phys. stat. sol. (a) **203**, No. 11, 2718–2722 (2006) / **DOI** 10.1002/pssa.200669619

Effect of co-doping of Ce^{3+} and alkaline metals on the photoluminescence in $CaGa_2S_4$ and $SrGa_2S_4$ hosts

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Received 24 February 2006, revised 14 June 2006, accepted 26 June 2006

PACS 42.70.Hj, 78.55.Hx, 78.60.Fi

Ce^{3+} doped alkaline-earth thiogallates represented as $M^{II}Ga_2S_4$ (M^{II} = Ca, Sr, Ba) are known as blue phosphors with high brightness and good purity of color. However the Ce concentration is limited below about 1 mol% in the process of the single crystal growth, presumably due to the charge imbalance of the dopant. Here in order to increase Ce^{3+} concentration, alkaline metals and Ce ions are codoped in the alkaline earth thiogallates and the effect of co-doping on the photoluminescence is studied. More than 15 mol% Ce doping is achieved, and PL intensity in Na codoped Ca and Sr thiogallates becomes three and five times stronger than that of the only Ce^{3+} 1 mol% doping case, respectively.

1 Introduction

Rare earth elements doped alkaline earth thiogallates exhibit various visible light emission and are expected as materials suitable for EL devices [1, 2]. Especially, as the blue emission of Ce^{3+} doped compounds shows high brightness and a broad spectrum, their application to laser devices is also expected [3]. In order to investigate their possibility, we have so far grown single crystals of the compounds and measured photoluminescence (PL) spectra. It was shown in our study that Ce ions could be incorporated in single crystals of the alkaline earth thiogallates up to a concentration of 1 mol%. We have also reported that excess Ce doping caused deterioration of the crystalinity of the compounds and reduction of the emission intensity. When Ce ions are incorporated in the compounds, the divalent alkaline earth metal ions are substituted by the trivalent Ce ions. The violence of the charge balance in the substitution is considered to be a reason why the overdoped Ce^{3+} leads to the poor crystalinity and the decrease in the emission intensity. Here, co-doping of Ce^{3+} with monovalent alkaline metals is performed to keep the charge balance. Actually, the luminescence spectra of the mixed compounds of $Sr_{1-2x}Ce_xNa_xGa_2S_4$ was already been reported [4], where it was shown that the solid solution was formed from $x = 0$ to 0.5 and the emission reached its maximum at $x = 0.1$. In the case of $CaGa_2S_4$ co-doped with Na^+ and Ce^{3+}, we have reported that Ce^{3+} could be introduced up to the concentration of 30 mol% and the PL intensity of the co-doped samples was enhanced three times in comparison to the case of only Ce doping samples (1 mol%) [5].

In this paper, three alkaline metals (Li, Na, K) are selected as co-dopants of Ce^{3+} and the effect of co-doping on the photoluminescence spectra will be discussed.

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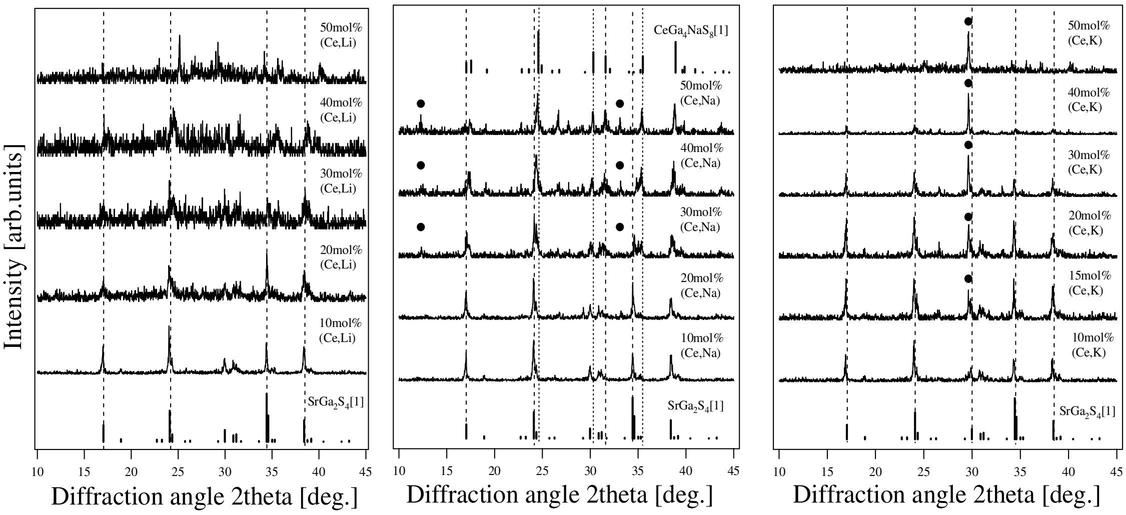
2 Sample preparation

Compounds of CaS, SrS, Ga_2S_3, Ce_2S_3, Li_2S, Na_2S and K_2S were used as starting materials. These compounds were weighed to about 0.4 g in Ar atmosphere at an appropriate composition of $M^{II}_{1-2x}Ce_xM^a_xGa_2S_4$ (M^{II} = Ca, Sr, M^a = Li, Na, K). About twenty samples were prepared by varying x from 0.0 to 0.5. The starting materials were sealed under a vacuum of 1×10^{-4} Pa in a quartz ampoule (7 mm × 40 mm), the inner surface of which was coated with carbon film by burning acetone gas.

The quartz ampoule was put in a furnace and heated up to 1120 °C a little above the melting point of Ga_2S_3 (1105 °C) for 1 h. The compounds were synthesized by the solid state reaction. The products after synthesis were identified by the powder X-ray diffraction analysis and the crystalline phases were identified. The measurements of powder X-ray diffraction (XRD) were performed by using a Cu K_α line (40 kV, 30 mA) at 300 K. It should be noted here that all the products were synthesized in evacuated quartz ampoules so that they were considered as being synthesized according to the scheduled compositions.

Figures 1 (a)–(c) show XRD patterns of $Sr_{1-2x}Ce_xM^a_xGa_2S_4$ (M^a = Li, Na, K) between $x = 0.1$ (10 mol%) and $x = 0.5$ (50 mol%). At low concentration up to $x = 0.1$ (10 mol%) a single phase belonging to the space group of D^{24}_{2h}-Fddd clearly appeared for all co-dopants. However unidentified lines emerged in the diffraction patterns according to the concentrations of Li, Na and K above $x = 0.3$ (30 mol%), $x = 0.2$ (20 mol%) and $x = 0.15$ (15 mol%), respectively. The diffraction lines do not shift within the accuracy of our measurement and stay constant up to these x-values. In the case of $Ca_{1-2x}Ce_xM^a_xGa_2S_4$ (M^a = Li, Na, K), the similar tendency was also observed, though undefined lines appeared above $x = 0.3$ (30 mol%), $x = 0.3$ (30 mol%) and $x = 0.4$ (40 mol%) for Li, Na and K co-dopants, respectively. The result dose not agree with that of the $Sr_{1-2x}Ce_xNa_xGa_2S_4$ case of Ronot-Limousin et al. [4] where they showed the variation in the lattice constants with Na concentration. They indicated, however, that this was not the case when Li was used as a co-dopant, presumably owing to its small ionic radius. They did not describe the case of K co-dopant. The discrepancy between our and their results may arise from the different synthetic methods used, and further detailed study should be made on this point.



a) b) c)

Fig. 1 Powder X-ray diffraction patterns of $Sr_{1-2x}Ce_xM^a_xGa_2S_4$ (M^a = Li (a), Na (b), K (c)) in the x-value between 0 and 0.5 together with the reported data of $SrGa_2S_4$ and $CeGa_4NaS_8$. Unidentified lines are shown by the solid circles except for (a) where most of the lines cannot be assigned owing to the large noises.

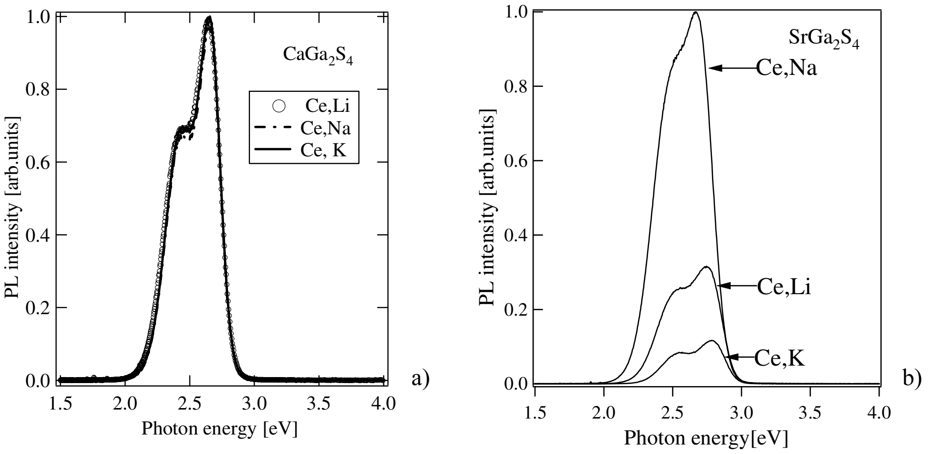


Fig. 2 Photoluminescence spectra of $Ca_{0.8}Ce_{0.1}M^{a}_{0,1}Ga_2S_4$ (a) and $Sr_{0.8}Ce_{0.1}M^{a}_{0.1}Ga_2S_4$ (b) for varying M^a as Li, Na and K at 300 K.

3 Photoluminescence spectra

3.1 $Ca_{1-2x}Ce_xM^a_xGa_2S_4$

The powdered samples were used in order to remove the effect of the shape of samples on the emission intensity. A 325 nm He–Cd laser line was used as an excitation light. Photoluminescence spectra were detected using a spectrometer equipped with a CCD detector (HAMAMATSU, PMA11) at room temperature. Figure 2 shows the typical photoluminescence spectra showing the effect of co-doping on Ca and Sr thiogallates. Two peaks of the emission spectra at 2.5 and 2.8 eV are due to the 5d–4f electronic transitions of the Ce^{3+} ions in the host crystals. The integrated intensities of the emission spectra were obtained and plotted as a function of the concentration of Ce and alkaline metal (Fig. 3(a)). The maximum intensity of $Ca_{1-2x}Ce_xM^a_xGa_2S_4$ (M = Li, Na, K) show little dependence on the co-doping concentration of the alkaline metal ions, but becomes three times stronger than that of the only Ce^{3+} 1 mol% doping case.

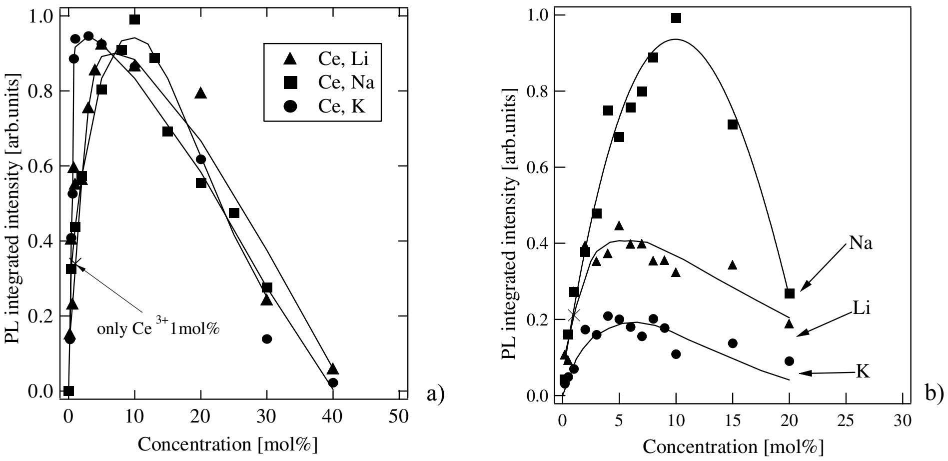


Fig. 3 Integrated intensity of photoluminescence spectra of $Ca_{1-2x}Ce_xM^a_xGa_2S_4$ (a) and $Sr_{1-2x}Ce_xM^a_xGa_2S_4$ (b) (M^a = Li, Na, K) as a function of x. The emission intensity of an only Ce^{3+} doped sample was marked as a cross. Solid lines are shown as guide for eye.

The peak energy of the emission shifts toward the low energy side with increasing *x*-value. It is considered that this is caused by the crystal field strengthened with increasing the number of Ce ions. When the crystal field becomes stronger, the split of the excited states of 5d levels broadens and the energy difference between the lowest excited state of 5d levels and 4f levels decreases.

3.2 $Sr_{1-2x}Ce_xM^a_xGa_2S_4$

The photoluminescence spectra of $Sr_{1-2x}Ce_xM^a_xGa_2S_4$ were also measured, some examples of which are shown in Fig. 2(b). The emission spectra have two peaks having the same origin as stated in the section above. Figure 3(b) shows the integrated intensities as a function of Ce, M^a concentration in this case. They have a maximum at 5–10 mol% for all compounds co-doped. In comparison to that of $SrGa_2S_4$ doped with only Ce^{3+} at 1 mol%, the maximum PL intensity was almost the same as that of K co-doped compounds, and two and five times stronger in the case of Li co-doped and Na co-doped samples, respectively. The Na co-doping was found to be the best. Since the charge compensation will be achieved by the two ions having the same mean valence as the host ion, both of the separation and the ionic radii of the two substituting ions should be made as close as possible to strengthen the effect. Thus the closeness of the ionic radii of Na^+ (1.18 Å [6]) and Ce^{3+} (1.14 Å [6]) might work very well in this case, which is expected to be more effective than to make smaller the difference in the ionic radii of alkaline earth ions (Ca or Sr) and the alkaline metal ions (Li, Na, K). Ronot-Limousin et al. reported that $Sr_{1-2x}Ce_xNa_xGa_2S_4$ shows high external luminescence efficiency in the range of $0.05 \leqq x \leqq 0.2$ though our emission intensity decreases in the concentration above $x = 0.1$ as shown in Fig. 3(b). This may be due to the undefined phase being included for *x* above 0.15 in our case.

The emission peak energies were determined only by Ce concentration independent of the kind of co-dopants and shifted to the low energy side with increasing it. The reason is the same as described previously.

4 Summary

We have prepared the compounds of $Ca_{1-2x}Ce_xM^a_xGa_2S_4$ and $Sr_{1-2x}Ce_xM^a_xGa_2S_4$ (M = Li, Na, K) and investigated the photoluminescence spectra in order to find the appropriate value of the Ce content for obtaining the maximum emission intensity. From the powder X-ray diffraction analysis, it is expected that the solid solution was formed up to 30 mol% for $Ca_{1-2x}Ce_xM^a_xGa_2S_4$ and 15 mol% for $Sr_{1-2x}Ce_xM^a_xGa_2S_4$. By incorporating alkaline metals as co-dopants, the content of Ce^{3+} in the thiogallates can be extremely increased above 1 mol%, the upper limit of Ce incorporation without co-doping.

The photoluminescence of these compounds has been measured at 300 K. Spectra due to the 5d–4f electronic transitions were obtained. In the both case of $Ca_{1-2x}Ce_xM^a_xGa_2S_4$ and $Sr_{1-2x}Ce_xM^a_xGa_2S_4$, the emission intensity estimated from the spectra has a maximum approximately at 5 mol% for the Li and K co-doped compounds and at 10 mol% for the Na co-doped ones. The difference in the maximum of the emission intensity according to host materials was found. The compounds of $Ca_{1-2x}Ce_xM^a_xGa_2S_4$ have almost the same maximum emission intensity independent of the doped alkaline metals. On the other hand, the PL intensity of the $Sr_{1-2x}Ce_xM^a_xGa_2S_4$ compounds was strikingly affected by alkaline metals. The reason for the difference in the two host compounds is not yet clarified and further detailed study should be required. However, the co-doping of rare earth element ions with alkaline metals is considered to be very effective to enhance the photoluminescence in (Ca, Sr) thiogallates.

Acknowledgement This work was partly supported by Research Grant from Nihon University.

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