel is due to its occurrence in the precursor nitrates, which are isolated from nitric acid solutions as crystal hydrates [24]. After the water is eliminated, at temperatures above $>80^{\circ}$ C the gel starts to decompose with gas bubble evolution, which becomes progressively vigorous; then, the process becomes uncontrollable, that is, it occurs spontaneously until the oxide is formed. Inasmuch as this process occurs without visible nitrogen oxide evolution, the reaction of the components of the redox system (which is the dehydrated gel based on a scandium and europium nitrate mixture and ethylene glycol) may be described by the following equation:

$$(2 - 2x)Sc(NO_3)_3 + 2xEu(NO_3)_3 + 3HOCH_2CH_2OH = Sc_{2-2x}Eu_{2x}O_3 (1) + 6CO_2 + 3N_2 + 9H_2O.$$

Dehydrated scandium and europium nitrates are also well soluble in ethylene glycol under heating; for this reason, reaction (1) can be carried out after the nitrate mixture is partially or completely dehydrated.

The phase analysis of the precursors, their thermolysis products, and the products of reaction (1) was carried out on a STADI-P (STOE) X-ray diffractometer using CuK_{α} radiation and a POLAM S-112 polarizing microscope in the transmitted light. Particle shapes and particle sizes were determined by scanning electron microscopy (SEM) using a JSM JEOL 6390LA instrument. The thermogravimetric analysis of $Sc_{1-x}Eu_x(CH_3COO)_3$ precursors was performed on a Q-1500D derivatograph (the heating rate was 10 K/min). Raman spectra were recorded at room temperature on a RENISHAW-1000 spectrophotometer ($\lambda = 514.5$ nm, Ar⁺ laser, W = 25 mW). Cathodoluminescence (CL) spectra were recorded on a KLAVI setup [25] in the pulsed cathodoluminescence mode, where $Sc_{2 - 2x}Eu_{2x}O_3$ samples having equal weights (30 mg) were exposed to short-duration (2-ns) electron beams with an energy of 170 keV (current density: 160 A/cm²). Reflection spectra were recorded in the range 190–900 nm on a UV-2401 PC (Shimadzu) spectrophotometer using a BaSO₄ reference. Emission spectra were recorded on a Varian Cary Eclipse fluorimeter (a 75-kW xenon lamp); test samples were prepared as disks 5 mm in diameter and 2 mm thick.

RESULTS AND DISCUSSION

According to microscopic analysis, $Sc_{1-x}Eu_x$ (CH₃COO)₃ ($0 \le x \le 0.1$) crystals prepared by spontaneous crystallization of a saturated solution are shaped as needles or rods with cross sections of about 0.2– 0.5 µm and lengths of up to 1–5 µm and tend to longitudinal intergrowth. The birefringence of these crystals is very high. Refractive indices for Sc_{0.9}Eu_{0.1}(CH_3COO)_3 are as follows: Ng = 1.612, Np = 1.504, Ng - Np = 0.108. In the samples where the composition corresponds to x > 0.1, shapeless flat chips of Eu(CH₃COO)₃ · nH₂O crystals and their random intergrowths, having non-uniform extinction, are encountered along with extended Sc_{1-x}Eu_x(CH₃COO)₃ crystals.

The thermal decomposition of $Sc_{1-x}Eu_x$ (CH₃COO)₃ to $Sc_{2-2x}Eu_{2x}O_3$ occurs in one stage within the temperature range ~300–425°C. The weight losses of Sc(CH₃COO)₃ and Sc_{0.95}Eu_{0.05}(CH₃COO)₃ samples as estimated from TG curves (Fig. 1) are close to the theoretical values calculated on the assumption of formation of Sc₂O₃ (68.96 wt %) and Sc_{1.9}Eu_{0.1}O₃ (67.33 wt %), and amount to 68.9 and 67.25 wt %, respectively.

The SEM image in Fig. 2a demonstrates that the conversion of $Sc_{0.975}Eu_{0.025}(CH_3COO)_3$ into $Sc_{1.95}Eu_{0.05}O_3$ under heating in air occurs with the inheritance of the precursor crystal shape by oxide particles. However, aggregates of the nascent oxide are bent in the course of the decomposition of the precursor with elimination of volatiles, likely because of the inconsistence of the oxide cubic structure and anisotropic shapes of aggregates and because of their constitutional specifics. The SEM images recorded at ×90000 magnification show that these aggregates represent rolls of very thin oxide layers. Reaction (1) occurs with vigorous evolution



Fig. 2. SEM images of the sesquioxide of composition $Sc_{1.95}Eu_{0.05}O_3$ prepared (a) by thermolysis of $Sc_{0.975}Eu_{0.025}(CH_3COO)_3$ and (b) by heating the nitrate mixture with ethylene glycol. In the inset: a SEM image of $Sc_{0.975}Eu_{0.025}(CH_3COO)_3$ precursor crystals.

of gaseous products (CO₂, N_2 , and H_2O), and this dictates the morphology of the nascent $Sc_{2-2x}Eu_{2x}O_3$. From the SEM image in Fig. 2b, one can see that the sesquioxide of composition $Sc_{1.95}Eu_{0.05}O_3$, which was prepared by reacting scandium and europium nitrates with ethylene glycol, has a loose spongelike structure and is built of very thin nanoparticles. This agrees with the absence of distinct reflections in the X-ray diffraction pattern of this sample, caused by its X-ray amorphous state. The crystallization of the X-ray amorphous phase to cubic $Sc_{1,9}Eu_{0,1}O_3$ occurs as a result of annealing the sample at temperatures above >700°C. For the $Sc_{1,95}Eu_{0,05}O_3$ sample after annealing the product of reaction (1) at 800°C for 2 h, the average crystallite size estimated according to Scherrer was 12.3 nm. The diffraction pattern for the $Sc_{1,9}Eu_{0,1}O_3$ sample prepared by heating $Sc_{0.95}Eu_{0.05}(CH_3COO)_3$ at 500°C has very broad lines and a large background, which is another piece of evidence for the high dispersity of the sample. Figure 3 displays X-ray diffraction patterns for Sc1.9Eu0.1O3 samples prepared by heating $Sc_{0.95}Eu_{0.05}(CH_3COO)_3$ to 500, 900, and 1100°C at a rate of 10 K/min followed by 2-h exposures at these temperatures.

Raman spectra of $Sc_{2-2x}Eu_{2x}O_3$ solid solutions prepared by the two above-described methods were recorded at $\lambda = 514.5$ nm. This excitation (which is closed to the excitation of the ${}^7F_0 \rightarrow {}^5D_1$ transition $(\lambda_{ex} = 525 \text{ nm})$ in Eu³⁺ [26]) gives rise to a very active emission spectrum of europium(III) (Fig. 4). Especially noteworthy is the Raman spectrum of the x =0.025 sample, where europium luminescence completely suppresses the Raman spectra of Sc₂O₃. The lines observed in the Raman spectra of Sc_{1.95}Eu_{0.05}O₃ samples synthesized by the two methods coincide in their positions regardless of the preparation method; that is, the macrostructure of these samples is the same (Fig. 5). Insignificant differences in line intensities can arise from the different degrees of crystallinity of the samples.

Europium(III) in the Sc_2O_3 cubic structure can substitute two positions (C_2 and C_{3i}) in the ratio $C_2/C_{3i} = 3:1$ [16]. Electric dipole transitions are allowed for Eu^{3+} ions in the C_2 positions, whereas the transitions from the C_{3i} positions are forbidden. When europium ions are in the C_{3i} positions, magnetic dipole transitions are observed. $4f \rightarrow 4f$ emission bands due to transitions from excited state to the ${}^{7}F_{J}$ lower-lying states (J = 0, 1, 2, 3, or4) in the Eu³⁺ ion appear in the range 2000–5000 cm⁻¹. The line at 3086 cm^{-1} (611 nm), which is the strongest line in the spectrum, and the line at 3702 cm^{-1} (635 nm) correspond to the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition in an Eu³⁺ ion in the C_{2} position [16]. Three weaker bands at 2373 (586), 2601 (594), and 2805 cm⁻¹ (601 nm) are associated with transitions from the ${}^{5}D_{0}$ level to ${}^{7}F_{1}$ Stark levels in an Eu³⁺ ion in the C_2 position. The weak line at 2283 cm⁻¹ (582 nm) may be identified as ${}^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition of an Eu³⁺ ion in the C_{3i} position. The luminescence line at 2212 cm^{-1} (580 nm) of the magnetic dipole transition is related to a more intense ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition of an Eu³⁺ ion in the C_2 position. The low-intensity line at 4040 cm⁻¹ (649 nm) corresponds to the ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ transition, and that at 4924 cm⁻¹ (689 nm) corresponds to the ${}^5D_0 \rightarrow {}^7F_4$ transition. Noteworthy, the probability of the ${}^5D_0 \rightarrow$ $^{7}F_{1}$ magnetic dipole transition (orange) is almost independent of the local surrounding of the europium in the host. The ${}^5D_0 \rightarrow {}^7F_2$ transition (red) has an electric dipole nature, is very sensitive to the europium ion surrounding, and is characterized as hypersensitive. The transition intensity ratio ${}^{5}D_{0} \rightarrow {}^{7}F_{2}/{}^{5}D_{0} \rightarrow {}^{7}F_{1}$ is the asymmetry ratio. The higher the ratio, the closer the local symmetry of the Eu³⁺ ion to a center of inversion. This ratio indicates the deviation of the Eu³⁺ ion from, or approaching to, centrosymmetric geometry as regards its first coordination sphere. The asymmetry ratio in favor of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition and the occurrence of the forbidden transition ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ (580 nm) are indicative of an asymmetric local surrounding of



Fig. 3. X-ray diffraction patterns of $Sc_{1.9}Eu_{0.1}O_3$ samples prepared by heating $Sc_{0.95}Eu_{0.05}(CH_3COO)_3$ to 500, 900, and 1100°C at a rate of 10 K/min followed by exposure at these temperatures for 2 h.

the europium ion and of the preferred occurrence of europium ions in the C_2 positions. Luminescence from levels higher than 5D_0 is not observed because of rapid radiationless relaxation to the 5D_0 level.

Strong lines in the reflection spectra for quasione-dimensional $Sc_{2-2x}Eu_{2x}O_3$ (x = 0.01, 0.025, 0.05) solid solutions, prepared by thermolysis of $Sc_{1-x}Eu_x(CH_3COO)_3$, correspond to ${}^7F_0 \rightarrow {}^5L_6$ (394 nm), and ${}^7F_0 \rightarrow {}^5D_2$ (465 nm) transitions and relate to internal configurational 4f-4f transitions of Eu^{3+} in Sc_2O_3 . Figure 6 is the Eu^{3+} emission intensity versus concentration plot with excitation with $\lambda_{ex} = 394$ nm in the range 550–800 nm. The emission spectra are dominated by an active line at 613 nm, which belongs to the ${}^5D_0 \rightarrow {}^7F_2$ transition. A weaker line at 701 nm corresponds to the ${}^5D_0 \rightarrow {}^7F_4$ transition. Weak emission lines at 591 nm (${}^5D_0 \rightarrow {}^7F_1$) prove that the europium ion occupies a noncentrosymmetric position in the Sc_2O_3 structure. The ${}^5D_0 \rightarrow {}^7F_3$ transition is



Fig. 4. Raman spectra of $Sc_{2-2x}Eu_{2x}O_3$ oxides where x = (1) 0.01, (2) 0.025, and (3) 0.05, prepared by thermolysis of the $Sc_{1-x}Eu_x(CH_3COO)_3$ precursor.

not observed in emission spectra for the specified excitation wavelength. The nonappearance of the line corresponding to the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition indicates that Eu^{3+} ions occupy both possible positions (C_2 and C_{3i}) in the scandium oxide lattice. The strongest emission is observed for the $Sc_{2-2x}Eu_{2x}O_3$ sample where x =0.025; up to x = 0.05, a well-known effect of concentration quenching of luminescence is observed, which is related to the transverse relaxation mechanism (Fig. 6). As the europium concentration increases, distances between Eu³⁺ ions (Eu–O–Sc bonds in the solid solution) become shorter and the cross-relaxation rate becomes higher, thereby decreasing luminescence intensity. Luminescence quenching can likewise arise from the increasing intensity of radiationless transitions to lower ${}^{7}F_{I}$ levels of Eu³⁺.

Pulsed cathodoluminescence appeared very sensitive to the occurrence of Eu³⁺ cations in Sc_{2-2x}Eu_{2x}O₃ [26]. In the CL spectrum of a Sc_{1.95}Eu_{0.05}O₃ sample prepared by thermolysis of the Sc_{0.975}Eu_{0.025}(CH₃COO)₃ precursor, there are nine lines of various intensities, which correspond to the ⁵D₀ \rightarrow ⁷F_J(J = 0, 1, 2, 3, or 4) transitions of the Eu³⁺ ion (Fig. 7). With high-energy excitation, the CL spectra for Sc_{1.95}Eu_{0.05}O₃ feature the same radiation transitions as in the Raman spectra of Sc_{2-2x}Eu_{2x}O₃ (Figs. 4, 5) excited by an Ar⁺ laser ($\lambda =$ 514.5 nm).

Noteworthy, europium-doped scandium acetate also has interesting optical properties, namely, luminescence in the visible spectral region. When exposed to the light of a domestic UV lamp with a wavelength range of 315-400 nm, Sc_{1-x}Eu_x(CH₃COO)₃ powders show a bright red luminescence with an intensity increasing in



Fig. 5. Raman spectra $Sc_{1.95}Eu_{0.05}O_3$ samples synthesized (1) by thermolysis of the $Sc_{1.95}Eu_{0.05}(CH_3COO)_3$ precursor and (2) by reaction (1).

response to increasing europium concentration. Reflection spectra for all $Sc_{1-x}Eu_x(CH_3COO)_3$ samples feature two strong lines, which are associated with internal configurational 4f-4f transitions of Eu³⁺ in the host and correspond to ${}^7F_0 \rightarrow {}^5L_6$ (394 nm) and ${}^7F_0 \rightarrow {}^5D_2$ (465 nm) transitions. An Eu³⁺ ion has a low excited level $({}^{5}D_{0})$ of the $({}^{5}D_{0})$ 4f₆ configuration, which lies below the $4f_55d$ configuration, and this gives rise to very narrow lines from the visible to near-IR. Emission spectra were recorded with $\lambda_{ex} = 394$ nm. The main radiation transitions in the range 550–720 nm from the ${}^{5}D_{0}$ level to ${}^{7}F_{2}$, ${}^{7}F_{1}$, and ${}^{7}F_{0}$ levels belong to Eu³⁺ local centers (Fig. 6). The line at 614 nm, which has the strongest emission, belongs to the ${}^5D_0 \rightarrow {}^7F_2$ transition. Other transitions from the ${}^{5}D_{J}$ excited levels to the ${}^{7}F_{J}$ ground levels are far less intense. In the short-wavelength spectral region, a peak appears at 594 nm $({}^{5}D_{0} \rightarrow {}^{7}F_{1})$ with an intensity commensurate to the strongest line of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition, and this proves rather a high symmetry of the local surrounding of Eu³⁺ ions in Sc_{1 – x}Eu_x(CH₃COO)₃. The absence of emission from the ${}^{5}D_{J}$ (J = 1, 2, or 3) excited levels is likely because of a high phonon energy in the host, which results from rapid radiationless relaxation to the ${}^{5}D_{0}$ level. A comparison of the emission spectra of $Sc_{1-x}Eu_{x}(CH_{3}COO)_{3}$ samples with different Eu³⁺ contents shows that the sample of composition Sc_{0.9}Eu_{0.1}(CH₃COO)₃ has the most pronounced luminescence.

In summary, our study resulted in the development and implementation of methods for preparing europium-doped scandium sesquioxide in two morphological types. Using thermolysis of $Sc_{1-x}Eu_x(CH_3COO)_3$, we prepared



Fig. 6. Emission spectra of $Sc_{2-2x}Eu_{2x}O_3$ solid solutions where x = (1) 0.01, (2) 0.025, and (3) 0.05).

 $Sc_{2-2x}Eu_{2x}O_3$ (0.005 $\leq x \leq$ 0.05) solid solutions with anisotropic shapes of aggregates which are atypical of the cubic structure of this oxide. Reacting the components of the redox system that consists of a mixture of scandium and europium nitrates (the oxidizer) and ethylene glycol (the reducer), we prepared nanodispersed $Sc_{2-2x}Eu_{2x}O_3$, which has a loose spongelike structure.



Fig. 7. Cathodoluminescence spectrum of $Sc_{1.95}Eu_{0.05}O_3$ prepared by thermolysis of $Sc_{0.975}Eu_{0.025}(CH_3COO)_3$.

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The nanosized condition of the $Sc_{2-2x}Eu_{2x}O_3$ samples was verified by SEM and Scherrer estimations of particle sizes. Inasmuch as mixtures of scandium and europium nitrates with ethylene glycol represent a homogeneous liquid mass (gel), they can be used to prepare $Sc_{2-2x}Eu_{2x}O_3$ supported on some porous support, for example, on silica, by impregnating the support followed by heat treatment of the supported sesquioxide. Nanoparticle sizes in $Sc_{2-2x}Eu_{2x}O_3$ powders prepared by reaction (1) are less than 12.3 nm, which renders them attractive for manufacturing high-density ceramics. The luminescence spectra of $Sc_{2-2x}Eu_{2x}O_3$ samples are identical, regardless of whether the samples were prepared from ultrafine powders or from pellets manufactured by cold compaction. Having a unique set of physical properties and fairly high radiation and chemical stability, europium-doped scandium sesquioxide is, undoubtedly, a promising luminophore material active in the visible spectral region and available due to the preparation methods developed in this study.

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