Luminescence of CaS:Bi

Chang-Hong Kim,* Chong-Hong Pyun, Han Choi,† and Sung-Jin Kim†

Division of Applied Science, Korea Institute of Science and Technology, Seoul 136-791, Korea
†Department of Chemistry, Ewha Womans University, Seoul 120-750, Korea

Received July 20, 1998

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.1−4 The s2-sp transition of Bi3+ is an allowed one: Bi3+ has an electronic configuration of 6s2 in the ground state and 6s6p in the excited state. Luminescence spectrum of ions with s2-sp transition such as Bi3+, Pb2+, Sn2+, and Sb3+ shows a very broad gaussian band. For example, the band halfwidth of Sn2+ is ~0.65 eV.5 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 s2-sp transition, and the excited p state is much wider than the ground s state. Therefore, luminescence from s2-sp transition is observed to be a very broad emission band.

The emitting state for Sn2+, Pb2+, and Bi3+ is the 3P1 state. But in a crystal field, this level splits into three sublevels, and the position of Bi3+ 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:Bi3+ at room temperature, and interpreted that the orange band is originated from the sulfur ion vacancy.6 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 Bi3+.7 Recently, Park assigned the emission band at 520 nm in CaS:Bi to the emission from the defect center formed by Bi3+-Na+ pair.8

In this work, we found the emission spectrum of Bi3+ in CaS is not only from the electronic energy levels transition of Bi3+, 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 Bi3+ by changing the host from CaS to BaS.

Experimental Section

Bismuth (Bi3+) doped alkaline earth sulfides (CaS, SrS, BaS) were prepared by two methods: reaction in Na2CO3+S flux and in H2S flow. The starting materials for the synthesis of Bi doped alkaline earth sulfides were CaCO3 (Aldrich, 99.9%), SrCO3 (Aldrich, 99.9%), BaCO3 (Aldrich, 99.9%), SrS:Bi and BaS:Bi were prepared in the stream of H2S gas flow. The mixture of SrCO3 or BaCO3 and Bi2O3 was heated at 1000 °C for 6 hrs. in the stream of H2S flow.

The products were analyzed by the X-ray diffraction technique and XRD data were obtained with Rigaku X-ray diffractometer using Cu Kα 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 Bi3+.
Excitation Spectra of CaS:Bi. The ground state of Bi$^{3+}$ with 6$s^2$ configuration is $^1S_0$. The excited levels have 6$s6p$ 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.$^{9,10}$

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 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 Bi$^{3+}$. The excitation band around 350 nm is stronger than any other bands when it was monitored at 515 nm and 580 nm. It suggests that another excitation center other than $^3P_1$ and $^1P_1$ 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.

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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.

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=Bi mole%.

Figure 4. The emission spectra of CaS:Bi (y=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$^{3+}$ ion is increased from 0.05% to 25%. In addition, the intensity of these bands is maximized under the excitation of 350 nm. As previously known, the band at 450 nm corresponds to $^3P_1 \rightarrow ^1S_0$ transition of the atomic energy level in Bi$^{3+}$, however, bands at 515 and 580 nm have not been explained in the literature until now.

When CaS:Bi is prepared in Na$_2$CO$_3$+S flux, Bi$^{3+}$ ions can easily be doped to Ca$^{2+}$ sites by compensating the charge with Na$^+$. Especially, two Ca$^{2+}$ (1.00 Å) sites can be easily replaced by a Bi$^{3+}$ (1.03 Å) ion and a Na$^+$ (1.02 Å) ion due to the similar size of their ionic radii. When CaS:Bi sites in CaS are replaced by Bi$^{3+}$ and Na$^+$, the following defect equations can be followed:

\begin{align*}
2\text{Ca}^{2+} & = 2\text{Na}^+ \text{Ca}^{2+} + \text{V}_S^{2-} \\
3\text{Ca}^{2+} & = 2\text{Bi}^{3+} \text{Ca}^{2+} + \text{V}_{\text{Ca}}^{2+} \\
2\text{Ca}^{2+} & = \text{Bi}^{3+} \text{Ca}^{2+} + \text{Na}^+ \text{Ca}^{2+}
\end{align*}

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$_2$CO$_3$+S flux. Especially, in CaS:La, La$^{3+}$ ion itself does not have d and f electrons. Therefore, possible vacancies ($\text{V}_{\text{Ca}}^{2+}$, $\text{V}_S^{2-}$) and defects formed by the substituted ions (Na$^+$$\text{Ca}^{2+}$, La$^{3+}$$\text{Ca}^{2+}$) are considered to be responsible for the luminescence of CaS:La. For example, the emission bands at 450 nm and 500 nm are assigned to the bands resulted from the two recombination process of La$^{3+}$$\text{Ca}^{2+}$ (or $\text{V}_S^{2-}$) with holes in the valence band and with vacancies of Ca$^{2+}$ ion, $\text{V}_S^{2-}$. Here La$^{3+}$$\text{Ca}^{2+}$ and $\text{V}_S^{2-}$ 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$^{3+}$$\text{Ca}^{2+}$ and Na$^+$$\text{Ca}^{2+}$ sites. Similar spectra can also be observed in CaS:Dy prepared in Na$_2$CO$_3$+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$^{3+}$.

In the same manner, we suggest that the luminescence spectra of CaS:Bi$^{3+}$ 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$^{3+}$ type materials. Both the energy states of Bi$^{3+}$ 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$^{3+}$$\text{Ca}^{2+}$/V$S^{2-}$ and $\text{V}_S^{2-}$, which is a different view from others. The latter band is associated with the recombination of Bi$^{3+}$$\text{Ca}^{2+}$/V$S^{2-}$ level with Na$^+$$\text{Ca}^{2+}$ 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 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$^{3+}$ 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.
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, cm⁻¹) of alkaline earth sulfides. The Stokes shift is taken as the energy difference between the maximum of 1S₀ → 3P₁ excitation and the maximum of 3P₁ → 1S₀ emission. The Stokes shift for Bi³⁺ in the host sulfide increases rounding anion as shown in the potential energy diagram. The effective distance between the central cation and 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. This may be possible, because ionic size of Bi³⁺ is similar to that of Ca²⁺, but is smaller than that of Sr²⁺ (1.18 Å) and Ba²⁺ (1.35 Å). The excited state of 3P₁ of Bi³⁺ splits into three levels in a crystal field by the Stark interaction. Therefore, the energy of emission bands of Bi³⁺ is changed by the crystal field. 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.

Figure 7 shows a simplified potential energy-configurational coordinate diagram of Bi³⁺ doped alkaline earth sulfides 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 1P₁, 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 3P₁ state is influenced much more by CaS. The minimum 3P₁ energy level of Bi³⁺ 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 1S₀ → 1P₁ transition and that at 420 nm is from 1S₀ → 3P₁. 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 Bi³⁺ transition, but from the recombination between Na⁺Ca²⁺ and the hole in the conduction band. The emission band at 450 nm is from 3P₁ → 1S₀ transition of Bi³⁺, that at 515 nm is due to the recombination of Bi³⁺Ca²⁻/V⁺S⁻ and V⁺Ca²⁻, and that at 580 nm is associated with the recombination of Bi³⁺Ca²⁻ and Na⁺Ca²⁻. 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.

Acknowledgment. S.-J. Kim thanks the KOSEF (96-0501-0601-3) for financial support of this research.

References