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Preparation and fluorescence properties of Eu^{3+}-doped strontium chloroapatite nanocrystals

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Abstract

Strontium chloroapatite nanocrystals doped with trivalent europium ions were prepared by an aqueous colloidal method. The mean diameter of the crystal was found to be ~ 3 nm by transmission electron microscopy, although, for the most part, they were agglomerated. The X-ray diffraction patterns show that the lattice constants of nanocrystals are contracted by $\sim 2\%$ compared to the corresponding bulk counterpart, and also that they further decrease by annealing at 200–300°C. The fluorescence spectrum of nanocrystals exhibited blue shifts of both the $^5D_0$–$^7F_2$ transition and the charge transfer excitation band, and an apparent enhancement in the strength of the hypersensitive $^5D_0$–$^7F_2$ transition.

Keywords: Trivalent europium; Apatite; Nanocrystal

1. Introduction

Eu^{3+}-doped fluorescence systems have been studied extensively because of their importance for applications in lighting and display phosphors, and also due to a basic interest in probing the local structure around the dopant. Furthermore, fluorescence properties of impurity-doped nanocrystals have been a subject of much controversy [1–3].

Apatites ($M_5(PO_4)_3X$, M = alkaline earths, X = halogens or OH) have been used as a matrix of industrial phosphors. This material has the advantage of incorporating many impurities by controlling the lattice size by changing the alkaline earth. We prepared Eu^{3+}-doped strontium chloroapatite nanocrystals by an aqueous colloidal method. Their fluorescence properties were compared with those in bulk crystals.

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2. Experimental

All the chemicals used to prepare nanocrystals are dissolved in distilled water (20 mM concentration). Solution A is made by mixing 6 ml of $(NH_4)_2HPO_4$, and 2 ml of NH_4Cl, whereas solution B is prepared by mixing 9.9 ml of $SrCl_2$ and 0.1 ml of $EuCl_3$ (Eu^{3+} concentration is 1 mol%). Then, solution B is poured into solution A with vigorous stirring. The mixed solution becomes turbid by the formation of strontium chloroapatite ($Sr_5(PO_4)_3Cl$, abbreviated as SCAP hereafter) nanocrystals. The stirring was continued for more than 20 min to complete the reaction. To prepare powder samples, the solution was centrifuged and repeatedly washed with water. The residue was put dropwise on a synthesized quartz plate and dried at ambient temperature. To investigate the annealing effect on fluorescence and X-ray diffraction patterns, the sample was annealed in an N_2 atmosphere for 5 h at various temperatures between 200°C and 300°C.

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For comparison, the bulk samples (Eu^{3+} concentration of 1 mol%) were prepared as described earlier [4].

A transmission electron microscope (TEM, Hitachi, H-9000) was used to observe the image of the nanocrystalline SCAP. X-ray diffraction patterns (Cu K_α line) were obtained with an X-ray diffractometer (Rigaku, Geigerflex or Shimadzu, XRD-6000). The fluorescence of an aqueous solution or its powder form on a quartz plate was measured at room temperature by using a conventional fluorometer (Hitachi F-4500).

3. Results and discussion

3.1. Transmission electron microscopy and X-ray diffraction

The TEM image in Fig. 1 shows that the mean particle size is ~ 3 nm, although mostly agglomerated.

Fig. 2 is the X-ray diffraction patterns of the bulk and nanocrystal samples annealed at different temperatures. The diffraction pattern of the bulk SCAP coincides well with the JCPDS data base (No. 16–666). The diffraction peak positions (a–h) for the nanocrystals are shifted towards the right. This means that the lattice parameters (d-value) are smaller than in the bulk counterpart by $\sim 2\%$. The lattice constant decreases with increasing annealing temperature. Decreases in d-values of 2.5% in nanocrystals have been reported for ZnSe [5]. The same phenomenon was also observed in Y_2O_3 nanocrystals [6]. This type of lattice contraction is considered to be due to some surface tension in the nanocrystals. The relative positions of the peaks in Fig. 2 give further information about the respective shrinkage ratios of a, b, and c axes in nanocrystals compared to the bulk.

The peak intensity ratios are quite different in nanocrystals from those in the bulk counterpart as seen in Fig. 2. In order to study the possibility of orientation of the nanocrystals, we made X-ray diffraction experiments for the nanocrystals shaved from the quartz plate and attached on another plate. It was found that the intensity of the broad peak around the diffraction angle of 30° is enhanced by about two times. This shows that the nanocrystals are partially oriented when they are created by pouring the solution on a quartz plate.

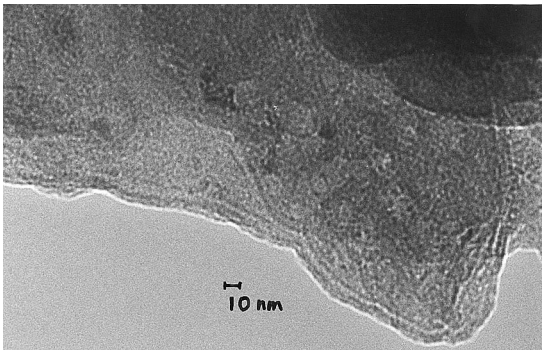

Fig. 1. Transmission electron microscope image of the sample.

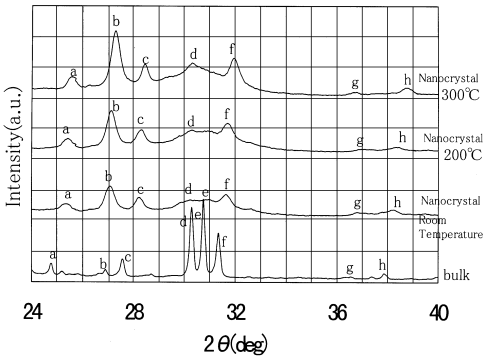

Fig. 2. X-ray diffraction patterns (2θ vs. intensity) of the nanocrystal (produced at room temperature, and annealed at 200°C and 300°C) and bulk strontium chloroapatite. Each peak in the four measurements is marked a–h. The resolution of the bulk sample (the lowest part) is determined by the apparatus limit.

3.2. Fluorescence

As shown in Fig. 3, the fluorescence of Eu^{3+} is shifted to the blue compared to that of the bulk for both the hypersensitive $^5D_0$–$^7F_2$ transition and the charge transfer band. There is a report that the $^5D_0$ –$^7F_2$ transition of Eu^{3+} in Y_2O_3 nanocrystals (~ 50 nm in diameter) prepared by an aqueous method shifts to the blue [6], although the fluorescence peak positions were the same

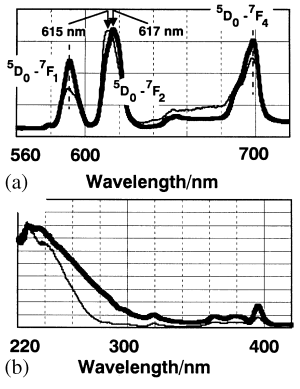

Fig. 3. Fluorescence spectra excited at 395 nm (a), and excitation spectra detected at 615 nm (b) of Eu^{3+}-doped nanocrystal in aqueous solution (fine line) and bulk (bold line) strontium chloroapatite at room temperatures.

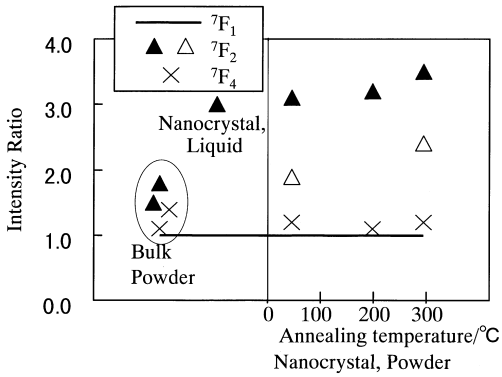

Fig. 4. The intensity ratio of the $^5D_0-^7F_2$ and $^5D_0-^7F_4$ fluorescence to the internal standard $^5D_0-^7F_1$ transition. Open and closed triangles correspond to two different series of samples.

as in the bulk for Eu^{3+} in Eu_2O_3 and Y_2O_3 nanocrystals ($\sim$ 5 nm in diameter) prepared by CO_2-laser vaporization [7], and also for Eu^{3+} in YVO_4 nanocrystals ($\sim$ 20 nm in diameter) prepared by a wet-chemical method [8]. Disorder due to lattice distortion is expected in nanocrystals. However, the line width of the emission is almost the same for the SCAP : Eu^{3+} nanocrystals and bulk crystals. Fig. 4 shows the intensity ratios of the fluorescence components to that of the $^5D_0-^7F_1$ transition. The intensity of this band can be used as an internal standard because it is due to the allowed magnetic dipole transition. The $^5D_0-^7F_4$ band intensity ratios in nanocrystals are the same as in the bulk, whereas the $^5D_0-^7F_2$ transitions are more intense in nanocrystals. It is well known that the intensity of the $^5D_0-^7F_2$ transition is very sensitive to the change in the environment. This has been accounted for by a dynamical coupling model [9]. This model may explain the enhancement of the intensity of this hypersensitive transition in nanocrystals. Since crystals of the same composition sometimes show different fluorescence properties (see open and closed triangles in Fig. 4), the surface state may play a role in the hypersensitive transition in nanocrystals. There was no significant difference in the fluorescence features due to annealing at different temperatures.

4. Conclusions

Eu^{3+}-doped strontium chloroapatite nanocrystals with $\sim$ 3 nm diameter were prepared and their fluorescence properties were studied at room temperature. It was found that the energy position and the intensity of the hypersensitive $^5D_0-^7F_2$ transition, besides the position of the charge transfer band, are different in nanocrystals compared with the bulk counterpart. Further, the SCAP nanocrystals produced by an aqueous colloidal method were found to be partially oriented on a quartz plate.

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