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The process of crystallization of CaSiO₃ gel and the luminescence of Eu³⁺ ions in gel-derived crystals

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Abstract. The process of crystallization of CaSiO₃ gel and the influence of crystallization on the luminescence of Eu³⁺ ions have been investigated. Differential thermal analysis and thermogravimetric analysis showed that residual solvents and organic compounds chemically bound to Ca and Si were eliminated for $T \leq 550$ °C. The exothermic effect corresponding to crystallization of the CaSiO₃ gel appeared at about 950 °C, and the activation energy of crystallization was about 580 kJ mol⁻¹. With the increase of temperature, x-ray diffraction patterns indicated a transformation from rankinite to wollastonite structure. The excitation and emission intensities for Eu³⁺ ions in the gel-derived crystals were much stronger than those for the dried gel. The excitation and emission spectra of Eu³⁺ ions changed during the process of crystallization, and the obvious level splitting by the crystal field can be observed in both the rankinite and wollastonite structures.

1. Introduction

Considerable success has been achieved in the application of Eu³⁺-activated oxide as a red phosphor, and the luminescence properties of Eu³⁺ in various hosts have been investigated extensively [1, 2]. The Eu³⁺-activated oxides, which are highly efficient, were generally prepared from intimate mixtures of high-purity raw materials by solid-state reaction. The luminescence of a Eu³⁺ ion depended predominantly on the chemical environment of that Eu³⁺ ion in the host lattices. Thus the requirements for producing a successful industrial phosphor are numerous: apart from having a well-defined composition with no impurity phases, the materials should also be free of crystal defects, and when an activator and/or a sensitizer are used, the distribution of the doping ions should be as uniform and random as possible in order to avoid non-radiative losses.

Crystallization of rare-earth-doped gel is a potential preparation method for rare-earth-activated phosphors. The gel, in which a small number of rare-earth ions can be mixed homogeneously on a molecular scale, can be obtained through hydrolysis–condensation reactions of metal alkoxides [3, 4], and then the rare-earth-activated phosphors can be prepared by crystallization of the gel at a lower temperature than that required for solid-state reactions. In this work, the process of crystallization of Eu³⁺-activated CaSiO₃ gel and the influence of the crystallization on the luminescence of the Eu³⁺ ions is investigated.

2. Experimental procedure

The solution was prepared by using tetraethoxysilane, calcium nitrate, reagent-grade ethanol, and deionized water. Eu³⁺ ions were introduced by adding Eu(NO₃)₃ to the solution. The

solution containing Eu^{3+} ions continued to react for 1 h at room temperature while being vigorously stirred, and was then placed at a closed container until the gelation point was attained. After being dried at $40\text{ }^\circ\text{C}$, the gel was heated in an air atmosphere at a rate of $60\text{ }^\circ\text{C h}^{-1}$ up to the temperature of the heat treatment for the crystallization, and then kept at that temperature for 8 h before being taken out of the electric furnace. The temperatures of the heat treatments were $750\text{ }^\circ\text{C}$, $850\text{ }^\circ\text{C}$, $950\text{ }^\circ\text{C}$, and $1050\text{ }^\circ\text{C}$.

An Lcp-1 differential thermal analyser was used for recording the DTA curves for the dried gel, and a PRT-1 thermogravimetric analyser was used for recording the TGA curve. X-ray diffraction analysis to identify the crystalline phase of the samples which were heat treated at various temperatures was carried out using a D/max-rA x-ray diffractometer. Excitation and emission spectra were recorded using a Hitachi 850 spectrofluorometer in which the slit width was 3 nm. All of the measurements were performed at room temperature.

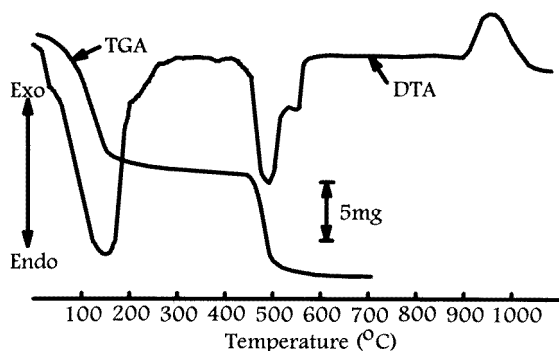


Figure 1. DTA and TGA curves for CaSiO_3 gel.

3. Results and discussion

3.1. The thermal evolution and crystallization of the CaSiO_3 gels

Figure 1 illustrates the differential thermal analysis and thermogravimetric analysis curves for CaSiO_3 gels (the heating rates were $10\text{ }^\circ\text{C min}^{-1}$). The DTA endothermic peak between room temperature and $300\text{ }^\circ\text{C}$ can be attributed to the vaporization of adsorbed water and residual organic molecules. The TGA curve shows marked weight losses in the same temperature range. The second weight loss indicated by the TGA curve and an endothermic effect indicated by the DTA curve, observed in the temperature range between $450\text{ }^\circ\text{C}$ and $550\text{ }^\circ\text{C}$, may be related to the elimination of the organic compounds chemically bound to Ca and Si.

The exothermic effect manifested at about $950\text{ }^\circ\text{C}$ in the DTA curve was caused by crystallization of the CaSiO_3 gel, and the broad and small exothermic peak suggests a very sluggish and complex process of crystallization. To obtain the activation energy of crystallization that governs the formation of the microcrystals, the modified Kissinger equation given by

$$\ln\left(\frac{\alpha}{T_p^2}\right) = -\frac{E}{RT_p}$$

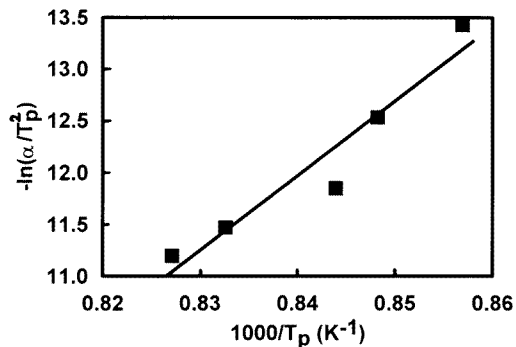


Figure 2. A Kissinger plot of the DTA results for CaSiO_3 gel.

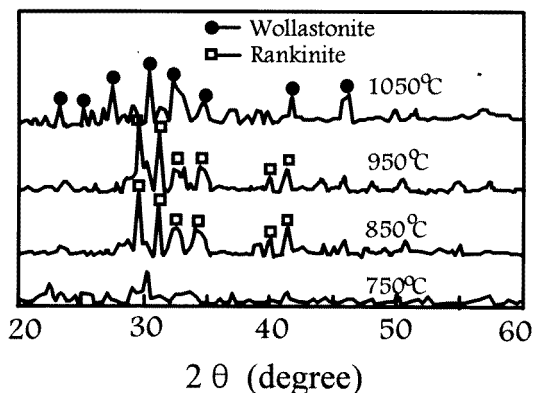


Figure 3. XRD patterns for samples which were heat treated at various temperatures.

was used, where α is the heating rate, E the activation energy, T_p the temperature of the exothermic crystallization peak, and R the gas constant [5]. A plot of $-\ln(\alpha/T_p^2)$ as a function of $10^3/T_p$ for the DTA results for the CaSiO_3 gel is shown in figure 2, and is approximately linear. The activation energy of crystallization was found to be about 580 kJ mol^{-1} . Hence a high activation energy also confirmed that the crystallization of CaSiO_3 gel is a complex process.

Figure 3 illustrates the x-ray diffraction patterns of CaSiO_3 gels which were heat treated at 750°C , 850°C , 950°C , and 1050°C . The XRD pattern of the sample which was heat treated at 750°C shows a very bad signal-to-noise ratio, which indicates that no obvious crystal was formed. After being heat treated at 850°C and 950°C , the gels showed better crystallization, and the crystalline phase was principally the rankinite one. (The excess SiO_2 in the samples cannot be detected by XRD because it was still amorphous.) However, the diffraction pattern shows formation of a crystalline phase corresponding to wollastonite in the sample which was heat treated at 1050°C , which suggests that rankinite structure transforms into wollastonite structure at higher temperature; that is, it appears that the following reaction occurs:



yet no exothermic effect corresponding to the proceeding transformation seems to be manifested in the DTA curve, due to the sluggish and complex nature of the transformation.

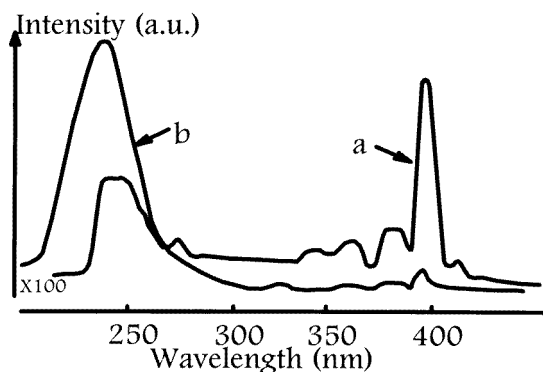


Figure 4. Excitation spectra of Eu^{3+} ions in dried gel (a) and in a sample which was heat treated at $1050\text{ }^{\circ}\text{C}$ (b).

3.2. Excitation spectra of Eu^{3+} ions

Figure 4 illustrates the excitation spectra of Eu^{3+} ions for ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ emission for the dried gel and for the sample which was heat treated at $1050\text{ }^{\circ}\text{C}$. The excitation spectra for samples which were heat treated at other temperature were quite similar to that for the sample which was heat treated at $1050\text{ }^{\circ}\text{C}$. They each consist of a broad band at about 240 nm and a number of narrow peaks on the longer-wavelength side, above 350 nm . It is obvious that the excitation spectra of Eu^{3+} ions in the gel-derived crystals were significantly different from that for the dried gel. The maximum in the excitation spectra was located at about 240 nm for gel-derived crystals and at 393 nm for dried gel, and the intensity of the excitation bands for the gel-derived crystals was also much stronger than that for dried gel.

In addition to $4f\text{--}4f$ direct excitation, the Eu^{3+} ion can undergo excitation in a broad excitation band that probably corresponds to a charge-transfer transition from oxygen to europium in Eu^{3+} -activated oxides. The direct excitation process can be analysed by the computation of free-ion energy levels as described by Ofelt [6], and is not strongly influenced by the electrical nature of the coordination polyhedron, because the $4f$ orbits are so deeply buried within the electronic shell that the energy levels of the $4f^n$ configuration are only slightly perturbed when an Eu^{3+} ion is placed within the solid. However, the excitation process via a charge-transfer transition from ligands (usually O^{2-} ions) to Eu^{3+} ions varies strongly with the nature of the ligand. The structural change of the host will significantly influence the broad excitation band of the Eu^{3+} ion. The higher the potential field at the O^{2-} ion due to the surrounding cations, the higher the energies of the band.

It can be considered that the CaSiO_3 dried gel consists of a continuous solid $\text{Si}\text{--}\text{O}$ network incorporating some metallic ions, residual water, and organic molecules. The bond between other metallic ions (e.g., Ca^{2+} and Eu^{3+}) and O^{2-} ions was very weak, so the intensity of the broad excitation band which was caused by a charge-transfer transition was relatively low, because the intensity of the charge-transfer band was determined by the mixing of the wave-function [7]. The main excitation bands of Eu^{3+} ions in the dried gel can be attributed to the $4f\text{--}4f$ direct excitation process (e.g. ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ transition, $\sim 393\text{ nm}$). After being heat treated at high temperature, however, the CaSiO_3 dried gels transformed

into gel-derived crystals, and the Si^{4+} , Ca^{2+} , and O^{2-} ions were arranged periodically according to the structure of rankinite or wollastonite, which leads to a decrease of the $\text{Ca}^{2+}-\text{O}^{2-}$ distance. Because the Eu^{3+} ion usually occupied an alkaline-earth-ion site, the decrease of the $\text{Eu}^{3+}-\text{O}^{2-}$ distance, and the increase of the interaction, would give rise to a predominant charge-transfer transition from ligands (O^{2-} ions) to Eu^{3+} ions in the gel-derived crystals.

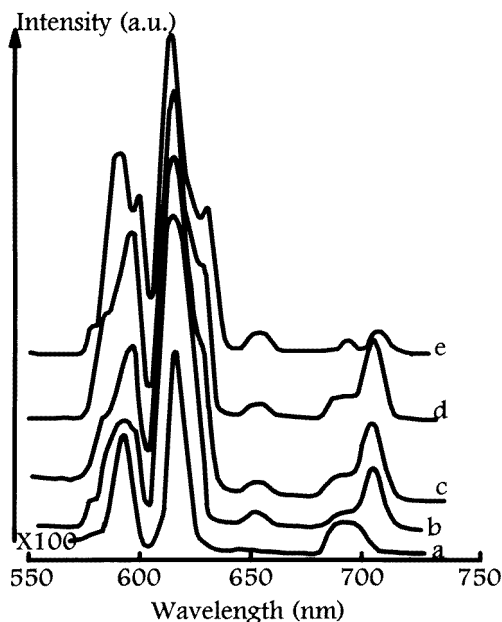


Figure 5. Emission spectra of the Eu^{3+} ions in the dried gel (a), and in samples which were heat treated at 750 °C (b), 850 °C (c), 950 °C (d), and 1050 °C (e).

3.3. Emission spectra of Eu^{3+} ions

Figure 5 illustrates the emission spectra of Eu^{3+} ions in the dried gel (excited at 393 nm) and in samples which were heat treated at 750 °C (excited at 249.5 nm), 850 °C (excited at 249.5 nm), 950 °C (excited at 248 nm), and 1050 °C (excited at 237 nm). For the dried gel, the emission spectrum of Eu^{3+} ions consists of some simple emission bands which correspond to $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (593 nm), $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (616 nm), and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ (690 nm) transitions. Due to the weakness of the interaction between Eu^{3+} and O^{2-} ions in the dried gel, very little level splitting can be caused by the crystal field, and no obvious splitting of Eu^{3+} emission bands has been observed. On the other hand, for low concentrations of rare-earth ions, the energy of the excited state can be transferred to the vibration of molecular groups (multiphonon relaxation), and the fluorescence decay rate of a level is the sum of the radiative decay and multiphonon relaxation rates. The rates of multiphonon relaxation between two successive electron levels decreased with the increase of the number of phonons matching the energy gap to the next lower level. For a given rare-earth ion, the multiphonon relaxation rates increased with the vibrational frequencies of the molecular groups of the host. Waters of hydration provide high-frequency vibration, and hydrated crystals are generally noted as poor fluorescers. From figure 1 it follows that there are some

water and organic molecules in the dried gel, and hence the intensity of the Eu^{3+} emission bands for the dried gel was much lower than that for the gel-derived crystals (see figure 5).

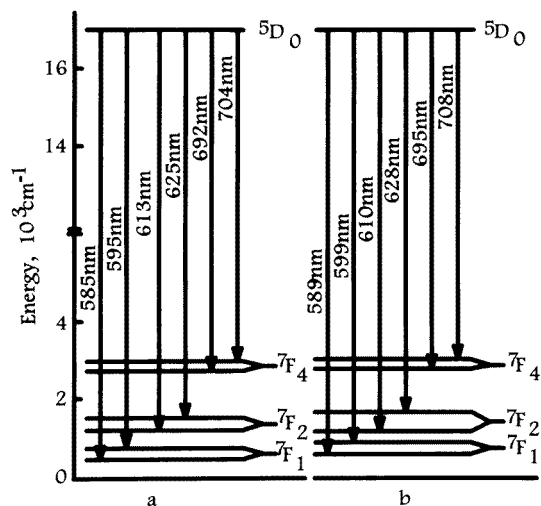


Figure 6. Energy levels of the Eu^{3+} ion in the rankinite (a) and in the wollastonite (b).

The emission spectra of Eu^{3+} ions in CaSiO_3 gel-derived crystals seem to be more complicated. For the sample which was heat treated at 750°C , except the band corresponding to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ (690 nm) transition—which was split into bands at 692 nm and 704 nm—no obvious level splitting by the crystal field can be observed. This may be attributed to the amorphous nature of this sample. In addition, the emission band at 613 nm corresponding to electric dipole transitions is much stronger than that at 593 nm corresponding to magnetic dipole transitions, which suggests that the Eu^{3+} ion would occupy a lattice site with no centre of symmetry in a sample which was heat treated at 750°C . With the increase of the temperature of the heat treatment, the main band corresponding to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transitions of the Eu^{3+} ion was obviously split by the crystal field into two bands, at 613 nm and 625 nm (610 nm and 628 nm for the sample which was heat treated at 1050°C), the band corresponding to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transitions was split into bands at 585 nm and 595 nm (589 nm and 599 nm for the sample which was heat treated at 1050°C), and the band corresponding to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ transitions was split into bands at 692 nm and 704 nm (695 nm and 708 nm for the sample which was heat treated at 1050°C). These transitions are illustrated in figure 6 by downward-pointing arrows. The emission spectrum of Eu^{3+} ions in the sample which was heat treated at 850°C was similar to that for the sample which was heat treated at 950°C ; this can be attributed to the same crystalline phase (rankinite) being predominant in the samples which were heat treated at 850°C and 950°C . The emission spectrum of Eu^{3+} ions in the sample which was heat treated at 1050°C , however, was obviously different from that for the samples which were heat treated at lower temperatures, because it shows a different crystal structure (wollastonite).

The 4f electrons in the rare-earth ion are shielded from the electric field of the neighbouring ions, and the effect of the crystal field on the 4f electrons is small, since the filled 5s and 5p shells are outside the 4f shell. When the rare-earth ions are introduced into the host materials, the energy levels are labelled by their ${}^{2S+1}\text{L}_J$ free-ion values. The

effect of the crystal field is to cause a fine splitting of these levels. In different hosts the energy levels of the trivalent ions are essentially in the same positions, but the splittings of the levels will be different, reflecting the different strengths and symmetries of the different crystal fields. If one knows the site symmetry of the RE ion from crystallographic data, then by group theory it is possible to determine exactly the number of crystal-field levels into which a free-ion term with total angular momentum J will be split, but the splittings of some levels are so small that they can be represented in the energy level scheme as a broadening of the levels. Both the rankinite structure and the wollastonite structure possess C_{2h} symmetry, and according to reference [8], the number of crystal-field states for the Eu^{3+} ion with an even number of 4f electrons is $2J + 1$. However, every 7F_J ($J = 1, 2,$ or 4) level of the Eu^{3+} ion is split into just two energy levels whether the ion is in rankinite and wollastonite. Obviously, the fine differences in spectral detail are difficult to observe without very high resolution.

From figure 6 one can also see that the crystal-field levels of Eu^{3+} in wollastonite are shifted to higher-energy states in comparison with those in rankinite. The probability of a transition from state i to state f , in which a photon of energy $\hbar\omega$ is absorbed, is given by [9]

$$P_{if} = (2\pi/\hbar)|V_{fi}|^2\delta(E_i - E_f - \hbar\omega)$$

where V_{fi} is the matrix element, $\langle f|V|i\rangle$, of the transition, and V is the operator denoting the energy of the interaction of the centre with the radiation. When the transition is an electric dipole process, the interaction term is $V = \mathbf{p} \cdot \mathbf{E}$, where \mathbf{p} is the electric dipole moment operator and \mathbf{E} is the electric field intensity of the radiation field. The transition can also be caused by a magnetic dipole process because of the interaction of the centre with the magnetic component of the radiation field. In this case the interaction term is $V = \boldsymbol{\mu} \cdot \mathbf{B}$, where $\boldsymbol{\mu}$ is the magnetic dipole operator and \mathbf{B} is the strength of the magnetic field of the radiation. In Eu^{3+} -doped oxides, the electric field and magnetic field intensity of the radiation field depend significantly on the number of nearest-neighbour O^{2-} ions and the distance between the Eu^{3+} ion and the O^{2-} ion. According to reference [10], the average of all of the Si–O distances in a silicate structure, $\langle d(\text{Si–O}) \rangle$, increases from 1.6 Å to 1.63 Å as the O:Si ratio (counting only those oxygen atoms that are linked to silicon atoms) increases from 2 for the three-dimensional tetrahedral frameworks of SiO_2 to 4 for monosilicates containing only $[\text{SiO}_4]$ tetrahedra not linked to other $[\text{SiO}_4]$ tetrahedra by common oxygen atoms. The $[\text{SiO}_4]$ tetrahedra in wollastonite structure are linked into chains, and the O:Si ratio is 3. The rankinite has a silicate structure containing $[\text{Si}_2\text{O}_7]$ groups, and the O:Si ratio is 7:3, which is smaller than that for wollastonite. Obviously, the electric and/or magnetic field intensity of the radiation field in wollastonite is stronger than that in rankinite due to the shorter distance between the cation and the O^{2-} ion in wollastonite, which leads to higher energies of crystal-field levels of the Eu^{3+} ion in wollastonite.

4. Conclusion

The two DTA endothermic peaks of CaSiO_3 gel can be related to the elimination of residual solvents and the organic compounds chemically bound to Ca and Si. The TGA curve also indicates marked weight losses in the same temperature ranges. The higher activation energy of crystallization suggests a very sluggish and complex process of crystallization for CaSiO_3 gel. The diffraction patterns show the evolution from rankinite to wollastonite structure at higher temperature. The intensities of the excitation and emission bands of the gel-derived crystals were much stronger than those of the dried gel, and the strongest

excitation band also transferred from 393 nm for the dried gel to 240 nm for the gel-derived crystals. The number of crystal-field levels into which a free-ion term with total angular momentum J is split is observed to be the same in both rankinite and wollastonite structures due to them having the same (C_{2h}) symmetry. Yet the relative intensities of the groups of emission bands corresponding to transitions from the state 5D_0 to the crystal-field states 7F_J vary significantly with the crystalline phases of the samples which were heat treated at various temperatures, and a difference in peak wavelength of the emission bands can also be observed.

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