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Influence of the technological conditions on the luminescence of Eu^{3+} ions in Sr_2SnO_4

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Different synthesis conditions have been used to prepare the stoichiometric compounds of the $Sr_{2-x}Eu_xSnO_4$ with $x = 0.00$, 0.01, 0.02 and 0.03. As the $^5D_0 \rightarrow {}^7F_0$ transition is forbidden by a selection rule of the Judd–Ofelt theory, the $J=0 \rightarrow J=0$ level gains some intensity from the mixing of J states in the $Sr_{2-x}Eu_xK_xSnO_4$ and $Sr_{1-x}Eu_xSnO_4$ samples. For $Sr_{2-x}Eu_xSnO_4$ samples prepared under a slightly reducing atmosphere, the $J=0 \rightarrow J=0$ transition is split into two peaks, which confirms the substitution of Eu^{3+} ions for different crystallographic sites. © *1998 Chapman & Hall*

1. Introduction

Quasi-two-dimensional oxides A_2BO_4 of the K_2NiF_4 structure have been investigated extensively with respect to their electrical [1, 2], magnetic [2, 3] and catalytic properties [4–6]. These compounds belong to the intergrowth structure family $AO(ABO_3)_n$.

Rao and co-workers [1, 2] have studied the magnetic and electrical properties of two-dimensional oxides of K_2NiF_4 type compared with those of three-dimensional perovskite oxides. These workers examined the two-dimensional $La_{1-x}Sr_{1+x}MnO_4$ (or $SrO \cdot La_{1-x}Sr_xMnO_3$) and then investigated how the electrical and magnetic properties of these compounds vary with three-dimensional character.

The luminescence of $Sr_{n+1}SnO_{3n+1}$ with doped Eu^{2+} ions was observed by Endo *et al.* [7]. Studies on Sr_2TiO_4 doped with Eu^{3+} ions have been carried out by several research groups [8, 9]. However, the optical properties of quasi-two-dimensional oxides have been investigated by very few research groups in contrast with the work on three-dimensional oxides. Thus, studies on the optical properties of quasi-two-dimensional oxides are much rarer than those for three-dimensional oxides [10–13].

The emission efficiency of doped rare-earth ions depends strongly on the crystallographic variety of energy migration in the excited state. In the present study, the influence of synthesis conditions on the optical properties of Sr_2SnO_4 doped with Eu^{3+} ions will be studied systematically.

2. Experimental procedure

2.1. Sample preparation

Samples of Sr_2SnO_4 doped with Eu^{3+} have been synthesized under various preparation conditions. The starting materials were $SrCO_3$, Eu_2O_3, SnO_2 and K_2CO_3 (the purities of all these are 99.99% or greater).

For the $Sr_{2-2x}Eu_xK_xSnO_4$ system with $x = 0.01$–0.03 mol%, the appropriate amounts of the starting materials were weighed, mixed, ground and then heated in air at 1300 °C for 4 h. K_2CO_3 was added to provide charge compensation as follows:

$$K^+ + Eu^{3+} = 2Sr^{2+}$$

For the $Sr_{2-x}Eu_xSnO_4$ system with $x = 0.01$–0.03, samples were also prepared at 1300 °C under a reducing atmosphere with the addition of active carbon. The added carbon was expected to react with oxygen to give reducing conditions. However, the amount of active carbon added to the compounds was too small to change the valence state of Eu^{3+} ions but caused oxygen vacancies in the compounds. The amount of oxygen vacancies was also too small to change the crystallographic structure of the matrix as shown in the X-ray diffraction patterns.

2.2. X-ray powder diffraction analysis

Powder XRD analyses of the samples have been carried out with monochromated CuK_α ($\lambda = 0.15418$ nm) radiation in the range $10° \leqslant 2\theta \leqslant 80°$. The crystal system and lattice parameters of the unit cell have been determined as reasonable values.

2.3. Optical measurements

Photoluminescence and excitation spectra measured using an Oriel spectrometer with monochromator models 77250 and 77276 under excitation with an XBO 151 xenon lamp. The spectra were recorded with a photomultiplier tube model 70680. Photoluminescence measurements were also carried out for comparison with an Opton monochromator under excitation with a nitrogen laser beam ($\lambda = 337$ nm). The spectra were recorded with an RCA 4832 photomultiplier and lock-in nanovoltmeter.

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3. Results and discussion

3.1. X-ray powder diffraction

From the XRD spectrum the crystallographic structure of the Sr_2SnO_4 was determined to be a tetragonal system with a K_2NiF_4-type structure whose space group is $I4/mmm$. The lattice parameters of the sample are $a = 0.4043$ nm and $c = 1.259$ nm, and the c/a ratio is about 3.114. The XRD pattern of the sample is shown in Fig. 1.

The XRD patterns suggest that the structures of all the samples of $Sr_{2-2x}Eu_xK_xSnO_4$ and $Sr_{2-x}Eu_xSnO_4$prepared in the reducing atmosphere are the same as tetragonal Sr_2SnO_4. It is also confirmed from the results of the XRD spectra analyses that the Eu^{3+} and/or K^+ ions substitute for Sr^{2+} ions site in all the homogeneous compounds of $Sr_{2-2x}Eu_xK_xSnO_4$ and $Sr_{2-x}Eu_xSnO_4$. The small amount of oxygen vacancies in the $Sr_{2-x}Eu_xSnO_4$ produced under the reducing atmosphere are randomly distributed. The Eu^{3+} ions substituted for the Sr^{2+} ions are coordinated with nine oxygen ions whose local symmetry is C_{4v}.

3.2. Excitation

The excitation spectra of $Sr_{1.98}Eu_{0.01}K_{0.01}SnO_4$ and $Sr_{1.99}Eu_{0.01}SnO_4$ are presented in Fig. 2. The peak at around 312 nm of the excitation spectra of Eu^{3+} ion is excited by the charge-transfer state that takes place from the 2p orbital of the oxygen ions to the 4f shell of the Eu^{3+} ions. The compound of $Sr_{1.99}Eu_{0.01}SnO_4$ exhibits a peak at 319 nm, which is induced by the charge transfer. The charge-transfer peak of $Sr_{1.99}Eu_{0.01}SnO_4$ is positioned at 319 nm is of lower energy than the peak of $Sr_{1.98}Eu_{0.01}K_{0.01}SnO_4$ at 312 nm. It seems that oxygen vacancies take part in the energy level of charge transfer from oxygen to the Eu^{3+} ions for the lower-energy $Sr_{1.99}Eu_{0.01}SnO_4$.

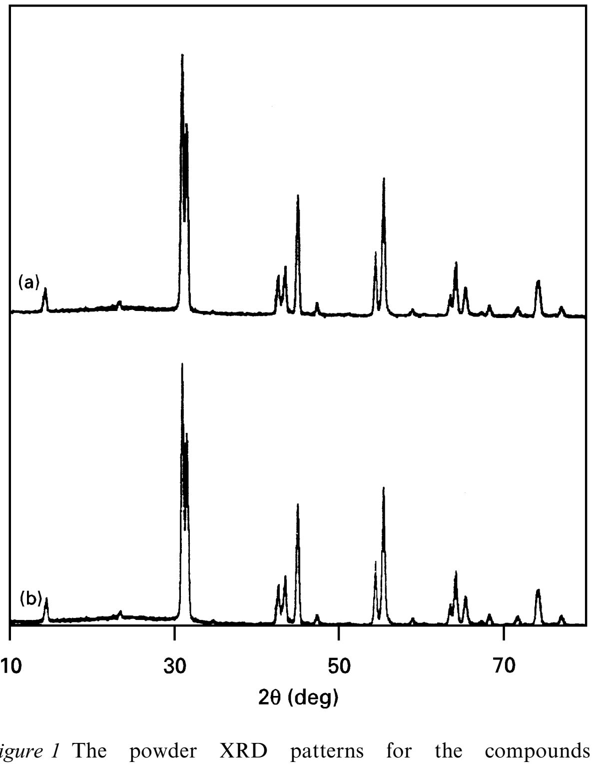

Figure 1 The powder XRD patterns for the compounds (a) $Sr_{1.99}Eu_{0.01}SnO_4$ and (b) $Sr_{1.98}Eu_{0.01}K_{0.01}SnO_4$.

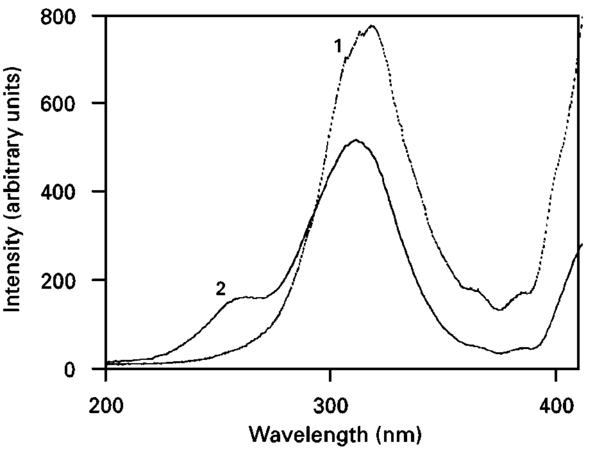

Figure 2 The excitation spectra of $Sr_{1.99}Eu_{0.01}SnO_4$ (curve 1) and $Sr_{1.98}Eu_{0.01}K_{0.01}SnO_4$ (curve 2) ($\lambda_{em} = 619$ nm).

The excitation spectrum of $Sr_{1.98}Eu_{0.01}K_{0.01}SnO_4$ is split by the charge transfer into two broad bands at around 259 and 312 nm. The peak appearing in the 259 nm region shows the formation of a deep centre by the K^+ ion in the Sr^{2+} site.

In the case of samples prepared by heating under a reducing atmosphere, the shift represents the excitation spectrum on curve 2 of Fig. 2 for a split in the $^5D_0 \rightarrow {}^7F_0$ transition into two peaks which will be discussed in the following section.

3.3. Photoluminescence

The luminescence spectra recorded for $Sr_{1.98}Eu_{0.01}K_{0.01}SnO_4$ obtained under the first reaction conditions and for $Sr_{1.99}Eu_{0.01}SnO_4$ obtained under the second reaction conditions are shown in Fig. 3. The red emission line induced by Eu^{3+} ions is observed at 625 nm in all samples but the line for Eu^{2+} ions does not appear. The intensity of the spectrum of $Sr_{1.99}Eu_{0.01}SnO_4$ is higher than that of $Sr_{1.98}Eu_{0.01}K_{0.01}SnO_4$.

The $^5D_0 \rightarrow {}^7F_J$ transition with $J = 0, 1, 2$ and 4 are seen at about 580 nm, 596 nm, 625 nm and 710 nm, respectively, as shown in Fig. 4. The $^5D_0 \rightarrow {}^7F_0$ transition was observed with a high intensity in all samples. In general, the $J = 0 \rightarrow J = 0$ level is forbidden by the selection rule of the Judd–Ofelt theory for an electric dipole transition of a rare-earth ion between $4f^n$-states. Some mixing states from different J levels or J mixing may occur by structural distortion.

In general, lower-symmetry cation sites produce more intensively emitting phosphors. The appearance of the $^5D_0 \rightarrow {}^7F_0$ line is always allowed by the observed site symmetry. The linear crystal-field theory based on the $4f^n$ wavefunctions with the effects of spin–orbit interaction and odd-parity crystal-field term with $L \geqslant 3$ accounts for the f–f transition corrected to the first order [10].

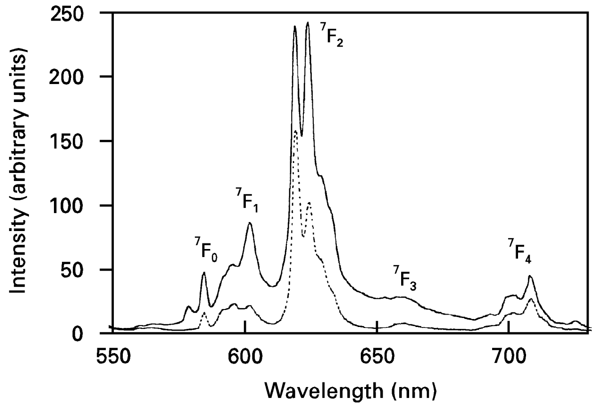

Figure 3 The luminescence spectra of the $Sr_{1.99}Eu_{0.01}SnO_4$ (——) and $Sr_{1.98}Eu_{0.01}K_{0.01}SnO_4$ (- - -), ($\lambda_{ex} = 311$ nm).

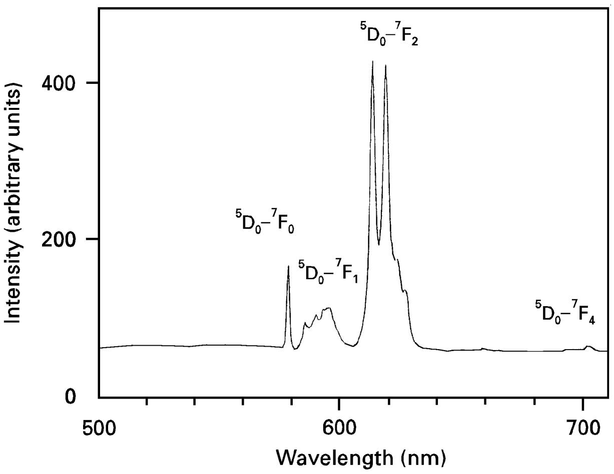

Figure 4 The emission spectrum of $Sr_{1.96}Eu_{0.03}K_{0.03}SnO_4$ ($\lambda_{ex} = 337.1$ nm).

The $^5D_0 \rightarrow {}^7F_0$ transition of $Sr_{1.98}Eu_{0.01}K_{0.01}$ SnO_4 with a single peak at about 580 nm is shown in curve 1 of Fig. 3. It is obvious that the emission intensity of Ln^{3+} ions is sensitive to the nature of the site symmetry of the host. The energy gap between $^7F_1$ and $^7F_0$ of the Eu^{3+} ions is so small [11] that the $^7F_1$ character may be mixed into the $^7F_0$ level of C_{4v} symmetry which is not centrospherical. The forbidden $^5D_0 \rightarrow {}^7F_0$ of transition gains some intensity from mixing of the J states by the coordination geometry around Eu^{3+} ions as C_{4v} symmetry.

The $^5D_0 \rightarrow {}^7F_0$ line for the $J = 0 \rightarrow J = 0$ levels cannot be split by the crystal field at the activator site. The $^5D_0 \rightarrow {}^7F_0$ transition of $Sr_{1.99}Eu_{0.01}SnO_4$ has been split into the two peaks at $^7F_{01} \approx 581$ nm and $^7F_{02} \approx 577$ nm. The presence of two lines in the emission spectrum given by curve 2 of Fig. 3 confirms that Eu^{3+} ions exist in different sites.

The larger Eu^{3+} ions occupy two crystallographic sites. One of them occupies a strongly distorted octahedron of site symmetry C_{2v}, and the other occupies an octahedron coordinated with five or six oxygen atoms of site symmetry C_{4v}. The substitution of Eu^{3+} in two site symmetries causes the two peaks of the $^5D_0 \rightarrow {}^7F_0$ transition as shown in curve 2 of Fig. 3.

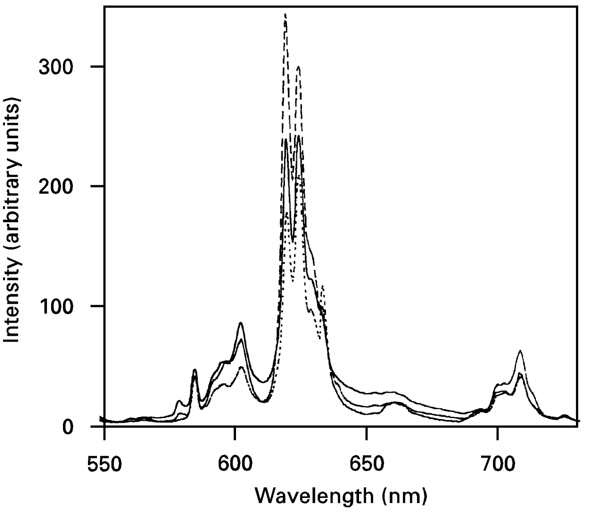

Figure 5 The luminescence spectra of the $Sr_{2-2x}Eu_xSnO_4$ with $x = 0.005$ (·····), 0.02 (——) and 0.03 (– – –) ($\lambda_{ex} = 311$ nm).

The luminescence spectrum of $Sr_{1.98}Eu_{0.01}K_{0.01}$ SnO_4 under excitation with a nitrogen laser of $\lambda = 337$ nm is shown in Fig. 4. The high-intensity peak of the $^5D_0 \rightarrow {}^7F_0$ transition is compared with the magnetic-dipole-allowed $^5D_0 \rightarrow {}^7F_1$ transition ($^5D_0$–$^7F_0$ to $^5D_0$–$^7F_1$ ratio, about 2.15). It is evident that the linear crystal-field term might be very important [9].

The luminescence spectra of $Sr_{2-x}Eu_xSnO_4$ with $x = 0.005$, 0.01 and 0.03 are shown in Fig. 5. The emission peaks of all compounds are displayed in the same positions. The luminescence intensity increase as the Eu^{3+} ion concentration increases. $^5D_0 \rightarrow {}^7F_J$ transitions with $J = 0$, 1, 2, 3 and 4 under the excitation with a xenon lamp of $\lambda = 311$ nm are observed. Since splitting of the $^5D_0 \rightarrow {}^7F_0$ transition appeared in all $Sr_{2-x}Eu_xSnO_4$ samples, the substituted Eu^{3+} ion might be placed in different crystallographic sites.

4. Conclusions

Stoichiometric samples of the $Sr_{2-x}Eu_x$ SnO_4 system with $x = 0.00$, 0.01, 0.02 and 0.03 have been prepared using different synthesis conditions. The samples obtained by firing in air have shown the appearance of a $^5D_0 \rightarrow {}^7F_0$ transition, which is allowed by the site symmetry C_{4v}. This is evidence that, on substitution of Eu^{3+} ions, these ions are located in an octahedron site with five or six oxygen atoms. For the samples heated under a reducing atmosphere, the $^5D_0 \rightarrow {}^7F_0$ transitions were observed to split into two peaks, which confirm that the substituted Eu^{3+} ions are in two different crystallographic sites with site symmetries such as C_{2v} and C_{4v}.

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