Valencies of Eu in CaS : Eu, La

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Photoluminescence of La and Eu codoped CaS prepared in sodium and potassium polysulfide flux was studied. The emission spectra of CaS : Eu prepared in both fluxes show a broad band at 650 nm due to the f–d transition of Eu^{2+}. When potassium polysulfide flux is used, the emission from Eu^{2+} decreases and the line emission of Eu^{2+} appears with concentration of codoped La^{3+}. However, when sodium polysulfide flux is used, clear line emission spectra of Eu^{3+} were observed, in addition to the broad band spectrum from recombination process of defects and vacancies in the host matrix. For the first time at room temperature, sharp line spectrum of Eu^{3+} is observed and this is a strong indication of La^{3+}–Eu^{3+} pairing in CaS : Eu, La. EPR intensity of Eu^{2+} increases with Eu concentration and decreases with La^{3+} concentration in CaS : Eu, La prepared in potassium polysulfide flux. However, the result of EPR study suggests that only Eu^{3+} is doped when CaS : Eu, La is prepared in sodium polysulfide flux. © 1998 Academic Press

INTRODUCTION

Luminescence properties of CaS : Eu have been studied by many investigators. Especially, Eu^{2+} doped alkaline-earth sulfides (CaS, SrS) have attracted interest due to their potential as phosphors for electroluminescence and cathodoluminescent display (1–4). From the viewpoint of chromaticity, CaS : Eu is considered to be the most promising candidate for red phosphor compared to ZnS : Sm, ZnS : Eu, and SrS : Eu (5).

Investigators suggested that there was coexistence of two valence states of Eu^{2+} and Eu^{3+} in alkaline oxides and sulfides (6–9): Yamashita et al. reported that ESR signal intensity of Eu^{2+} in CaO : Eu prepared in H_2 was about 7 times higher than that in CaO : Eu prepared in N_2 (10).

They suggested that Eu^{3+} had two kinds of sites in CaS, forming center A (isolated Eu^{3+} center) and center B (paired Eu^{3+}–Eu^{2+}) (11). M. Pham-Thi *et al.* observed two oxidation states of Eu^{3+} and Eu^{2+} in CaS prepared in alkaline polysulfide flux, however, they observed Eu^{3+} luminescence in CaS only at low temperature as many other investigators (6, 12).

We have reported that the spectral change depends on the vacancy concentration which was controlled chemically with La^{3+} substitution in CaS (refer to $Ca_{1-x}La_xS$). Since La^{3+} itself is transparent to UV excitation, the assignment of vacancy state to the spectra could be clearly explained with arguments in our previous paper (13).

This paper reports luminescence properties of La and Eu codoped CaS, hereafter denoted as CaS : Eu, La. For the first time at room temperature, highly resolved emissions due to Eu^{2+} and Eu^{3+} in addition to the emission from defects in the host matrix were observed. The nature of spectra observed in CaS : Eu, La was interpreted relating to the concentration of codopant and cation of flux materials.

EXPERIMENTAL

Eu and La codoped CaS, CaS : Eu, La, was prepared in two different fluxes, sodium polysulfide (Na_2CO_3–S) and potassium polysulfide(K_2CO_3–S). Starting materials for the synthesis of CaS : Eu, La were $CaCO_3$ (Aldrich 99 + %), La_2O_3 (Shin-Etsu, 99.99%), Eu_2O_3 (Shin-Etsu, 99,99%), S (Kanto, E.P), Na_2CO_3 (Aldrich, 99.95%), and K_2CO_3 (Aldrich, 99.95%). Required amounts of starting materials were well mixed and heated in a covered alumina crucible at 1000°C for 2 hrs. The product was cooled to room temperature and residual fluxes (Na_2S_x, Na_2SO_4, K_2S_x, and K_2SO_4 etc.) were washed out with distilled water. The final product was dried after rinsing with ethyl alcohol.

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X-ray diffraction data were obtained with Rigaku X-ray diffractometer using Cu $K\alpha$ radiation and EPR spectra were obtained with Bruker ER2000D-SRC. For photoluminescence measurements, monochromated 150 W Xenon lamp was used as an excitation source. Photoluminescence spectra were obtained using monochromator equipped with photomultiplier tube.

RESULTS AND DISCUSSION

1. X-ray Diffraction

X-ray diffraction patterns of CaS : Eu, La prepared in both fluxes consist of typical diffraction peaks of a rock-salt structure. The lattice parameter of CaS : Eu, La prepared in potassium polysulfide flux does not change with concentration of doped La and Eu. Extra diffraction peaks of Eu_2O_2S are observed above 10 mole% of Eu in CaS : Eu, La as shown in Fig. 1b.

X-ray diffraction patterns of CaS : Eu, La prepared in sodium polysulfide flux shift to low angle with concentration of doped La ($0 \sim 30$ mole%) as previously reported (Fig. 1a) (13). The lattice parameters calculated from the X-ray diffraction increase linearly in the range of $5.69 \sim 5.77$ Å following Vegard's law.

2. Photoluminescence of CaS : Eu, La Prepared in Potassium Polysulfide (K_2CO_3-S) Flux

The body color of CaS : Eu is pink and gets deeper with increasing Eu content. The pink color indicates an absorption of Eu^{2+} in the blue region. The oxidation state of Eu is
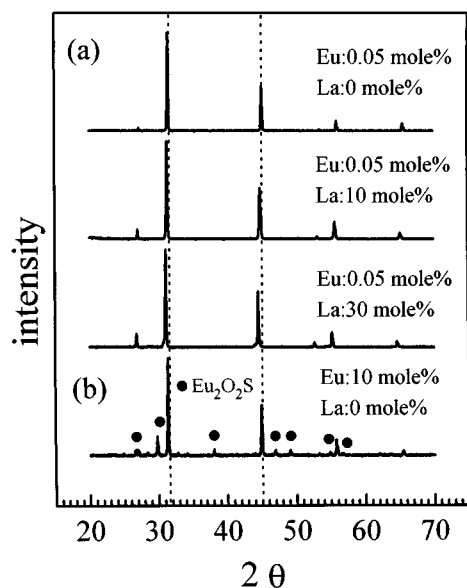
known to be dependent on the alkaline flux used in the synthesis (14). Excitation spectrum of CaS : Eu prepared in potassium polysulfide flux is shown in Fig. 2. The excitation spectrum shows two bands in $260 \sim 300$ nm region and a broad band with some feature in $400 \sim 600$ nm region: the peak at 260 nm can be assigned to the band gap of host material CaS, the peak around 275 nm to the f–d(e_g) transition of Eu^{2+}, and the band in $400 \sim 600$ nm region to the f–d(t_{2g}) transition. The assignment has reasonable agreement comparing the luminescence spectra of host material itself, CaS, and considering the energy states of Eu^{2+} ion in octahedral environment. Previously, excitation and emission peaks of pure CaS prepared by H_2S are observed at 260 nm and 450 nm, respectively. In the spectrum of pure CaS, the excitation peak at 260 nm corresponds to the band gap of CaS and the emission peak at 450 nm were assigned to be the transition from the trapped electron in the intrinsic $V_{S^{2-}}^{2+}$ level to the valence band of host material (13).

When La is codoped to CaS : Eu (CaS : Eu, La), a new broad band appears in 330 nm region in addition to the band gap and the f–d transition, which is also shown in Fig. 2. This can be assigned to a charge transfer band of Eu^{3+} from the ligand S^{2-} as in the case of Y_2O_2S : Eu (15). The pink color of CaS : Eu, La changed from deep to light with increasing La content, which is due to reduced excitation of the f-d transition.

The emission spectrum of CaS : Eu prepared in potassium polysulfide flux is shown in Fig. 3. The spectrum shows only a broad band at 650 nm due to f–d transition of Eu^{2+}. The Eu^{2+} emission decreases drastically with La^{3+} doping and a sharp line spectrum of Eu^{3+} emission appears.

When CaS : Eu and CaS : Eu, La are prepared in potassium polysulfide flux, possible ions to be doped could be
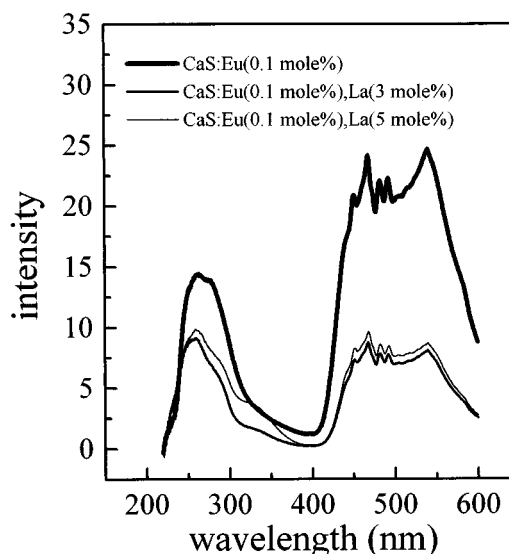

FIG. 1. X-ray diffraction patterns of CaS : Eu, La prepared in (a) sodium polysulfide flux (Eu 0.05 mole%, La $0 \sim 30$ mole%) and (b) potassium polysulfide flux (Eu 10 mole%, La 0 mole%)

FIG. 2. Excitation spectra of CaS : Eu, La prepared in potassium polysulfide flux (λ_{em}: 624.5 nm)

FIG. 3. Emission spectra of CaS : Eu, La prepared in potassium polysulfide flux (λ_{ex}: 335 nm)
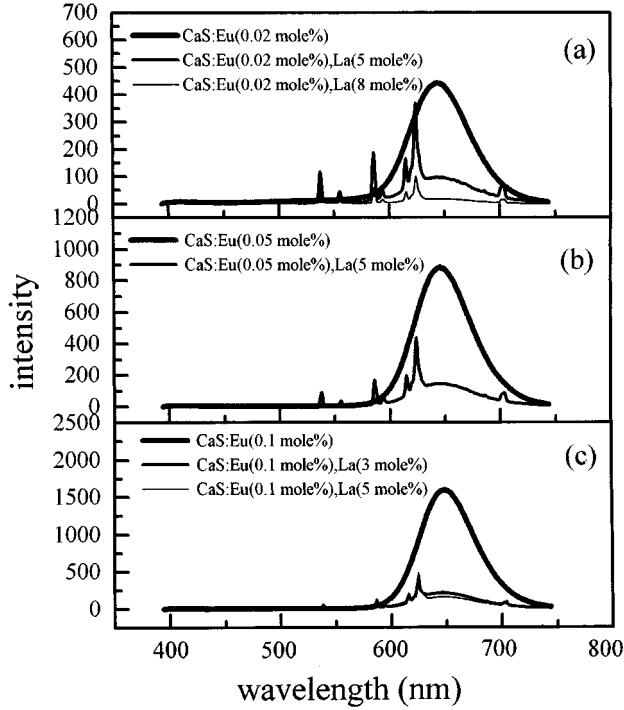
FIG. 4. f–f line spectra of Eu^{3+} in CaS : Eu, La (λ_{ex}: 335 nm).

Eu^{2+}, Eu^{3+}, K^+, and La^{3+}. The ionic sizes of the dopants are: K^+ (1.38 Å), Eu^{2+} (1.17 Å), Eu^{3+} (1.03 Å), La^{3+} (1.03 Å), and Ca^{2+} (1.00 Å) (16). Since K^+ and Eu^{2+} are much larger than Ca^{2+}, substitution of both ions to Ca^{2+} sites may cause large lattice distortion. According to the previous result, K^+ is expected to be dissolved in CaS with solubility limit around 5 mole% (13). The substitution of cations to Ca^{2+} sites may follow in either way of followings.

$$2Ca^{2+} \rightarrow K^+_{Ca^{2+}} + Eu^{3+}_{Ca^{2+}} \qquad [1]$$

$$Ca^{2+} \rightarrow Eu^{2+}_{Ca^{2+}} \qquad [2]$$

$$3Ca^{2+} \rightarrow 2La^{3+}_{Ca^{2+}} + V_{Ca^{2+}} \qquad [3]$$

Since Eu^{2+} is much smaller than K^+, substitution of Eu^{2+} to Ca^{2+} site may cause less distortion in CaS lattice than that of K^+, therefore, the case [2] is more probable than the case [1]. But when La^{3+} is doped to CaS : Eu in potassium polysulfide flux, the case [3] may occur, because the ionic size of La^{3+} (1.03 Å) is similar to that of Ca^{2+}. Especially, in case [3], a vacancy at Ca^{2+} site ($V_{Ca^{2+}}$) for two La^{3+} ions would be produced. As vacancies increase in CaS lattice, the deficiencies of positive charges are enhanced and some of Eu^{2+} would be oxidized to Eu^{3+}. The line emission spectra of Eu^{3+} are observed with La doping as in Fig. 3. On substitution of Ca^{2+} wit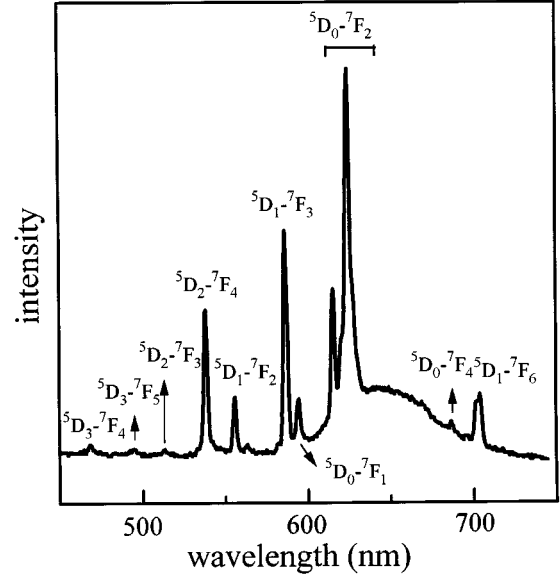h La^{3+} in CaS lattice, a dramatic decrease of Eu^{2+} emission is observed, which suggests that $2La^{3+}_{Ca^{2+}}$ acts as a trap.

The sharp emission line spectrum of Eu^{3+} in CaS : Eu, La can be clearly assigned to the f–f transition as shown in Fig. 4. Especially, emissions from the electric dipole transitions of $^5D_2 \rightarrow {}^7F_4$, $^5D_1 \rightarrow {}^7F_3$, and $^5D_0 \rightarrow {}^7F_2$ with $\Delta J = 2$ are intense due to the hypersensitive transition (15, 17). Magnetic dipole transition of $^5D_0 \rightarrow {}^7F_1$ ($\Delta J = 1$) shows only weak one line which is known to be due to centrosymmetrical site of Eu^{3+} ion in cubic system of CaS : Eu, La. It is known that if Eu^{3+} is on noncentrosymmetric center, electrical dipole transition predominates due to forced electric dipole transition. Therefore, contrary to the previous reports, the most of Eu^{3+} ion in CaS : Eu, La likely to be located at noncentrosymmetric sites and it seems to be due to $(La–Eu)^{3+}$ pair formation (6, 11). The role of doped La^{3+} ion seems to be breaking symmetry of Eu^{3+} site, which causes highly resolved strong dipole transition at room temperature.

3. Photoluminescence of CaS : Eu, La Prepared in Sodium Polysulfide (Na₂Co₃–S) Flux

The excitation spectrum of CaS : Eu prepared in sodium polysulfide flux is shown in Fig. 5. This spectrum shows one broad band at 250~300 nm due to the band gap of CaS. Substitution of La^{3+} to Ca^{2+} causes large decrease of the excitation intensity and shows some weak bands which are similar to the bands from the recombination process of various defects (13). A new sharp band appears around 420 nm, which can probably be assigned to excitation from valence band to $2La^{3+}_{Ca^{2+}}$.
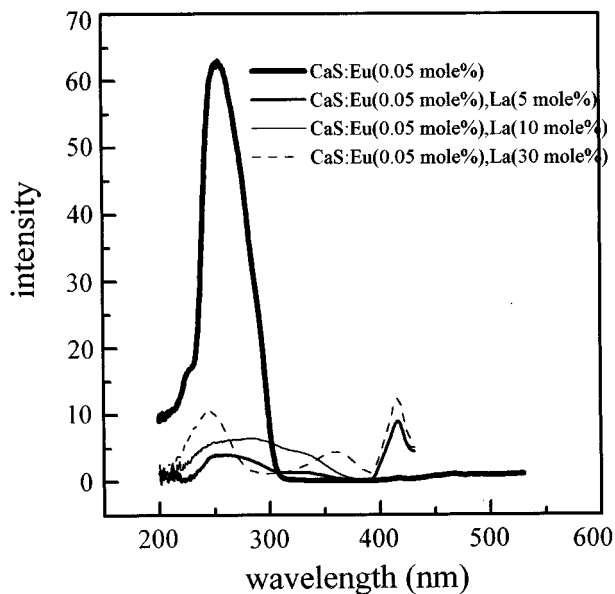
FIG. 5. Excitation spectra of CaS:Eu, La prepared in sodium poly-sulfide flux (λ_{em}: 624.5 nm)

The emission spectra of CaS:Eu, La prepared in sodium polysulfide flux are shown in Fig. 6. The spectrum of CaS:Eu shows typically broad emission band of octahedrally coordinated Eu^{2+}. Since the size of Eu^{3+} is similar to that of Ca^{2+}, it can easily be substituted to Ca^{2+} site through charge compensation with Na^{+} in sodium polysulfide flux. The Eu^{2+} ($4f^6 5d^1$–$4f^7$) emission in CaS is explained as it is due to the induction of trapping electrons from the conduction band via excited state, Eu^{2+} ($4f^6 5d^1$)*. Exciting
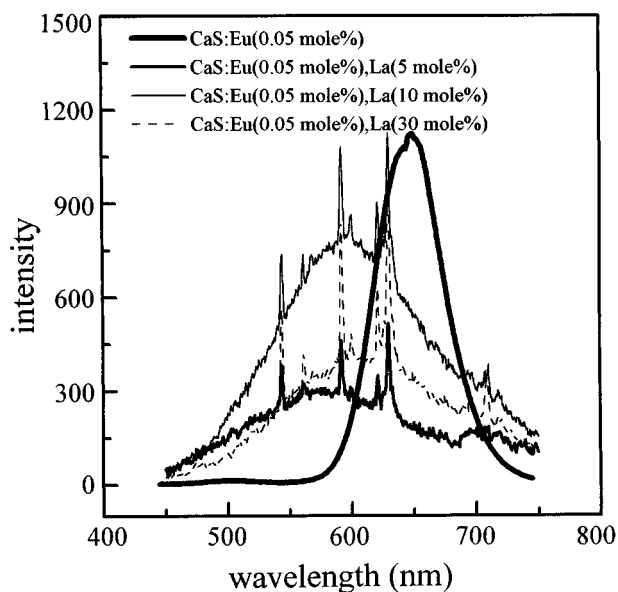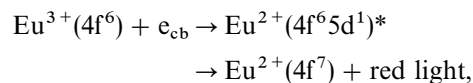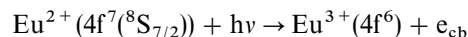

FIG. 6. Emission spectra of CaS:Eu, La prepared in sodium polysulfide flux (λ_{ex}: 335 nm)

light ($h\nu = 2.41$ eV) is high enough to induce a direct photoionization (18, 19). The mechanism of photoionization transition can be expressed as:
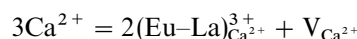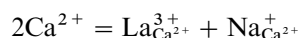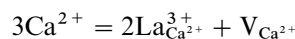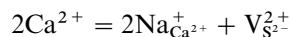
$$Eu^{2+}(4f^7(^8S_{7/2})) + h\nu \rightarrow Eu^{3+}(4f^6) + e_{cb}$$

$$Eu^{3+}(4f^6) + e_{cb} \rightarrow Eu^{2+}(4f^6 5d^1)*$$

$$\rightarrow Eu^{2+}(4f^7) + red\ light,$$

where e_{cb} represents electron of conduction band. According to the previous study, Eu^{2+} band spectrum is observed at room temperature. On the other hand, Eu^{3+} line spectrum is observed only at low temperature (11).

Emission of CaS:Eu, La prepared in sodium polysulfide flux shows line spectrum of Eu^{3+} even at room temperature and a broad band spectrum, which differs from Eu^{2+} emission. This observation is somewhat different from the previous study (11).

The La^{3+}-substituted Ca^{2+} site may form a trap with the depth between the excited states of Eu^{2+} and Eu^{3+}. The depth of $La^{3+}_{Ca^{2+}}$ trap is considered to be rather in the same energy level with the excited state of Eu^{3+} and may easily transfer energy to Eu^{3+} near La^{3+}, that is, to (La–Eu)$^{3+}$ pair. Therefore, as the number of Eu^{3+} near La^{3+} site or the concentration of (La–Eu)$^{3+}$ pair and the energy transfer rate increase, much of the emission may be expected to be quenched.

The broad band spectrum may be explained with the recombination processes between the luminescence centers from various vacancies ($V_{Ca^{2+}}$, $V^{2+}_{S^{2-}}$) and defects ($La^{3+}_{Ca^{2+}}$, $Na^{1+}_{Ca^{2+}}$, (La–Eu)$^{3+}_{Ca^{2+}}$) (13). The mechanism of the defects and vacancies formation can be proposed as;

$$2Ca^{2+} = 2Na^+_{Ca^{2+}} + V^{2+}_{S^{2-}}$$

$$3Ca^{2+} = 2La^{3+}_{Ca^{2+}} + V_{Ca^{2+}}$$

$$2Ca^{2+} = La^{3+}_{Ca^{2+}} + Na^+_{Ca^{2+}}$$

$$3Ca^{2+} = 2(Eu–La)^{3+}_{Ca^{2+}} + V_{Ca^{2+}}$$

And these band spectra shift to a longer wavelength with increasing La^{3+} content (Fig. 6). This is due to the increments of the lattice parameter with the substitution of La^{3+} (13).

4. EPR Properties of CaS:Eu, La

The Eu^{2+} ion with f^7 configuration can be detected by EPR at room temperature, but Eu^{3+} ion with $^7F_0$ ground state is nonmagnetic ($J = 0$) and cannot be detected. Europium has two isotopes of ^{151}Eu and ^{153}Eu with nuclear spin 5/2 (the natural abundance and nuclear g_n factor of ^{151}Eu and ^{153}Eu are: 47.8%, 1.39 and 52.2%, 0.61, respectively) (10,12), therefore, Eu^{2+} in cubic symmetry is expected to show two sets of six hyperfine lines with equal intensity.

Figure 7(a)∼(e) show EPR spectra of CaS:Eu and CaS:Eu,La prepared in potassium polysulfide flux. Fig. 7(a) shows the EPR spectrum of Eu^{2+}. When the concentration of doped Eu is increased (0.02, 0.05, 0.1 mole% to 1 mole of CaS), the EPR signal of Eu^{2+} increases as shown in Fig. 7(a), (c) and (d). But when La^{3+} is codoped to CaS:Eu, the intensity of EPR absorption of Eu^{2+} decreases significantly as shown in Fig. 7(b) and (e). On the other hand, when CaS:Eu and CaS:Eu,La are prepared in sodium polysulfide flux, only impurity Mn^{2+} signals in the EPR spectrum are observed and the EPR of Eu^{2+} signal are not observed. This observation indicates that europium is doped mainly in 3+ oxidation state when it is prepared in sodium polysulfide flux.

Since the ionic sizes of Eu^{3+} (1.03 Å) and Na^{+} (1.02 Å) are similar to the size of Ca^{2+} (1.00 Å), Eu^{3+} can easily be doped to CaS with charge compensator Na^{+} in sodium polysulfide flux, while Eu^{2+}-doping (1.17 Å) may be limited because of large lattice distortion of CaS.

In potassium polysulfide flux, europium may be doped to CaS lattices upto the solubility limit in Eu^{2+} (1.17 Å) state and/or in Eu^{3+} state by forming calcium vacancies. But K^{+} ion (1.38 Å) may not be easily doped to CaS lattices by forming K^{+}–Eu^{3+} charge compensation pair. Thus europium, in CaS prepared in potassium polysulfide flux may exist in two oxidation states of Eu^{2+} and Eu^{3+}, and shows only Eu^{2+} signal at room temperature in the EPR spectrum.

When La^{3+} is codoped to CaS:Eu in potassium polysulfide flux, Eu^{2+} emission decreases significantly and Eu^{3+} emission appears with the La^{3+} content increase. With the increment of La^{3+} doping, the concentration of Ca^{2+} vacancy ($V_{Ca^{2+}}$) may increase and enhance the deficiency of positive charges, which may bring the driving force for Eu^{2+} oxidation.

CONCLUSIONS

Eu in CaS:Eu,La prepared in fluxes (sodium polysulfide flux, potassium polysulfide flux) exists in two oxidation states of Eu^{3+} and Eu^{2+} at room temperature. CaS:Eu shows broad red emission band independent of the flux used in the preparation process. But the oxidation state of europium is 3+ when CaS:Eu is prepared in sodium polysulfide flux, and in two oxidation states of 2+ and 3+ when CaS:Eu is prepared in potassium polysulfide flux. When La^{3+} is codoped to CaS:Eu, $La^{3+}_{Ca^{2+}}$ trap is formed and f–f transition of Eu^{3+} can be observed with intense hypersensitive transition of $\Delta J = 2$, which is due to the change of local symmetry of Eu^{3+} through the (La–Eu)$^{3+}$ pair formation.

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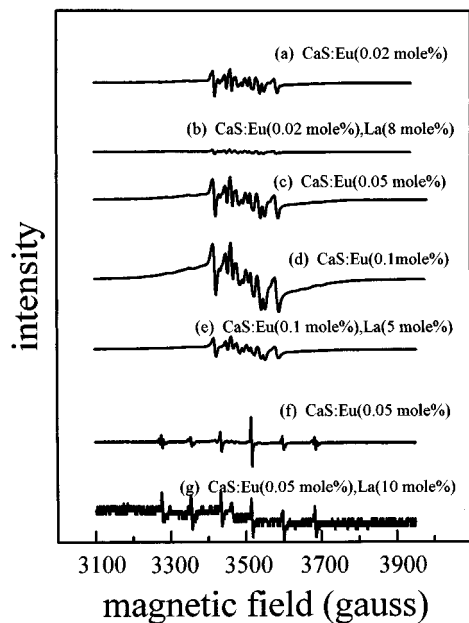

FIG. 7. EPR spectra of CaS:Eu,La with different Eu,La concentration and flux methods at room temperature. The sample for (a)∼(e) prepared in potassium polysulfide flux and for (f) and (g) prepared in sodium polysulfide flux. (a) CaS:Eu(0.02 mole%), (b) CaS:Eu(0.02 mole%),La(8.0 mole%), (c) CaS:Eu(0.05 mole%), (d) CaS:Eu(0.10 mole%), (e) CaS:Eu(0.10 mole%), La(5.0 mole%), (f) CaS:Eu(0.05 mole%), (g) CaS:Eu(0.05 mole%), La(10 mole%).