

## Luminescence of CaS:Bi

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Luminescence of bismuth activated CaS, CaS:Bi, prepared in sodium polysulfide is studied. Excitation spectrum of CaS:Bi shows a band at 350 nm due to the recombination process between holes in  $\text{Na}^+_{\text{Ca}^{2+}}$  and electrons in conduction bands, in addition to bands at 260 nm from band gap of CaS, and at 320 nm ( $^1\text{S}_0 \rightarrow ^1\text{P}_1$ ) and at 420 nm ( $^1\text{S}_0 \rightarrow ^3\text{P}_1$ ) from electronic energy transitions of Bi. Emission band at 450 nm is from  $^3\text{P}_1 \rightarrow ^1\text{S}_0$  transition of  $\text{Bi}^{3+}$ , bands at 500 nm and 580 nm correspond to recombinations of electron donors ( $\text{Bi}^{3+}_{\text{Ca}^{2+}}$  and  $\text{V}_{\text{S}^{2-}}$ ) with acceptors ( $\text{V}_{\text{Ca}^{2+}}$  and  $\text{Na}^+_{\text{Ca}^{2+}}$ ). Emission band of  $^3\text{P}_1 \rightarrow ^1\text{S}_0$  transition is shifted to longer wavelength from CaS:Bi to BaS:Bi, due to the increase of the Stokes shift by the decrease of the crystal field parameter from CaS:Bi to BaS:Bi.

### Introduction

Bismuth activated CaS, CaS:Bi, has been well known for a long time as a blue phosphor and used as a photoluminescence, electroluminescence, cathodoluminescence and thermoluminescence material.<sup>1-4</sup>

The  $s^2$ - $sp$  transition of  $\text{Bi}^{3+}$  is an allowed one:  $\text{Bi}^{3+}$  has an electronic configuration of  $6s^2$  in the ground state and  $6s6p$  in the excited state. Luminescence spectrum of ions with  $s^2$ - $sp$  transition such as  $\text{Bi}^{3+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sn}^{2+}$ , and  $\text{Sb}^{3+}$  shows a very broad gaussian band. For example, the band halfwidth of  $\text{Sn}^{2+}$  is  $\sim 0.65$  eV.<sup>5</sup> The characteristics of a broad band can be explained with their configurational coordinate energy diagram. The potential energy curve of the luminescent center in the lattice can be plotted as a function of the distance  $r$  between the central cation and surrounding anions. In the potential energy diagram, the coordinate of the excited state minimum is shifted from that of the ground state minimum. This shift is very large for  $s^2$ - $sp$  transition, and the excited  $p$  state is much wider than the ground  $s$  state. Therefore, luminescence from  $s^2$ - $sp$  transition is observed to be a very broad emission band.

The emitting state for  $\text{Sn}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Bi}^{3+}$  is the  $^3\text{P}_1$  state. But in a crystal field, this level splits into three sublevels, and the position of  $\text{Bi}^{3+}$  emission band can be changed depending on the host matrix.

Vij and Mathur found a weak orange band at 590 nm in addition to the strong blue band at 450 nm in the emission spectrum of CaS:Bi<sup>3+</sup> at room temperature, and interpreted that the orange band is originated from the sulfur ion vacancy.<sup>6</sup> Yamashita and Asano obtained blue (450 nm), green (515 nm), and orange (588 nm) emission bands at 300 K, and these bands were assigned to bands from electronic transition of  $\text{Bi}^{3+}$ .<sup>7</sup> Recently, Park assigned the emission band at 520 nm in CaS:Bi to the emission from the defect center formed by  $\text{Bi}^{3+}$ - $\text{Na}^+$  pair.<sup>8</sup>

In this work, we found the emission spectrum of  $\text{Bi}^{3+}$  in CaS is not only from the electronic energy levels transition of  $\text{Bi}^{3+}$ , but also from the emission centers of defects and

vacancies in the CaS:Bi system. We could also observe Stokes shift in the emission band of  $\text{Bi}^{3+}$  by changing the host from CaS to BaS.

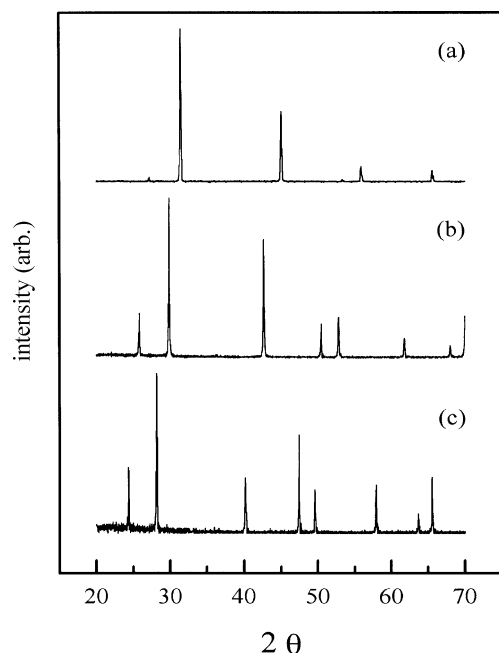
### Experimental Section

Bismuth ( $\text{Bi}^{3+}$ ) doped alkaline earth sulfides (CaS, SrS, BaS) were prepared by two methods: reaction in  $\text{Na}_2\text{CO}_3$ +S flux and in  $\text{H}_2\text{S}$  flow. The starting materials for the synthesis of Bi doped alkaline earth sulfides were  $\text{CaCO}_3$  (Aldrich, 99+),  $\text{SrCO}_3$  (Aldrich, 99.9%),  $\text{BaCO}_3$  (Aldrich, 99.9%),  $\text{Bi}_2\text{O}_3$  (Aldrich, 99.9%),  $\text{Na}_2\text{CO}_3$  (Aldrich, 99.95%) and S (Kanto, E.P.). For the synthesis of CaS:Bi, the stoichiometric amounts of starting materials with excess amount of flux were well mixed and heated in a covered alumina crucible at 1000 °C for 2 hrs. The residual flux in the product was washed out with distilled water at room temperature and the final product was dried after rinsing with ethyl alcohol. SrS:Bi and BaS:Bi were prepared in the stream of  $\text{H}_2\text{S}$  gas flow. The mixture of  $\text{SrCO}_3$  or  $\text{BaCO}_3$  and  $\text{Bi}_2\text{O}_3$  was heated at 1000 °C for 6 hrs. in the stream of  $\text{H}_2\text{S}$  flow.

The products were analyzed by the X-ray diffraction technique and XRD data were obtained with Rigaku X-ray diffractometer using Cu  $K\alpha$  radiation. For photoluminescence (PL) measurements, monochromated 150 W Xenon lamp was used as an excitation source. The PL spectra were obtained using monochromator equipped with photomultiplier tube.

### Results and Discussion

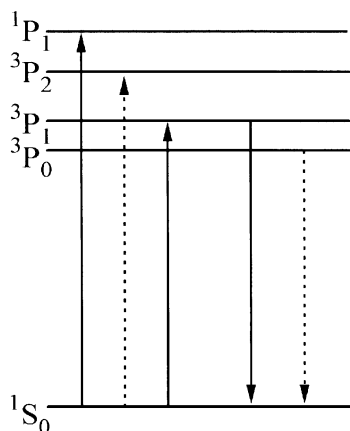
Figure 1 shows X-ray diffraction patterns of CaS:Bi, SrS:Bi and BaS:Bi. The structure of host materials are rock-salt type and the lattice parameter of CaS:Bi was 5.69 Å and those of SrS:Bi and BaS:Bi were 6.02 Å and 6.38 Å, respectively. No extra peaks except rock-salt structure sulfides were observed. The body color of CaS:Bi is changed from light yellow to black depending on the concentration of  $\text{Bi}^{3+}$ .



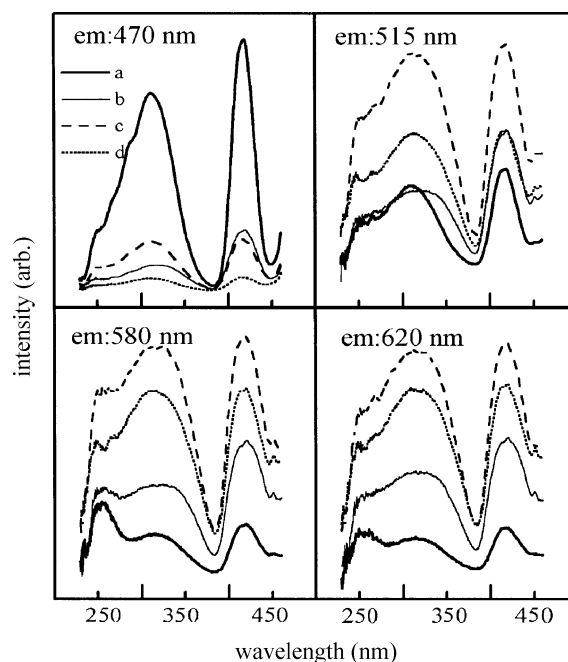
**Figure 1.** The X-ray diffraction patterns of (a) CaS:Bi, (b) SrS:Bi, and (c) BaS:Bi. Bi concentration was 0.05 mole% for each phosphors.

**Excitation Spectra of CaS:Bi.** The ground state of  $\text{Bi}^{3+}$  with  $6s^2$  configuration is  $^1S_0$ . The excited levels have  $6s6p$  configuration. Thus,  $^3P_0$ ,  $^3P_1$ ,  $^3P_2$ , and  $^1P_1$  are possible states. Figure 2 shows the energy levels of  $ns^2$  ion in the  $O_h$  symmetry. The transitions from  $^1S_0$  to  $^3P_0$  and  $^3P_2$  are completely spin forbidden, but the two levels  $^3P_1$  and  $^1P_1$  are mixed by spin-orbital coupling. Therefore, the transitions  $^1S_0 \rightarrow ^3P_1$  and  $^1P_1$  are allowed transitions and are expected to have reasonable absorption intensity.<sup>9,10</sup>

The excitation spectra of CaS:Bi are shown in Figure 3. These spectra show three broad bands: the band at 260 nm corresponds to the band gap of CaS, and that at 380–450 nm corresponds to  $^1S_0 \rightarrow ^3P_0$  transition of  $\text{Bi}^{3+}$ . But the band 250–350 nm in CaS is not clear, because it changed with the monitoring wavelength and the doping concentration of  $\text{Bi}^{3+}$ . The excitation band around 350 nm is stronger than



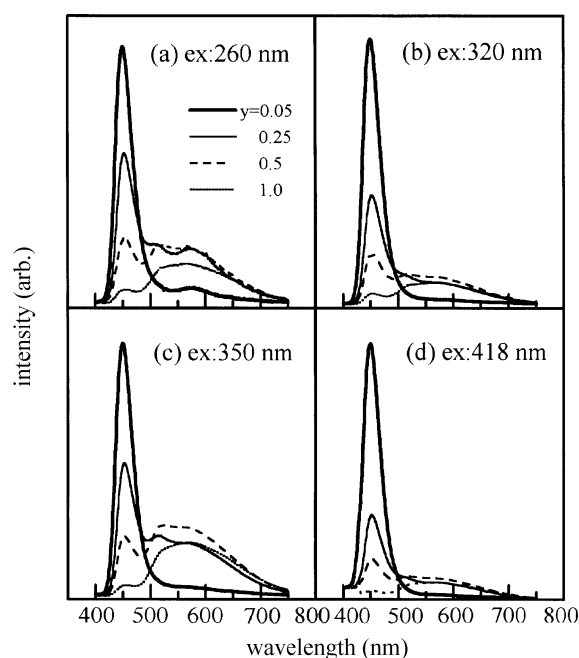
**Figure 2.** Energy level diagram of a  $ns^2$  ion in the  $O_h$  symmetry. Solid lines are allowed transition and dashed lines are forbidden transitions.



**Figure 3.** The excitation spectra of CaS:Bi. (a)  $y=0.05$ , (b)  $y=0.25$ , (c)  $y=0.5$ , and (d)  $y=1.0$ , where  $y=\text{Bi mole\%}$ .

any other bands when it was monitored at 515 nm and 580 nm. It suggests that another excitation center other than  $^1P_1$  and  $^3P_1$  states exist in CaS:Bi.

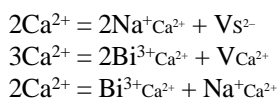
**Emission Spectra of CaS:Bi.** Bismuth doped CaS shows different colors of emission depending on the doping concentration of Bi. For example, the emission color is changed to blue, white, yellow, and deep yellow when the Bi concentration is increased to 0.05 mole%, 0.25 mole%, 0.5 mole%, and 1.0 mole%, respectively.



**Figure 4.** The emission spectra of CaS:Bi ( $y=\text{mole\%}$ ) under the excitation by (a) 260 nm, (b) 320 nm, (c) 350 nm and (d) 418 nm.

Figure 4 shows that the emission spectra of CaS:Bi depend on the Bi concentration and the excitation wavelength. The emission spectra of CaS:Bi consist of three broad bands of 450, 515 and 580 nm. The bands at 515 and 580 nm are considerably enhanced as the concentration of the Bi<sup>3+</sup> ion is increased from 0.05% to 25%. In addition, intensity of these bands are maximized under the excitation of 350 nm. As previously known, the band at 450 nm corresponds to <sup>3</sup>P<sub>1</sub> → <sup>1</sup>S<sub>0</sub> transition of the atomic energy level in Bi<sup>3+</sup>, however, bands at 515 and 580 nm have not been explained in the literature until now.

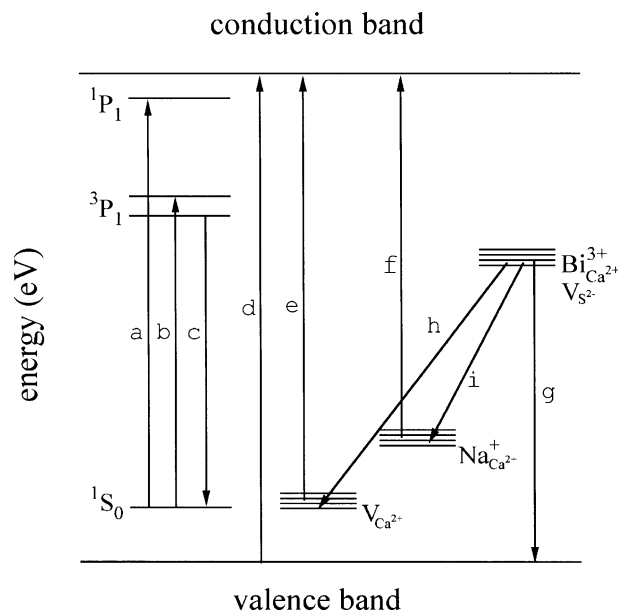
When CaS:Bi is prepared in Na<sub>2</sub>CO<sub>3</sub>+S flux, Bi<sup>3+</sup> ions can easily be doped to Ca<sup>2+</sup> sites by compensating the charge with Na<sup>+</sup>. Especially, two Ca<sup>2+</sup> (1.00 Å) sites can be easily replaced by a Bi<sup>3+</sup> (1.03 Å) ion and a Na<sup>+</sup> (1.02 Å) ion due to the similar size of their ionic radii.<sup>11</sup> When Ca<sup>2+</sup> sites in CaS are replaced by Bi<sup>3+</sup> and Na<sup>+</sup>, the following defect equations can be followed:



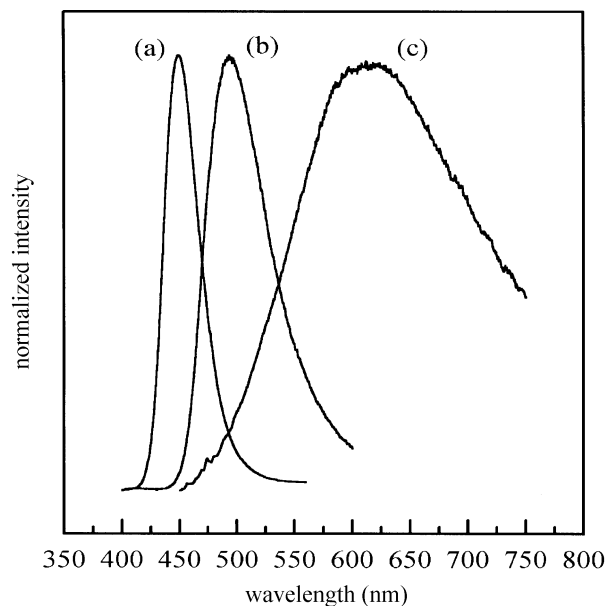
Previously, similar defect formation mechanisms could be used to explain the nature of excitation and emission bands of CaS:La, CaS:Dy and CaS:Ce prepared in Na<sub>2</sub>CO<sub>3</sub>+S flux. Especially, in CaS:La, La<sup>3+</sup> ion itself does not have d and f electrons. Therefore, possible vacancies (V<sub>Ca<sup>2+</sup></sub>, V<sub>S<sup>2-</sup></sub>) and defects formed by the substituted ions (Na<sup>+</sup>Ca<sup>2+</sup>, La<sup>3+</sup>Ca<sup>2+</sup>) are considered to be responsible for the luminescence of CaS:La. For example, the emission bands at 450 nm and 500 nm are assigned to the bands resulted from the two recombination process of La<sup>3+</sup>Ca<sup>2+</sup> (or V<sub>S<sup>2-</sup></sub>) with holes in the valence band and with vacancies of Ca<sup>2+</sup> ion, V<sub>Ca<sup>2+</sup></sub>. Here La<sup>3+</sup>Ca<sup>2+</sup> and V<sub>S<sup>2-</sup></sub> are the electron donor and the acceptor, respectively. The band at 580 nm is assigned to the band resulted from the recombination process of La<sup>3+</sup>Ca<sup>2+</sup> and Na<sup>+</sup>Ca<sup>2+</sup> sites.<sup>9-12</sup> Similar spectra can also be observed in CaS:Dy prepared in Na<sub>2</sub>CO<sub>3</sub>+S flux. The emission spectrum of CaS:Dy has two bands at 520 nm and 580 nm in addition to the weak lines from the f-f transition of Dy<sup>3+</sup>.

In the same manner, we suggest that the luminescence spectra of CaS:Bi<sup>3+</sup> consist of two kinds of bands: one is due to the atomic energy level transitions and the other one is due to the recombination processes of the defects in CaS:M<sup>3+</sup> type materials. Both the energy states of Bi<sup>3+</sup> ion and the energy bands of defects in CaS are shown in Figure 5. Both the emission bands at 515 and 580 nm are suggested to be associated with the lattice defects: The former is due to the recombination of Bi<sup>3+</sup>Ca<sup>2+</sup>/V<sub>S<sup>2-</sup></sub> and V<sub>Ca<sup>2+</sup></sub>, which is a different view from others.<sup>8</sup> The latter band is associated with the recombination of Bi<sup>3+</sup>Ca<sup>2+</sup>/V<sub>S<sup>2-</sup></sub> level with Na<sup>+</sup>Ca<sup>2+</sup> level.

The emission intensity at 450 nm decreases with Bi concentration above 0.05 mole % (refer to Figure 4), where the concentration quenching seems to begin from relatively low concentration of Bi. However, the emissions due to defects and vacancies in the range of 500-600 nm continue to



**Figure 5.** The atomic energy levels of Bi<sup>3+</sup> and energy levels of defects and vacancies in CaS:Bi. a: 320 nm (3.87 eV), b: 420 nm (2.95 eV), c: 450 nm (2.76 eV), d: 260 nm (4.76 eV), e: 300 nm (4.13 eV), f: 350 nm (3.54 eV), g: 450 nm (2.76 eV), h: 515 nm (2.40 eV), and i: 580 nm (2.14 eV).



**Figure 6.** Emission spectra of (a) CaS:Bi (0.05 mole%), (b) SrS:Bi (0.05 mole%), and (c) BaS:Bi (0.05 mole%).

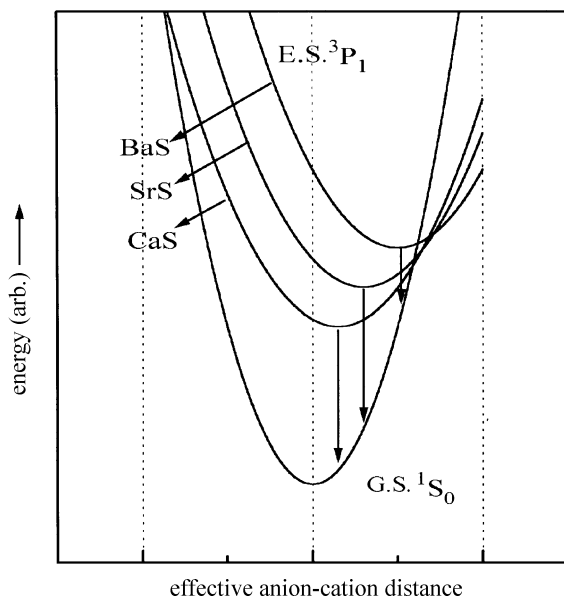
increase beyond the quenching concentration point of Bi. This relatively early quenching point of Bi may be due to the interaction of the activator Bi<sup>3+</sup> with the luminescence centers at lattice defects.

#### Emission Spectra of Bi Doped Alkaline Earth Sulfides.

The emission color of Bi doped alkaline earth sulfides are different depending on the alkaline earth metals: The emission color of CaS:Bi is blue (450 nm), that of SrS:Bi is green (497 nm) and that of BaS:Bi is red (608 nm). The emission spectra of SrS:Bi and BaS:Bi are shown in Figure 6.

**Table 1.** The Stokes shift and crystal field parameter of Bi doped alkaline earth sulfides

	Stokes shift (cm <sup>-1</sup> )		Crystal field parameter (10 Dq, cm <sup>-1</sup> )
CaS:Bi	1,340 <sup>a</sup>	1,588 <sup>c</sup>	18,750 <sup>b</sup>
SrS:Bi	2,570 <sup>a</sup>	3,239 <sup>c</sup>	17,400 <sup>b</sup>
BaS:Bi	4,490 <sup>a</sup>	5,082 <sup>c</sup>	16,100 <sup>b</sup>

<sup>a</sup>from ref. 9. <sup>b</sup>from ref. 14. <sup>c</sup>this study.**Figure 7.** Simplified potential energy curve of Ca:Bi. Excited state level is only shown the lowest state of <sup>3</sup>P<sub>1</sub> Stokes states. Only the lowest allowed Stark state, <sup>3</sup>P<sub>1</sub>, is indicated in excited states.

The positions of each emission band of SrS:Bi and BaS:Bi was shifted toward longer wavelength from that of CaS:Bi. Table 1 shows the Stokes shift and the crystal field parameter (10 Dq) of alkaline earth sulfides. The Stokes shift is taken as the energy difference between the maximum of <sup>1</sup>S<sub>0</sub> → <sup>3</sup>P<sub>1</sub> excitation and the maximum of <sup>3</sup>P<sub>1</sub> → <sup>1</sup>S<sub>0</sub> emission. The Stokes shift for Bi<sup>3+</sup> in the host sulfide increases going from CaS to BaS. Bimuth ion would be tightly bonded by the surrounding anions in CaS, whereas it would be loosely bonded in SrS and BaS due to the increase of the effective distance between the central cation and the surrounding anion as shown in the potential energy diagram.<sup>9</sup> This may be possible, because ionic size of Bi<sup>3+</sup> is similar to that of Ca<sup>2+</sup>, but is smaller than that of Sr<sup>2+</sup> (1.18 Å) and Ba<sup>2+</sup> (1.35 Å).<sup>11</sup> The excited state of <sup>3</sup>P<sub>1</sub> of Bi<sup>3+</sup> splits into three levels in a crystal field by the Stark interaction. Therefore, the energy of emission bands of Bi<sup>3+</sup> is changed by the host matrix. The lattice parameters of CaS:Bi, SrS:Bi, and BaS:Bi are obtained as 5.69 Å, 6.02 Å, and 6.38 Å, respectively. Thus the crystal fields, 10 Dq, may be decreased from CaS:Bi to BaS:Bi as shown in Table 1.<sup>13</sup>

Figure 7 shows a simplified potential energy-configuration coordinate diagram of Bi<sup>3+</sup> doped alkaline earth sul-

fides from CaS to BaS. From this diagram, we can explain the increase of the Stokes shift to longer wavelength from CaS to BaS. The lowest state of <sup>3</sup>P<sub>1</sub> Stark state goes higher in energy from CaS to BaS, which is due to the fact that CaS has larger 10 Dq than SrS and BaS. So splitting of <sup>3</sup>P<sub>1</sub> state is influenced much more by CaS. The minimum <sup>3</sup>P<sub>1</sub> energy level of Bi<sup>3+</sup> in BaS is located at a large <r> value, and accordingly it leads to a large Stokes shift of BaS.

## Conclusions

The excitation spectra of CaS:Bi show three broad bands: the band at 260 nm is from band gap transition of CaS, that at 320 nm is from <sup>1</sup>S<sub>0</sub> → <sup>1</sup>P<sub>1</sub> transition and that at 420 nm is from <sup>1</sup>S<sub>0</sub> → <sup>3</sup>P<sub>1</sub>. The excitation intensity at 350 nm is increased with the increase of Bi concentration, especially at 515 nm and 580 nm emission. It is indicated the excitation band at 350 nm is not from Bi<sup>3+</sup> transition, but from the recombination between Na<sup>+</sup>Ca<sup>2+</sup> and the hole in the conduction band. The emission band at 450 nm is from <sup>3</sup>P<sub>1</sub> → <sup>1</sup>S<sub>0</sub> transition of Bi<sup>3+</sup>, that at 515 nm is due to the recombination of Bi<sup>3+</sup>Ca<sup>2+</sup>/ VS<sup>2-</sup> and VCa<sup>2+</sup>, and that at 580 nm is associated with the recombination of Bi<sup>3+</sup>Ca<sup>2+</sup> and Na<sup>+</sup>Ca<sup>2+</sup>. The positions of emission bands of CaS:Bi to BaS:Bi are shifted to longer wavelength by the Stokes shift due to the crystal field effect.

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