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The structure and luminescence characteristics of $SrSiO_3:Eu^{3+}:Bi^{3+}$ synthesized at a high pressure and high temperature

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Abstract

The $SrSiO_3:Eu^{3+}:Bi^{3+}$ samples were first synthesized using a high temperature of 1200 °C and a high pressure of 3.15 GPa. The structure of the samples and the influence of pressure and temperature on the luminescence properties have been studied in comparison with those prepared at atmospheric pressure. This shows that there is a structural transformation under pressure; the samples prepared at atmospheric pressure have a hexagonal phase structure; in the pressure range 2.34–4.10 GPa this structure transforms into a pseudo-orthorhombic phase (monoclinic). The effects of high pressure obviously make the intensity and quantum luminescence efficiency decrease, the half-width increase and the red shift of the emission peak increase to 756 cm^{-1}. The variation in the luminescence characteristics is due to the pressure-induced change in crystal structure.

1. Introduction

Study of the luminescence of rare earth solid state materials is an interesting research field in both rare earth physics and chemistry. Europium is a special element in the lanthanides; besides the common properties of rare earth elements, it may exhibit the phenomenon of valence fluctuation, *i.e.* the valence state is divalent or trivalent, and it has different luminescence characteristics due to the different valences. Thus the study of europium-activated materials is important. Much work has been done on the luminescent properties of europium-activated phosphors under atmospheric pressure [1, 2]; some important conclusions about the luminescence of europium cations in the lattice have been reached. Over recent years, besides the research of *in-situ* luminescence properties using the diamond anvil cell, the luminescence characteristics of the products synthesized or treated at a high pressure and a high temperature have also been studied under atmospheric and room temperature [3–5]. It has been shown that a high pressure and high temperature can effectively change the interatomic distance of the phosphor and the interaction between atoms; this therefore changes the luminescence characteristics of the europium cations and makes the emission spectrum shift to the red edge or blue edge and the intensity to increase or decrease. In particular, when the pressure-induced change in structure occurs, these changes are more obvious. Since the phosphor materials synthesized or treated at a high pressure and a high temperature are metastable products and most of them are irreversible normally, and since the high pressure experiments are performed using a large press which has a larger sample chamber, it is beneficial to study the luminescence effect of the high pressure, high temperature treatment as applied to the products. Therefore studying the effect of the high pressure and high temperature on the luminescence not only supplies an effective and sensitive means of studying the micromechanism of luminescence but also provides a new way to probe the synthesis of luminescent materials. In this paper, some metasilicates in which a structural transition easily takes place under a high pressure [6] were selected as the host, Eu^{3+} ions as the activator and Bi^{3+} ions as the sensitizer. By studying the structure and luminescence of $SrSiO_3:Eu^{3+}:Bi^{3+}$ synthesized and

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treated at a high pressure and a high temperature, we expect to obtain some information about the luminescence micromechanism of Eu^{3+}.

2. Experimental details

The starting materials used in this experiment were SiO_2, SrO and Bi_2O_3 of analytical purity and Eu_2O_3 of 99.95% purity. The appropriate stoichiometric proportions of $SrSiO_3:Eu^{3+}:Bi^{3+}$ were determined and mixed; then samples were prepared by three different methods, namely the atmosphere pressure, high temperature method, the sol–gel method and the high pressure, high temperature method.

During the sintering under atmospheric pressure and high temperature, the homogeneous mixture was firstly fired in air at 800 °C for 4 h reground and pressed into pellets and then sintered in air at 1350 °C for 8h. The sol–gel method was performed as follows. According to the nominal composition, $Sr(NO_3)_2$, $Eu(NO_3)_3$, $Bi(NO_3)_3$ and ethylsilicate were taken as the starting materials and dried in a drying oven; then the diluted nitric acid of five-times in volume was added to form a homogeneous transparent solution. The above solution was constantly refluxed in a refluxing crucible at 650 °C using the silicon sol as the silicon source until a homogeneous transparent gel was formed. After drying, the gel was fired at 700 °C for 3 h and then ground and sintered at 950 °C. Finally the samples were obtained by sieving the products with the 220 mesh sieve.

The high pressure, high temperature synthesis was performed using a 4.9 MN (500 t) Bridgman press. The mixture was ground and fired at 850 °C for 4 h in air and then put into the sample chamber of the press. During the synthesis, a pressure of 3.15 GPa was first applied; then the temperature was increased to 1200 °C and maintained for 30 min; finally the samples were quenched to room temperature under this pressure. In addition, the other samples sintered in air were treated under a hot pressure and a cold pressure respectively.

The X-ray diffraction spectra of the above samples were determined with the Rigaku D/max r-A X-ray diffractometer. The emission and excitation spectra were determined using a RF540 spectrometer with a xenon lamp of 398 nm excitation wavelength. The quantum luminescence efficiencies were determined using a MPF-4 fluorophotometer.

3. Results and discussion

The X-ray diffraction analysis showed that the $SrSiO_3:Eu^{3+}:Bi^{3+}$ samples prepared at atmospheric pressure and high temperature and by the sol–gel method have the same structure; both are all hexagonal structure. The samples synthesized at a high pressure and high temperature have a monoclinic structure, which has a wide stable range of pressure and may be synthesized from 2.34 to 4.10 GPa. The X-ray diffraction spectra and calculated results for these samples are given in Fig. 1 and Table 1. For the samples prepared by atmospheric sintering, their structure transformed from hexagonal to pseudo-orthorhombic (monoclinic) at 3.0 GPa and 1200 °C, which means that there is a phase transition under pressure. So the samples synthesized at a high pressure and high temperature can be considered to be located in the high pressure phase region of the $SrSiO_3$ samples.

The luminescence characteristics of the $SrSiO_3:Eu^{3+}:Bi^{3+}$ samples prepared by the three different methods were measured and studied. The emission spectra are shown in Fig. 2 and the peak locations, half-widths and relative intensities of emission peak are given in Table 2. It can be seen that the luminous intensity of the samples prepared by the sol–gel method is the best, that prepared at atmospheric pressure the second best and that prepared at a high pressure the worst of these samples prepared by the three different methods. The luminescence characteristics of the sample synthesized at a high pressure undergo a large change; the relative intensity is obviously decreased, the red shift of the emission peak is increased to 756 cm^{-1} which is much more than that of $Sr_2SiO_4:Eu^{3+}:Bi^{3+}$ [4] and the half-width is five times that of the samples prepared at atmospheric pressure and a high temperature. The quantum efficiencies of the samples prepared by the different methods were measured (Table 3); this

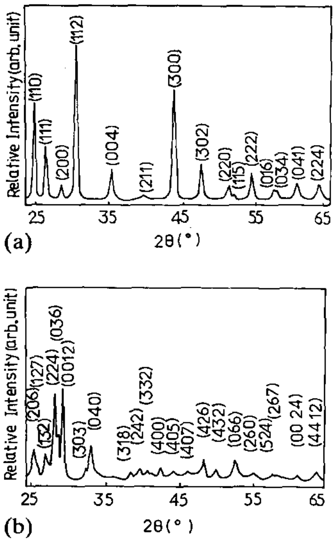

Fig. 1. X-ray diffraction spectra of $SrSiO_3:Eu^{3+}:Bi^{3+}$: (a) atmospheric pressure and high temperature; (b) high pressure and high temperature.

TABLE 1. The lattice parameters of $SrSiO_3$:Eu^{3+}:Bi^{3+} (±0.5 pm)

Method of synthesis	*a* ($\times10^{-1}$ nm)	*b* ($\times10^{-1}$ nm)	*c* ($\times10^{-1}$ nm)	*β* (deg)	*v* ($\times10^{-3}$ nm^3)
High pressure, high temperature	8.532	10.792	36.364	90.326	3348.5
Sintering at atmospheric pressure	7.123		10.005	120	439.49

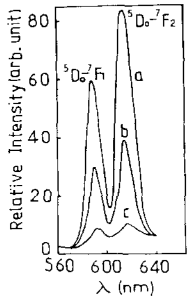

Fig. 2. Emission spectra of $SrSiO_3$:Eu^{3+}:Bi^{3+}: curve a, sol–gel; curve b, atmospheric pressure; curve c, high pressure.

TABLE 2. The luminescence characteristics of $SrSiO_3$:Eu^{3+}:Bi^{3+}

Method of synthesis	Peak location (cm^{-1})	Half-width (cm^{-1})	Relative intensity (%)
Sol–gel	16260	428	82
Sintering at atmospheric pressure	16260	428	40
High pressure, high temperature	15504	2420	10

table shows that the efficiency of $SrSiO_3$:Eu^{3+}:Bi^{3+} synthesized at a high pressure and high temperature is only 11.9% of that prepared by the sol–gel method.

The dramatic decrease in the relative intensity of the samples synthesized at a high pressure and a high temperature may result from several factors due to the high pressure action. The samples prepared at atmospheric pressure have a hexagonal structure. According to the lattice cell of this structure [7], the Eu^{3+} ions may substitute on the Sr (2) site which has a larger space and 12 oxygen neighbours around it. The oxygen neighbours consist of two different kinds of oxygen site; O(1) and O(2). The estimated bond lengths of Sr–O are 2.8(25) nm (three O(1)), 2.7(26) nm (three O(2)) and 3.5(67) nm (six O(2)). This indicates that the Eu^{3+} ions have a non-inverse symmetric center, which breaks up the forbidden condition of the electric dipole transition (EDT) $^5D_0 \rightarrow {}^7F_2$ and then cause the luminescence intensity of the (EDT) $^5D_0 \rightarrow {}^7F_2$ to be greater than that of magnetic dipole transition (MDT) $^5D_0 \rightarrow {}^7F_1$. The high pressure changes the structure from hexagonal to monoclinic, which causes further destruction of the inverse symmetry and further removal of the forbidden condition of $^5D_0 \rightarrow {}^7F_2$. So the results using high pressure should make the intensity of the EDT $^5D_0 \rightarrow {}^7F_2$ in the monoclinic structure greater than that in the hexagonal structure; however, the measurement results shown in Fig. 2 do not indicate this. It should be noted that the luminescence intensities of both the EDT $^5D_0 \rightarrow {}^7F_2$ and the MDT $^5D_0 \rightarrow {}^7F_1$ of $SrSiO_3$:Eu^{3+} obviously increase after doping with the sensitizer Bi^{3+}. As a resonable explanation it may be considered that the high pressure changes the crystal structure (makes the hexagonal structure transform to monoclinic) and induces the difference between the excitation spectrum of the activator Eu^{3+} and the emitting spectrum of the sensitizer Bi^{3+}; therefore it greatly weakens the sensitivity of Bi^{3+} and greatly reduces the energy transfer between Bi^{3+} and Eu^{3+}, which result in a decrease in luminescence intensity of the EDT. This decrease in intensity exceeded the decrease in the luminescence intensity due to the effect of inversion symmetry. So it appears that the intensity of $^5D_0 \rightarrow {}^7F_2$ is close to that of $^5D_0 \rightarrow {}^7F_1$, as shown in Fig. 2(c). The dramatic weakening of the above sensitizing action is also reasonable from the viewpoint of the high-pressure-induced red shift increase for $SrSiO_3$:Eu^{3+}:Bi^{3+}.

The inhomogeneous distribution of Eu^{3+} in $SrSiO_3$:Eu^{3+}:Bi^{3+} synthesized at a high pressure can also cause the luminescence intensity to decrease and the

TABLE 3. The relative quantum efficiencies of $SrSiO_3$:Eu^{3+}:Bi^{3+}

Method of synthesis	Peak height *M* (arbitrary units)	Peak area *S* (arbitrary units)	Quantum efficiency *MS* (arbitrary units)	Relative quantum efficiency (%)
Sol–gel	1790.5	458	820049	100
Sintering at atmospheric pressure	236.5	926	218999	26.7
High pressure, high temperature	127.5	766	97665	11.9

half-width to increase. According to calculation, the distance between Eu^{3+} ions in the samples with stoichiometric composition exactly satisfies the condition for the probability of energy transference between the luminescence centres to be minimized if the distribution of Eu^{3+} in this sample is homogeneous. In high pressure synthesis, the distribution of Eu^{3+} is not very homogeneous, which will result in an increase in the energy transference probability between Eu^{3+} ions to some extent and cause the radiative transition and luminescence intensity to decrease.

In addition, the luminescence properties of the sintering sample treated by a cold pressure have been studied. This shows that after treatment the half-width increases, the peak shift increases and at the same time the quantum luminescence efficiency decreases (Fig. 3). These effects increase with increasing pressure and become similar to those of samples synthesized at a high pressure, but the extent is weaker than that for the latter samples.

The structural phase transition induced by the high pressure and the high temperature has an important influence on the luminescence intensity of the luminous body. In ref. 3 the orthorhombic structure SrB_2O_4 having Eu^{2+} luminescence centres was transformed to the cubic structure at 2.0 GPa and 700 °C, and there is a pressure zone of stable cubic phase above 2.0 GPa. The relative quantum efficiency for this cubic phase is 80–100 times that for the orthorhombic phase. The reason is that the coordination of Eu^{2+} ions changes from the open type in the orthorhombic phase to the closed type in the cubic phase. In this paper and ref. [4], however, the high-pressure-induced structural phase transition makes the relative quantum efficiency decrease greatly. The reason for this is the change in the coordination. Therefore systematic research on the influence of high pressures and high temperatures on the coordination, crystal field and luminescence properties of phosphors will be important in establishing a unified crystal field theory and in searching for high efficiency luminescent materials.

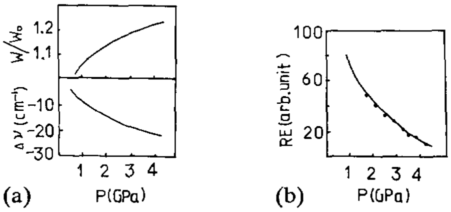

Fig. 3. Effect of cold-pressure treatment on the luminescence characteristics of $SrSiO_3:Eu^{3+}:Bi^{3+}$: (a) peak shift $\Delta\tilde{\nu}$ and half-width ratio W/W_0; (b) relative quantum efficiency (RE).

Acknowledgments

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