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Interaction of Sb^{3+} ions with Eu^{3+} ions during the room temperature synthesis of luminescent Sb_2O_3 nanorods: Probed through Eu^{3+} luminescence

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ABSTRACT

The interaction of Eu^{3+} with Sb^{3+} ions during the room temperature synthesis of luminescent Sb_2O_3 nanorods is investigated using luminescence and vibrational spectroscopic techniques. Our results demonstrate that well crystalline, oriented Sb_2O_3 nanorods having length of around 3–4 μm, a width of around 100–200 nm and luminescence at around 390 nm can be synthesized at room temperature. Incorporation of Eu^{3+} in these nanorods has been attempted and it is found that Eu^{3+} ions do not have any interaction with nanorods and their orientation. Detailed Eu^{3+} luminescence and XRD studies confirmed that a part of Sb^{3+} ions reacts with Eu^{3+} ions in the presence of hydroxyl ions (present in the medium) to form an amorphous antimony europium hydroxide compound. The amorphous compound on heating at high temperatures leads to its decomposition, giving hydrated Sb(V) oxides and Eu_2O_3 as major phases.

1. Introduction

Sb_2O_3 is a transparent semiconducting material with an indirect band gap of 3.3 eV and has got number of applications in the fields of catalysis, fire retardants, nonlinear optical glasses, sensors and anode material for the Li-ion batteries [1–8]. It exists mainly in two crystalline modifications, namely the cubic senarmonite form and the orthorhombic valentinite form. Depending on the nature of crystallographic modifications, they exhibit different properties. For example, cubic senarmonite form of Sb_2O_3 is used as an additive to improve the flame retardency of polymer resins whereas valentinite form of Sb_2O_3 is an essential component in Sb_2O_3–B_2O_3 glasses showing enhanced nonlinear optical properties [9]. Recently a number of reports have appeared regarding the synthesis and characterization of different one-dimensional forms of Sb_2O_3 nanorods, nanowires, nanobelts and nanotubes [10–17]. However in all these studies the luminescence properties of the nanorods have been given only limited attention, particularly when luminescent species like lanthanide ions are associated with them. The reason for the lack of such studies is the difficulty in the incorporation of lanthanide ions in the Sb_2O_3 lattice. The factors considered to be responsible for this is the significant difference in the ionic radius between Eu^{3+} ions (0.95 Å under 6 coordination) and Sb^{3+} ions (0.76 Å under four coordination) [18] and the difference in the stable coordination numbers of Eu^{3+} and Sb^{3+} ions. There is also a vast difference in their electronegativity values. Generally Eu^{3+} ions prefer higher coordination numbers like 6, 8 and 9, whereas in orthorhombic Sb_2O_3, antimony has a slightly distorted tetrahedral geometry with oxygen atoms at three corners and the lone pair of electrons of antimony at the fourth corner with all the O–Sb–O bond angles different [19].

Even though there exists significant difference in terms of ionic radius, electronegativity, stable coordination numbers, etc. between Sb^{3+} and Eu^{3+} ions, it will be of interest to understand the chemical interaction taking place between them, particularly in aqueous/organic solvents under alkaline conditions. This is because many technologically important luminescent oxide nanoparticles doped with lanthanide ions and Sb^{3+} are prepared by this method. For example Wen et al. [20] demonstrated that by suitably modifying the Eu^{3+}/Sb^{3+} ratio in YBO_3 crystal, nearly white light emission can be obtained. The interaction between Eu^{3+} and Tb^{3+} ions under high temperature heat treatment is also important as lanthanide ions are co-doped with Sb^{3+} ions in many of the oxide based glasses, which are prepared at high temperatures [21,22]. It is reported that presence of Sb_2O_3 in silicate glass doped with Er^{3+} has got significant effect on the spontaneous emission rates of $^4I_{13/2}$ level of Er^{3+} in the glass [21].

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Keeping this in mind we have investigated the chemical interaction of Sb^{3+} with Eu^{3+} ions. Eu^{3+} ion is chosen because its luminescence is very sensitive to the nature of the chemical environment around it, and the results obtained by this study will be useful for understanding the luminescence properties of other lanthanide ions or their nature of interaction with Sb^{3+}. We report in this study that there exists a strong tendency for Eu^{3+} and Sb^{3+} ions in the presence of hydroxide ions to form amorphous antimony europium hydroxide even at room temperature. A few literatures are available on the interaction of lanthanide ions with Sb^{3+} ions. To the best of our knowledge this is the first time that studies are being carried to understand the interaction of Sb^{3+} with Eu^{3+} ions.

2. Experimental

2.1. Preparation of Sb_2O_3 nanorods with and without Eu^{3+} ions

For the synthesis of nanorods without Eu^{3+}, first 0.5 g of $SbCl_3$ was dissolved in concentrated HCl and evaporated repeatedly by adding water dropwise while stirring. Repeated evaporation is done to remove excess HCl and dropwise addition of water is necessary for preventing the rapid hydrolysis of $SbCl_3$ and formation of $Sb(OH)_3$ precipitate. Around 2 ml solution of $SbCl_3$ left over after the repeated evaporation was mixed with 20 ml of iso-propanol followed by the addition of 20% ammonium hydroxide solution dropwise while stirring until precipitate was formed. This precipitate was centrifuged and washed several times with ethanol and acetone to remove free solvent and unreacted species. For samples containing different amounts of Eu^{3+} ions (2.5, 5 and 10 atom% Eu^{3+} with respect to Sb^{3+} as nominal compositions), same procedure was used except that Eu_2O_3 was dissolved in concentrated HCl and added to the acidic solution of $SbCl_3$ prior to the reaction. The resulting material was used for characterization. Bulk Sb_2O_3 sample with Eu^{3+} (5 atom% with respect to Sb^{3+}) ions was obtained by the hydrolysis of $SbCl_3$ and $EuCl_3$ in water at room temperature. For the purpose of comparison Eu^{3+} ions were also subjected to same reaction conditions as that used for Sb_2O_3 nanorods and the resulting precipitate was centrifuged, washed and dried. Eu^{3+} content in all the samples was analysed by fluorimetry and the results are in conformity with the inductive coupled plasma atomic emission spectroscopic (ICP-AES) analysis. The relative atom percentages of the Sb^{3+} and Eu^{3+} ions are shown in Table 1.

2.2. Characterization

X-ray diffraction (XRD) studies were carried out using a Philips powder X-ray diffractometer (model PW 1071) with Ni filtered Cu-K_α radiation. The lattice parameters were calculated from the least square fitting of the diffraction peaks. Average crystallite size was calculated from diffraction line width based on the Scherrer relation $D=0.9\lambda/\beta\cos\theta$, where D is the average crystallite size, λ is the wavelength of X-rays and β is the full width at half maximum (FWHM).

All luminescence measurements were carried out at room temperature with a resolution of 5 nm, using Edinburgh instruments' FLSP920 system with an excitation source of 450 W Xe lamp for steady state measurements and a 60 W Xe microsecond flash lamp for lifetime measurements. Atomic force microscopic (AFM) measurements were performed in contact mode using an AFM instrument from Ms. NT-MDT (solver model) having a 50 μm scanner head. Highly oriented pyrolytic graphite (HOPG) was used as the substrate. Transmission electron microscopic (TEM) measurements (bright field low magnification and lattice imaging) were performed using 200 keV electrons in JEOL 2000 FX TEM microscope. The Raman measurements were carried out on a CCD (Peltier cooled) based home made spectrograph using an excitation wavelength of ~633 nm (from diode pumped solid state laser). Fourier transformed infrared (FTIR) patterns were recorded for thin pellets of the samples made with KBr using a Bomem MB102 machine.

Table 1
Relative concentrations of Sb^{3+} and Eu^{3+} ions in as prepared Sb_2O_3 samples containing different amounts of Eu^{3+} ions.

Samples with their nominal compositions	Measured Sb^{3+} (at%)	Measured Eu^{3+} (at%)
Sb_2O_3 with 2.5 at% Eu^{3+}	97.6	2.4
Sb_2O_3 with 5 at% Eu^{3+}	95.7	4.3
Sb_2O_3 with 10 at% Eu^{3+}	92.1	7.9
Bulk Sb_2O_3 with 5 at% Eu^{3+}	95.8	4.2

3. Results and discussions

Fig. 1(a) and (b) shows the AFM images of the methanol dispersion of as prepared Sb_2O_3 samples. The images consist of long rod shaped species with a length of around 3–4 μm and a width of around 100–200 nm. Several such rods can be seen very clearly from the images. A closer look of the image demonstrates that in addition to the long rods there also exist small rods having length roughly in the range of around 1 μm. A representative TEM image along with the selected area electron diffraction (SAED) pattern of the sample is shown in Fig. 1(c) and (d). Dimension of the nanorods obtained from TEM images agrees well with that obtained from AFM images. As the SAED pattern taken along the [1 0 0] zone axis consists of only spots, it is confirmed that each nanorod is a single crystal of Sb_2O_3 with [1 0 0] orientation.

Fig. 2 shows the XRD patterns of Sb_2O_3 nanorods prepared in both the presence and absence of Eu^{3+} ions. For the purpose of comparison XRD pattern corresponding to bulk Sb_2O_3 prepared in the presence of Eu^{3+} is also shown in the same figure. Sharp peaks in the XRD patterns indicate the highly crystalline nature of the samples. The peak positions in the XRD patterns confirm that the Sb_2O_3 samples crystallize in the orthorhombic structure. From the line width of the diffraction peaks the average crystallite sizes were calculated using the Debye–Scherer formula and found to be around 40 nm for the nanorods. Lattice parameters were calculated based on the least square fitting of the diffraction peaks. The values are found to be comparable within error limits for both type of samples (i.e. the ones prepared in presence and absence of Eu^{3+} ions) and the values are $a=4.916(1)$ Å, $b=12.471(2)$ Å and $c=5.418(2)$ Å. The corresponding values for bulk Sb_2O_3 prepared in the presence of Eu^{3+} are $a=4.918(3)$ Å, $b=12.453(2)$ Å and $c=5.427(2)$ Å. For bulk Sb_2O_3 sample the highest intensity peak corresponds to (1 2 1) plane at around a 2θ value of 28.42° (Fig. 2(c)). However for the nanorods prepared in iso-propanol, the highest intensity of XRD peaks corresponds to (1 1 0) and (2 0 0) planes at around 2θ values of 19.66 and 36.62°, respectively. These results indicate a preferred crystallographic orientation existing in the sample prepared by iso-propanol route, which leads to selective enhancement in the intensity of some of the Bragg reflections. Similar increase in intensity for (1 1 0) and (2 0 0) planes has also been observed by Deng et al. [16] for Sb_2O_3 nanorods prepared by oxidation of Sb metal. These results agree well with the inferences obtained from SAED pattern shown in Fig. 1(d). Eu^{3+} ions do not have any effect on the crystallinity and orientation of the nanorods as revealed by the identical line width