CHEMISTRY LETTERS, pp. 283-286, 1990.

Effects of Reduction Temperatures on Electron Spin Resonance Spectra of CaS:Eu

Hiroshi MATSUI,* Genzo HASHIZUME, and Gin-ya ADACHI†
Industrial Research Institute of Hyogo Prefecture, Suma, Kobe 654
†Department of Applied Chemistry,
Faculty of Engineering, Osaka University, Suita 565

Polycrystalline CaS:Eu^{2+} phosphors have been prepared by the reduction of $CaSO_3$:Eu·1/2H_2O in a stream of H_2S gas at 450, 600, and 900 °C for 3 to 24 h. All samples have been examined by means of ESR and photoluminescence spectroscopy. The emission intensity due to Eu^{2+} increased with the increase of reduction temperatures. The interstitial Eu^{2+} ions were observed for the CaS host prepared even at as low as 450 °C. At a higher reduction temperature, the Eu^{2+} ion may enter a Ca cite in the CaS host lattice substitutionally.

A considerable amount of investigation has been done and reviewed[1] recently on the alkaline-earth sulfides. Driving force behind these efforts is the potential applications of these materials as a host in PL, CRT, EL-panel and IR detector phosphors. The purpose of this study on europium activated CaS phosphors (CaS:Eu) is to show effects of reduction temperatures on ESR spectra of Eu in CaS host crystal.

Europium containing calcium sulfite hemihydrate, $CaSO_3$:Eu·1/2H_2O, of spherical particles was prepared as starting material by precipitation using a reaction between a Na_2SO_3 solution, and a $CaCl_2$ solution containing a given concentration of $EuCl_3$ (III). Resulting calcium sulfite hemihydrate was reduced to CaS:Eu of spherical particles in a stream of hydrogen sulfide at 450, 600, and 900 °C for 3 to 24 h at a single process.

ESR spectra were obtained by using an X-band spectrometer system (Japan Elec-

tron Optics Co. JM-PE-3X) operating at about 9.20 GHz and a modulation frequency of 100 kHz at room temperature.

Photoluminescences were measured under excitation by 254 nm ultraviolet using a Shimazu RF-502 spectrofluorophotometer. Emission spectra due to Eu^{2+} obtained were composed of a broad band emission and were similar to the other results.[2] These profiles were independent of reduction temperatures. As shown in Table 1, the relative emission intensity due to Eu^{2+} increases with the increase of reduction temperatures. The intensity also increases with increasing Eu^{2+} concentration. The ESR spectra of $CaS:Eu^{2+}$, which are dependent on reduction temperatures, are shown in Fig.1.

A Eu^{2+} state has a $4f^7$ spin configuration, i.e. a half filled f-shell with $^8S_{7/2}$ at a ground state. The electronspin, S, of the Eu^{2+} ion is 7/2 and the nuclear spin, I, is 5/2 for both ^{151}Eu and ^{153}Eu. An analysis of the ESR spectrum for $^8S_{7/2}$ of the Eu^{2+} ion in a quasi-cubic field is performed. We may have six groups of lines that consist of seven lines where positions are in touch with one another. Each distance between the neighboring groups is almost equal and there exist two kinds of structure patterns due to two isotopes ^{151}Eu and ^{153}Eu. The characteristic hyperfine patterns due to the ^{151}Eu isotope (natural

Table 1. Photoluminescence intensity[a] of $CaS:Eu^{2+}$ in varying reduction temperatures and Eu concentrations

(a.u.)

Reduction	Eu concentration / mol%		
temperature/°C	0.001	0.01	0.1
450	13	21	21
600	36	67	84
900	37	69	85

a) Observed at an excitation wavelength of 254 nm.

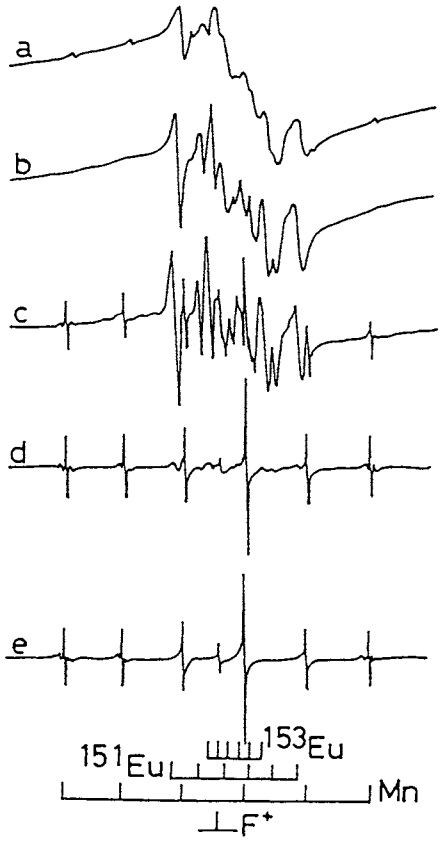

Fig. 1. ESR spectra of CaS:Eu.
a:450 °C,0.1 mol%, b:600 °C,0.1 mol%, c:900 °C,0.1 mol%, d:900 °C,0.01 mol%, e:900 °C,0.001 mol%.

abundance 47.8% and magnetic moment 3.441) and ^{153}Eu isotope (natural abundance 52.2% and nuclear magnetic moment 1.521) can be used to identify Eu^{2+} by ESR. The hyperfine interaction constant, A, of ^{151}Eu is about twice as large as that of ^{153}Eu ($^{151}Eu/^{153}Eu$ = 3.441/1.521 = 2.262), and, the peak intensity ratio of ^{151}Eu to ^{153}Eu is about 1 ($^{151}Eu/^{153}Eu$ = 47.8/52.2 = 0.916).

The ESR spectra are composed of four components due to ^{151}Eu, ^{153}Eu, Mn^{2+}, and F^{+}, as assigned in Fig.1. These clear hyperfine structure revealed an isotropic crystal field of the CaS cubic crystal phase. A series composed of 6-lines due to Mn^{2+}, having a nuclear spin of 5/2, which was a minor impurity contained in the host lattice, is recognized. The ESR spectra of Mn^{2+} in CaS:Mn were discussed in detail by Yamase.[3] An F^{+} center signal at g=2.0032 due to a sulfur vacancy, V_S, which was discussed in detail by Auzin[4] and Shanker,[5] could be also identified. Table 2 lists values for g factors and hyperfine interaction constants, A, obtained in this study and other investigators. These results agree with those in the literature.[5-8]

The ESR absorption lines of CaS:Eu are brought to broadening compared to that of SrS:Eu,[9] because ionic radii of Ca^{2+} and Eu^{2+} are different from one another. If a Ca ion is substituted by a Eu ion, the substitution may lead to some distortion of the host crystal. We examined the crystalline lattice distortion by the line broadening method with X-ray diffraction method. We could not obtain an accurate information, because the resulting crystalline size was much larger than 1000 Å. However, if the instrument correction is not applied, the higher the reduction temperature becomes, the less the resulting distortion becomes relatively.

As is seen from Fig.1, deviation from the baseline became smaller with increasing the reduction temperature. The hyperfine structure superimposes upon the broad signal appeared in the whole field. It was recognized that the Eu^{2+} ions existed in interstitial positions in the CaS crystal and the interaction between Eu^{2+} ions increased with increase in the Eu concentration. The interstitial Eu^{2+} ions were observed for the CaS host prepared even at as low as 450 °C. At a higher reduction temperature, the Eu^{2+} ion may enter a Ca site in the CaS host lattice substitutionally .

Table 2. Comparison of ESR parameters of CaS phosphors.
All values of A are in cm^{-1}

Activator	g factor	A(Mn)	A(^{151}Eu)	A(^{153}Eu)	F^+ g factor	Meas.temp	Ref.
En^{2+}	1.990		30.4	13.4		300 K	5
Eu^{2+}	-		30.6	-		R.T.[a)]	6
Mn^{2+}	2.001	75.7				R.T.	7
None					2.0032	R.T.	8
Eu^{2+}	1.9952		31.1	13.7	2.0032	R.T.	This work
Mn^{2+} b)	2.0115	76.0				R.T.	This work

a) R.T.: Room temperature. b) Minor impurity.

References

1) R. P. Rao, J. Mate. Sci., 21, 3357(1986).

2) T. V. Samulski, P. T. Chopping, and B. Haas, Phys. Med. Biol., 27, 107(1982).

3) T. Yamase, Inorg. Chim. Acta, 114, L35(1986).

4) A. Auzins, J. W. Orten, and J. E. Wertz, "Paramagnetic Resonance," Academic Press, New York (1960), Vol.1, p.90.

5) V. Shanker, P.K. Ghosh, and T. R. S. Reddy, Indian J. Pure Appl. Phys., 14, 193(1976).

6) K. Kojima, T. Komaru, T. GHihira, and Y. Koi, J. Phys. Soc. Jpn., 40, 1570 (1976).

7) O. Matsumura, J. Phys. Soc. Jpn., 14, 108(1959).

8) P. K. Ghosh and V. Shanker, J. Lumin., 20, 139(1979).

9) Y. Kanaji, Private Communication.

(Received November 10, 1989)