

## New Observations on the Pressure Dependence of Luminescence from Eu<sup>2+</sup>-Doped MF<sub>2</sub> (M = Ca, Sr, Ba) Fluorides

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The luminescence from Eu<sup>2+</sup> ions in MF<sub>2</sub> (M = Ca, Sr, Ba) fluorides has been investigated under the pressure range of 0–8 GPa. The emission band originating from the 4f<sup>6</sup>5d<sup>1</sup> → 4f<sup>7</sup> transition of Eu<sup>2+</sup> ions in CaF<sub>2</sub> and SrF<sub>2</sub> shows the red-shift as increasing pressure with pressure coefficients of −17 meV/GPa for CaF<sub>2</sub> and −18 meV/GPa for SrF<sub>2</sub>. At atmospheric pressure, the emission spectrum of BaF<sub>2</sub>:Eu<sup>2+</sup> comprises two peaks at 2.20 and 2.75 eV from the impurity trapped exciton (ITE) and the self-trapped exciton (STE), respectively. As the pressure is increased, both emission peaks shift to higher energies, and the shifting rate is slowed by the phase transition from the cubic to orthorhombic phase at 4 GPa. Due to the phase transition at 4–5 GPa pressure, the ITE emission disappears gradually, and the STE emission is gradually replaced by the 4f<sup>6</sup>5d<sup>1</sup> → 4f<sup>7</sup> transition of Eu<sup>2+</sup>. Above 5 GPa, the pressure behavior of the 4f<sup>6</sup>5d<sup>1</sup> → 4f<sup>7</sup> transition of Eu<sup>2+</sup> in BaF<sub>2</sub>:Eu<sup>2+</sup> is the same as the normal emission of Eu<sup>2+</sup> in CaF<sub>2</sub> and SrF<sub>2</sub> phosphors.

### Introduction

The Eu<sup>2+</sup> ion is a very efficient emitter with emissions from ultraviolet (UV) to near infrared (NIR) depending on the crystal field strength of the host crystals,<sup>1,2</sup> and Eu<sup>2+</sup>-doped phosphors have been investigated extensively.<sup>3–7</sup> In Eu<sup>2+</sup>-doped fluoride host MF<sub>2</sub> systems, a dipole-allowed radiative transition from 4f<sup>6</sup>5d<sup>1</sup> to 4f<sup>7</sup> may take place, which can produce a broad bright emission. The occurrence of the f–d transition in compounds doped with divalent lanthanide ions depends on the location of the 5d levels relative to the conduction edge of the host.<sup>1,2</sup> In general, the d–f emission takes place when the 5d excited state lies inside the band gap of the host. For example, CaF<sub>2</sub>:Eu<sup>2+</sup> and SrF<sub>2</sub>:Eu<sup>2+</sup> compounds meet the above condition, and thus the emission bands from the d–f transition have been observed.<sup>1,2</sup> However, if the lowest 5d excited state is above or close to the conduction band of the host, the recombination process becomes more complicated. For instance, because all the Eu<sup>2+</sup> excited states lie in the conduction band of the BaF<sub>2</sub> host, different observations have been reported in photoluminescence of BaF<sub>2</sub>:Eu<sup>2+</sup>. Kobayashi et al.<sup>3</sup> detected the d–f emission peak around 403 nm at low temperature. But in most cases, the d–f emission is absent. Instead, a strong broadband luminescence extending from 500 to 600 nm was observed due to the recombination of the impurity trapped exciton.<sup>1,2,4</sup> A broad blue band was also found and interpreted as the recombination of perturbed self-trapped excitons in BaF<sub>2</sub>:Eu<sup>2+</sup>.<sup>4</sup> A similar case also occurred in a ZnS:Eu<sup>2+</sup> nanocrystal, where the 5d state of Eu<sup>2+</sup> near the band edge of ZnS interacted with the sd-like conduction band of the host.<sup>6,8</sup> As a result, the emission band had some similarities to the band gap of the host in temperature and pressure behavior,<sup>7</sup> which is different from the common d–f transition.

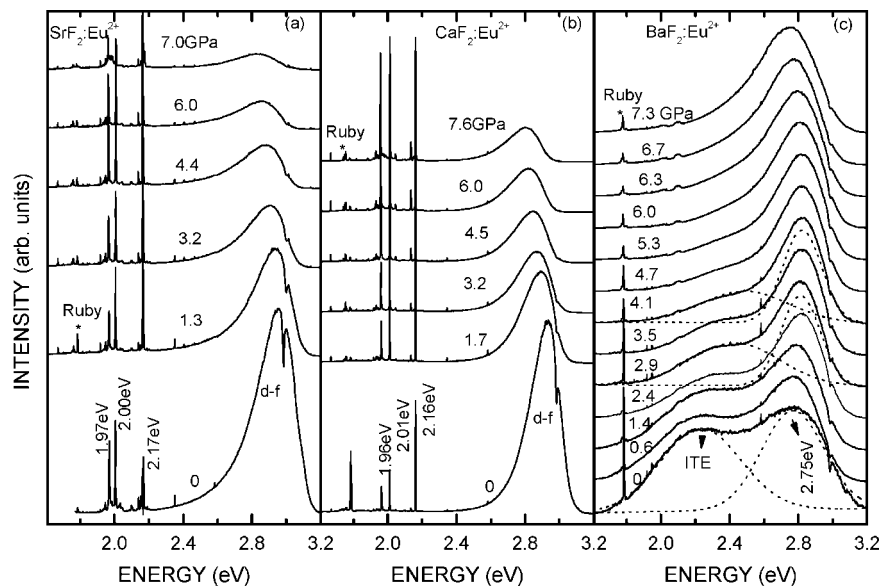
Temperature- and pressure-dependent photoluminescence (PL) techniques are frequently used to investigate the properties of luminescence centers in materials.<sup>9,10</sup> Variation of hydrostatic pressure can change the interatomic distance and the overlap among adjacent electronic orbits. The pressure dependence of luminescence can provide useful information about the electronic states of the emitters and the interactions between the luminescence centers and their hosts. The temperature-dependent PL spectra help to reveal the thermal quenching effect, carrier transfer process between two emission centers, electron–phonon coupling, etc.<sup>9,10</sup> At ambient conditions, fluoride MF<sub>2</sub> (M = Ca, Sr, Ba) compounds have the cubic fluoride type structure with the *Fm3m* group. The high-pressure crystal structures of the three compounds have been investigated extensively by theory and experiment.<sup>11,12</sup> The orthorhombic and hexagonal phases are formed in sequence upon compression, but little is known about the effect of pressure on electronic structures in Eu<sup>2+</sup>-doped MF<sub>2</sub> compounds. Kobayashi et al.<sup>13</sup> reported the Eu<sup>2+</sup> emission spectra under static high pressures in a CaF<sub>2</sub>:Eu<sup>2+</sup> sample, where the emission from the f–d transition showed a red-shift with a rate of 2.2 nm/GPa and lost its intensity suddenly at 12 GPa. Gatch et al.<sup>14</sup> studied the pressure behavior of anomalous emission in BaF<sub>2</sub>:Eu and d–f luminescence in SrF<sub>2</sub>, in which the anomalous emission exhibited a red-shift and disappeared in the high-pressure orthorhombic phase. Here we report the pressure and temperature behaviors of luminescence in MF<sub>2</sub>:Eu<sup>2+</sup> (M = Sr, Ca, Ba) phosphors. For the first time, we observed the nonlinear pressure behavior of the emission band in BaF<sub>2</sub>:Eu<sup>2+</sup> in the 0–8 GPa pressure range.

**Samples and Experiments.** BaF<sub>2</sub>:Eu<sup>2+</sup>, SrF<sub>2</sub>:Eu<sup>2+</sup> and CaF<sub>2</sub>:Eu<sup>2+</sup> phosphors were prepared by solid state diffusion. Calculated amounts of MF<sub>2</sub> (95%) and EuCl<sub>2</sub> (5%) were mixed thoroughly by stirring in an alcohol solution. The mixture was dried at room temperature and then placed in a crucible covered with charcoal powder and heated at 800 °C for 6 h. The luminescence measurements under hydrostatic pressure were performed in a diamond-anvil cell (DAC) at room temperature.

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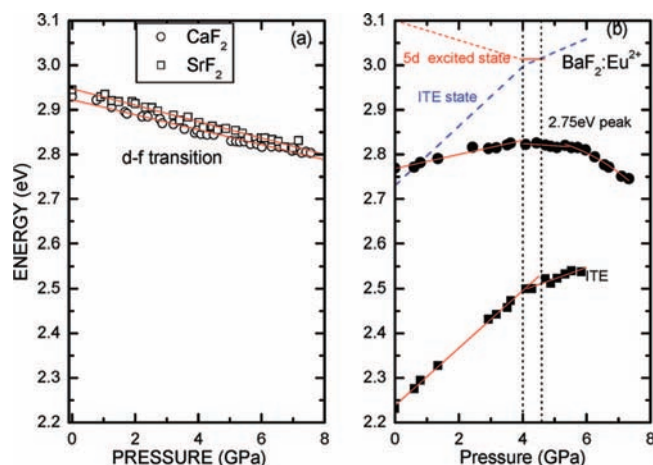
**Figure 1.** Emission spectra at different pressures for MF<sub>2</sub>:Eu<sup>2+</sup> (M = Ca, Sr, Ba) measured at room temperature. The dotted lines in panel c represent the fitting to the PL spectra of BaF<sub>2</sub>:Eu<sup>2+</sup> by Gaussian functions. The emission lines from the ruby are marked by asterisks.

The samples, together with a small piece of ruby, were placed in a stainless-steel gasket with a hole 300  $\mu\text{m}$  in diameter. A 4:1 methanol–ethanol mixture was used as the pressure-transmitting medium. The pressure was determined using the standard ruby-fluorescence technique and varied from 0 to 8 GPa. The luminescence was measured at different temperatures by fixing samples on the cold finger of a closed-cycle refrigeration system. The temperature varied from 10 to 300 K. The 325 nm line of a He–Cd laser was used as the excitation source. The emitted light was dispersed by a JY-HRD1 double grating monochromator and detected by a cooled GaAs photomultiplier tube operating in photon-counting mode.

## Experimental Results

**1. Pressure-dependent PL spectra in CaF<sub>2</sub>:Eu<sup>2+</sup> and SrF<sub>2</sub>:Eu<sup>2+</sup>.** The emission spectra from Eu<sup>2+</sup>-doped SrF<sub>2</sub> and CaF<sub>2</sub> measured at room temperature under different pressures are shown in Figure 1a and Figure 1b. In SrF<sub>2</sub>:Eu<sup>2+</sup>, the broad peak at 2.91 eV is from the 4f<sup>6</sup>5d<sup>1</sup>  $\rightarrow$  4f<sup>7</sup> transition of Eu<sup>2+</sup> ions. The three sharp peaks at 2.17, 2.00, and 1.97 eV are from the <sup>5</sup>D<sub>0</sub>  $\rightarrow$  <sup>7</sup>F<sub>1</sub>, <sup>5</sup>D<sub>0</sub>  $\rightarrow$  <sup>7</sup>F<sub>2</sub>, and <sup>5</sup>D<sub>0</sub>  $\rightarrow$  <sup>7</sup>F<sub>4</sub> transitions of Eu<sup>3+</sup> ions, respectively.<sup>15,16</sup> These sharp peaks remain almost constant at different pressures. At low pressures, the dip superimposed on the PL spectra is due to the absorption by a defect state of the front diamond in the DAC.<sup>7</sup> The red-shift and broadening in the Eu<sup>2+</sup> peak profile can be observed with increasing pressure. As shown in Figure 1b, there is a broad emission at 2.96 eV from CaF<sub>2</sub>:Eu<sup>2+</sup> at zero pressure from the 4f<sup>6</sup>5d<sup>1</sup>  $\rightarrow$  4f<sup>7</sup> transition of Eu<sup>2+</sup> ion. In CaF<sub>2</sub>:Eu<sup>2+</sup>, the three similar sharp emission peaks due to <sup>5</sup>D<sub>0</sub>  $\rightarrow$  <sup>7</sup>F<sub>1</sub>, <sup>5</sup>D<sub>0</sub>  $\rightarrow$  <sup>7</sup>F<sub>2</sub> and <sup>5</sup>D<sub>0</sub>  $\rightarrow$  <sup>7</sup>F<sub>4</sub> transitions of Eu<sup>3+</sup> ions are also observed. As these f–f transitions from Eu<sup>3+</sup> are not sensitive to pressure, they will not be discussed in this article.

Figure 2a shows the d–f emission energy of Eu<sup>2+</sup> in CaF<sub>2</sub>:Eu<sup>2+</sup> and SrF<sub>2</sub>:Eu<sup>2+</sup> as a function of pressure. The d–f emissions of Eu<sup>2+</sup> in these two samples show a typical red-shift with the increase of pressure. The pressure coefficients by a linear fitting are listed in Table 1. The pressure coefficients are  $-18 \pm 1$  meV/GPa for SrF<sub>2</sub>:Eu<sup>2+</sup> and  $-17 \pm 1$  meV/GPa for CaF<sub>2</sub>:Eu<sup>2+</sup>, which agrees with the results reported.<sup>13,14</sup>



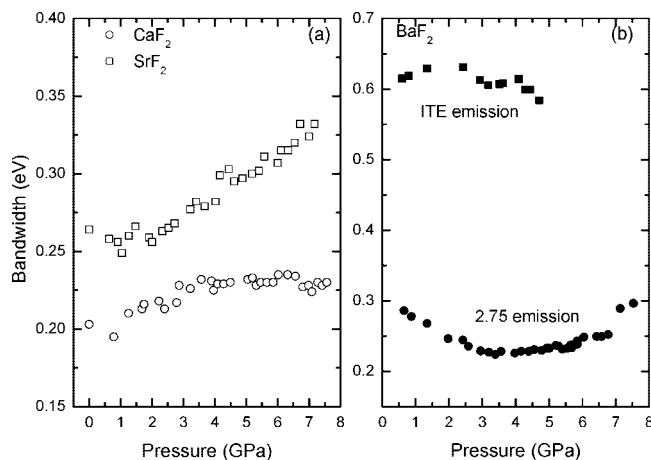
**Figure 2.** The peak energies from MF<sub>2</sub>:Eu<sup>2+</sup> (M = Ca, Sr, Ba) as a function of pressure. In panel a, the solid lines are obtained by linear fitting to the pressure dependence of the d–f emission energies in CaF<sub>2</sub>:Eu<sup>2+</sup> and SrF<sub>2</sub>:Eu<sup>2+</sup>. In panel b, the dashed lines denote the pressure dependence of the 5d excited level and the ITE level. The energy positions of the 5d and ITE states at atmospheric pressure come from ref 4. The 5d excited state shows linear pressure dependence with the slope of  $-22$  meV/GPa, as estimated by the crystal field method. The ITE state follows the pressure induced shift of the ITE emission bands. The maximum crossover between the 5d excited state and the ITE state occurs around 4.6 GPa, as shown by the horizontal line. We performed the linear fitting to the pressure dependence of ITE peak energies. The solid lines through the data of 2.75 eV emission below 5 GPa represent the linear fitting results. Above 5 GPa, the solid curve is derived from the fitting by the quadratic polynomial function,  $E(P) = E_0 + B_0(P - 5.0) + B_1(P - 5.0)^2$ .

**2. Pressure and Temperature Dependence of Emission Bands in BaF<sub>2</sub>:Eu<sup>2+</sup>.** The pressure dependence of Eu<sup>2+</sup> luminescence in CaF<sub>2</sub> and SrF<sub>2</sub> as shown in Figures 1a and 1b is basically the same as reported in the literature.<sup>13,14</sup> However, the pressure behavior of Eu<sup>2+</sup> luminescence in BaF<sub>2</sub> is different and more interesting. As shown in Figure 1c, BaF<sub>2</sub>:Eu<sup>2+</sup> has two emission peaks. The emission peak at 2.20 eV (563 nm) corresponds to the well-known anomalous emission in BaF<sub>2</sub>:Eu<sup>2+</sup>, which is attributed to the recombination of impurity trapped exciton (ITE).<sup>17</sup> When the pressure increases, the intensity of the ITE band diminishes rapidly. The emission at

**TABLE 1: Pressure Coefficients Obtained by Experiments and Estimations According to the Crystal Field Method<sup>a</sup>**

	fluorite phase					orthorhombic phase	
	transition	$E_0$ (eV)	pressure coeff (meV/GPa)			pressure coeff (meV/GPa)	
			exptl	estimation	refs	exptl	refs
SrF <sub>2</sub>	d-f	2.91	-18(1)	-17	-21.6 <sup>11</sup>		
CaF <sub>2</sub>	d-f	2.96	-17(1)	-17.3	-15.0 <sup>10</sup>		
BaF <sub>2</sub>	d-f			-22		-10(2)	-17.2 <sup>11</sup>
	ITE	2.20	64(1)		-20.5	25(1)	
	STE	2.92	15 (1)				

<sup>a</sup> The results from references are also listed for comparison.



**Figure 3.** Variation of the bandwidth from the PL spectra of SrF<sub>2</sub>:Eu<sup>2+</sup>, CaF<sub>2</sub>:Eu<sup>2+</sup> (a) and BaF<sub>2</sub>:Eu<sup>2+</sup> (b) with pressure.

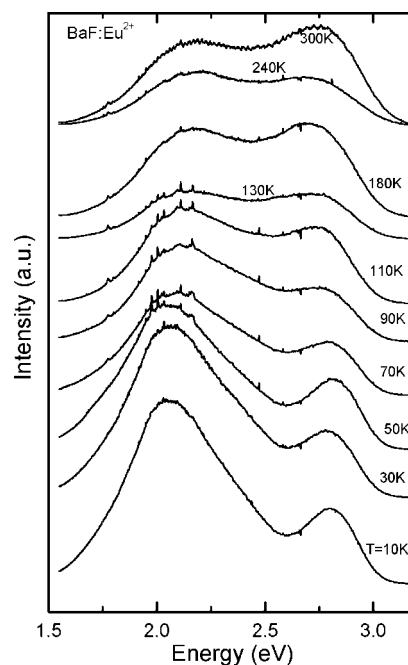
2.75 eV (451 nm) is similar to the blue emission reported by Moine et al.<sup>4</sup> Moine suggested that this blue emission was associated with the self-trapped exciton (STE).<sup>4</sup>

With increasing pressure, the 2.75 eV peak increases as the ITE decreases in intensity. The peak energies [Figure 2b] and bandwidths [Figure 3b] were obtained by Gaussian fitting to the emission spectra and were plotted as a function of pressure. The ITE peak shifts toward higher energies with increasing pressure below 4 GPa. The pressure coefficient of the ITE peak obtained by linear fitting is  $64 \pm 1$  meV/GPa, which is greater than the  $-20.5$  meV/GPa reported by Catch et al. who conducted their measurement at 20 K.<sup>14</sup> The 2.75 eV emission peak shows a nonlinear pressure dependence in both peak energy and bandwidth in the studied pressure range. In the 0–4 GPa pressure range, the 2.75 eV emission peak shifts to higher energies with increasing pressure. It is nearly constant from 4 to 5 GPa, and then gradually shifts toward lower energies from 5 to 8 GPa. The pressure coefficient obtained by a linear fitting in the low pressure range is  $15 \pm 1$  meV/GPa. The pressure dependence of the peak energy of the 2.75 eV emission band above 5 GPa is consistent with the quadratic polynomial function

$$E(P) = 2.82 - 0.010(P - 5.0) - 0.011(P - 5.0)^2 \quad (1)$$

The obtained pressure coefficient ( $-10 \pm 1$  meV/GPa) of peak energy of 2.75 eV emission is comparable to the reported pressure coefficient ( $-17.2$  meV/GPa) of the d-f emission from the orthorhombic BaF<sub>2</sub>:Eu<sup>2+</sup>.<sup>14</sup>

The bandwidth of the 2.75 eV emission exhibits an abnormal pressure behavior, i.e. the emission band initially becomes narrower with increasing pressure, and above 4 GPa it tends to broaden with the pressure. The XRD (X-ray diffraction) experiments under high pressure and theoretical studies demonstrated that the transformation from the cubic to orthorhombic phase happened between 3.5 and 5 GPa in BaF<sub>2</sub>.<sup>11,18,19</sup> The



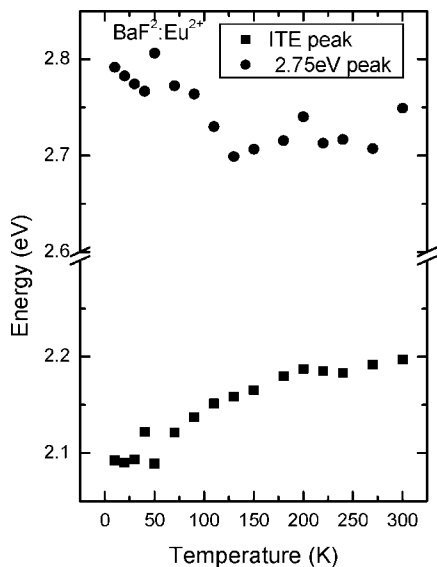
**Figure 4.** Emission spectra from BaF<sub>2</sub>:Eu<sup>2+</sup> at different temperatures.

sudden decrease in the slope of the pressure dependence of ITE and 2.75 eV emission energies as well as the abnormal change in bandwidth at around 4 GPa are the results of the transition from the cubic to orthorhombic phase.

Figure 4 depicts the emission spectra at different temperatures for BaF<sub>2</sub>:Eu<sup>2+</sup>. The two emissions decrease in intensity as the temperature increases. The remarkable quenching of the emission intensity of the 2.20 eV emission band with increasing temperature is the typical temperature behavior of impurity-trapped exciton luminescence.<sup>1,14</sup> The temperature dependence of the peak energies from ITE and 2.75 eV emissions is presented in Figure 5. As the temperature increases, the 2.75 eV emission peak has a slight red-shift, but the ITE has a large blue-shift. These behaviors are consistent with those of Ba<sub>x</sub>Sr<sub>1-x</sub>F:Eu<sup>2+</sup> reported by Gatch et al.<sup>14</sup>

## Discussion

**1. Pressure Behaviors of Eu<sup>2+</sup>-Doped SrF<sub>2</sub> and CaF<sub>2</sub>.** The ground state of the free Eu<sup>2+</sup> ion is <sup>8</sup>S<sub>7/2</sub> with 4f<sup>7</sup> configuration, and its lowest lying excited configuration is 4f<sup>6</sup>5d<sup>1</sup>. In Eu<sup>2+</sup>-doped cubic-phase MF<sub>2</sub> fluorides, the doped Eu<sup>2+</sup> ions replace the metal M ions and feel the cubic symmetrical crystal field of near neighboring F<sup>-</sup> ions. The 4f<sup>6</sup>5d<sup>1</sup> electron state of the Eu<sup>2+</sup> ion splits into two levels, i.e., the triply degenerate state t<sub>2g</sub> and doubly degenerate state e<sub>g</sub>. The t<sub>2g</sub> is higher than the original d-level by 4(Dq), and the e<sub>g</sub> is lower by 6(Dq).<sup>20</sup> Dq



**Figure 5.** Peak energies of the ITE and 2.75 eV emission bands from BaF<sub>2</sub>:Eu<sup>2+</sup> at atmospheric pressure as a function of temperature.

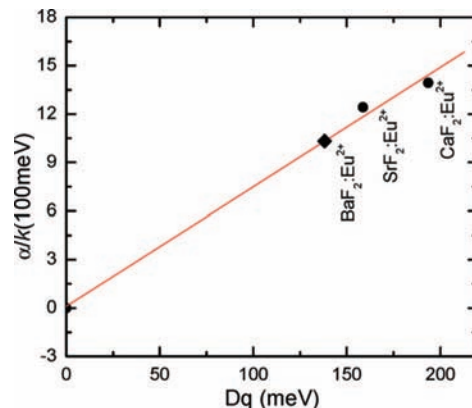
denotes the strength of the crystal field surrounding the doping ion. The transition from the lowest 5d<sup>1</sup> excitation state ( $e_g$ ) to the 4f<sup>7</sup> ground state produces a so-called d–f emission. The increase of the crystal field strength is expected because of the compression in bond length when an external pressure is applied. Consequently, the lowest  $e_g$  excited state should move downward relative to its original position. The average radius of 4f electrons is much smaller than those of 5s and 5p electrons, and thus 4f electrons are well screened. It is reasonable that the 4f<sup>7</sup> configuration forms a highly localized ground state in the band gap of MF<sub>2</sub> and is not sensitive to the applied pressure. Therefore, the pressure dependence of the d–f transition energy mainly depends on the pressure behavior of the crystal field level. Based on the above discussion, the derivative of the pressure dependence of d–f transition can be described simply as<sup>20</sup>

$$\alpha = \frac{dE_{d-f}}{dP} = -6 \frac{d(Dq)}{dP} \quad (2)$$

In general,  $Dq$  is proportional to  $R^{-n}$ ,<sup>21–23</sup> where  $R$  represents the distance between the impurity ion and the nearest neighboring F ions and  $n$  is a constant related to the local lattice symmetry surrounding the impurity ion. As a result, the following expression can be derived from eq 2:

$$\frac{dE_{d-f}}{d \ln V} = \frac{\alpha}{k} = 2n(Dq) \quad (3)$$

where  $k = (-1/V)(dV/dP)$  is the volume compressibility of the MF<sub>2</sub> host crystal. We suggest that the cubic MF<sub>2</sub>:Eu<sup>2+</sup> has the same  $n$  value because of the similar local symmetry around the doped Eu<sup>2+</sup> ion. The reported  $k$  values under the cubic phase are  $-0.02 \text{ GPa}^{-1}$  for BaF<sub>2</sub>,  $-0.012 \text{ GPa}^{-1}$  for CaF<sub>2</sub>, and  $0.0145 \text{ GPa}^{-1}$  for SrF<sub>2</sub>.<sup>11,12,18,19,24–26</sup> The estimated  $Dq$  values from the excitation and absorption spectra in ref 3 for compounds doped with Eu<sup>2+</sup> ions are 138 meV for BaF<sub>2</sub>, 193 meV for CaF<sub>2</sub>, and 159 meV for SrF<sub>2</sub>. According to the experimental points ( $\alpha/k, Dq$ ) for CaF<sub>2</sub>:Eu<sup>2+</sup> and SrF<sub>2</sub>:Eu<sup>2+</sup>, we performed linear fitting using the function  $y = bx$  as shown in Figure 6. The obtained value of  $n$  is about 3.7. The estimated pressure coefficients of the d–f transition for the three samples based on the linear fitting are listed in Table 1. The obtained value of  $\alpha$  for BaF<sub>2</sub>:Eu<sup>2+</sup> is



**Figure 6.** The value of  $\alpha/k$  versus  $Dq$ . Here  $k = -(1/V)(dV/dP)$  is the volume compressibility of the MF<sub>2</sub> host crystal, and  $\alpha = dE_{d-f}/dP$  is the pressure coefficient of the d–f emission band from the samples. The solid line is determined by fitting to the experimental points for CaF<sub>2</sub>:Eu<sup>2+</sup> and SrF<sub>2</sub>:Eu<sup>2+</sup> using the linear function  $y = bx$ . The value of  $\alpha/k$  for BaF<sub>2</sub>:Eu<sup>2+</sup> is estimated and denoted as the symbol  $\blacklozenge$ .

about  $-22 \text{ meV/GPa}$ , which is in the typical range for MF<sub>2</sub>:Eu<sup>2+</sup> fluorides.

**2. The Emission Bands from BaF<sub>2</sub>:Eu<sup>2+</sup>. a. The Impurity Trapped Exciton Emission.** The impurity trapped exciton recombination occurs as follows.<sup>2,17</sup> Some electrons excited into the 5d excitation state tend to autoionize because the 5d level lies above the conduction band of BaF<sub>2</sub>. The ionized Eu<sup>3+</sup> together with the possible reduced Madelung potential at the nearby Ba<sup>2+</sup> sites creates a Coulomb potential and attracts an electron in the conduction band. The electron delocalizes over the surrounding Ba<sup>2+</sup> cations, and a trapped exciton-like state near the Eu<sup>3+</sup> ion is formed. The Eu<sup>3+</sup> impurity returns to the 4f ground state and is radiative by the anomalous ITE emission. The pressure coefficient of the ITE emission band is as large as  $64 \text{ meV/GPa}$  when the pressure is  $<4 \text{ GPa}$ . Since the 4f electrons are well shielded from the ligand field, the 4f ground state is less sensitive to the applied pressure, but the electronic orbit of ITE extends to twelve next-neighbor metal-ion sites.<sup>2,17</sup> Such a delocalization makes the ITE state behave like the conduction band of the BaF<sub>2</sub> host in pressure dependence. Therefore, we suggest that the pressure dependence of conduction of the BaF<sub>2</sub> host is responsible for the large positive pressure coefficient of the ITE emission band. Unfortunately, there is no experimental data available about the pressure coefficient of the BaF<sub>2</sub> band gap. Jiang et al.<sup>19</sup> and Kanchana et al.<sup>18</sup> predicted theoretically that the BaF<sub>2</sub> band gap would increase with increasing pressure in the cubic phase. Normally, the exciton-to-defect bounding energy increases with rising pressure because the compression leads to the increase of the dielectric constant in the ion crystal. Thereby, it implies that the conduction band of BaF<sub>2</sub> increases with increasing pressure by a rate higher than  $64 \text{ meV/GPa}$  in the cubic phase.

When the pressure exceeds 4 GPa, BaF<sub>2</sub> undergoes a transition from the cubic to orthorhombic phase. The phase transition induces the sudden slope decrease of the peak energy pressure dependence of the ITE emission. The slight blue-shift of the ITE emission with increasing pressure presents its pressure behavior in the orthorhombic phase. Also the pressure dependence of ITE in the high-pressure phase indicates that the pressure-induced blue-shift of the conduction band could be small in the orthorhombic phase.

**b. The 2.75 eV Emission.** The nature of the emission at 2.75 eV (451 nm) in BaF<sub>2</sub>:Eu<sup>2+</sup> is not yet clear, but it is certain that the 2.75 eV emission below 4 GPa is not from the d–f transition



of  $\text{Eu}^{2+}$  ions in  $\text{BaF}_2:\text{Eu}^{2+}$ . First, emission energy at 2.75 eV is lower than that of d–f recombination (3.07 eV or 403 nm) from the  $\text{Eu}^{2+}$  ion.<sup>4</sup> Second, the 2.75 eV emission shifts to the blue with increasing pressure below 4 GPa, which is opposite of the pressure dependence of the d–f emission from  $\text{CaF}_2:\text{Eu}^{2+}$  and  $\text{SrF}_2:\text{Eu}^{2+}$ . The crystal field theory also predicted that the pressure coefficient of d–f emission in  $\text{BaF}_2:\text{Eu}^{2+}$  should be negative, as discussed in the previous section. In addition, the pressure coefficient (15 meV/GPa) of the 2.75 eV emission is far smaller than that of ITE emission (64 meV/GPa). This indicates that its shift with pressure is much smaller than that of the  $\text{BaF}_2$  conduction band. Therefore, the possibility of the electronic transition from the conduction band to the 4f ground state for the 2.75 eV emission is excluded.

The 2.75 eV emission at lower pressure most likely arises from the STE and follows the model proposed by Moine et al.<sup>4</sup> In this model, the  $\text{Eu}^{2+}$  impurity ion is photoionized and captures an electron from a neighboring  $\text{F}^-$  ion, thereby returning to the ground state of the  $\text{Eu}^{2+}$  ion. Two neighboring F atoms constitute an  $(\text{F}_2)^-$  center, and the self-trapped exciton is created by bonding an electron ejected by  $\text{Eu}^{2+}$  ion to the center. It returns the  $(\text{F}_2)^-$  to two  $\text{F}^-$  ions at the normal lattice sites by the STE recombination. Similar to ITE, the conduction band is partly involved in the recombination of the STE. Therefore, the STE also exhibits positive pressure dependence. The pressure coefficient of the 2.75 eV emission peak is much smaller than that of the ITE emission peak. This means that the self-trapped exciton is more localized than the impurity trapped exciton.

In order to understand the mechanism of the transition for the 2.75 eV emission band under pressure higher than 4 GPa, we plotted the impurity trapped exciton level state and 5d excited level of  $\text{Eu}^{2+}$  in  $\text{BaF}_2$  as a function of pressure in Figure 2. The initial values of the ITE (2.73 eV) and 5d levels (3.1 eV) with respect to the 7f ground position of the  $\text{Eu}^{2+}$  ion at atmosphere pressure are adopted from ref 4. Here we assume the following. (1) The 6f ground state of  $\text{Eu}^{2+}$  ion is independent of external pressure. (2) The Stokes shift of the ITE and the d–f transition are independent of pressure. Therefore, the pressure dependences of the ITE configuration and the 5d excited state of  $\text{Eu}^{2+}$  ion are equivalent to those of 2.20 eV emission and the d–f emission, respectively. (3) The 5d excited state has linear pressure dependence with a slope of about  $-22$  meV/GPa as estimated by the crystal field method in the cubic phase. (4) The peak energy of the d–f emission band in the orthorhombic phase should decrease with increasing pressure, i.e., the maximum slope of the pressure dependence is zero as shown in Figure 2b. Then, the maximum crossover point of the ITE state and the 5d excited state is about 4.6 GPa.

As shown in Figure 2b, the ITE state moves upward and the 5d excited state moves downward as pressure increases. In the 4–4.6 GPa pressure range, the crossover between the two states can take place. Upon further compression, the 5d excited state can occupy a lower position than the ITE configuration in the band gap of  $\text{BaF}_2$ . Consequently, the ITE emission band will decrease in intensity because the relaxation efficiency of the electron at the 5d excited state to the ITE state is decreased. The vanishing of the 2.20 eV emission peak above 6 GPa proves the above assumption. Instead, the emission from the d–f transition of  $\text{Eu}^{2+}$  ion is expected to appear under higher pressure because the lowest excited 5d state is lower than the ITE level. The 2.75 eV emission peak shifts toward lower energies upon compression when the pressure is above 5 GPa, which is a typical pressure behavior of the d–f emission band in  $\text{MF}_2:\text{Eu}^{2+}$  compounds. Therefore, it is reasonable that the

emission from  $\text{BaF}_2:\text{Eu}^{2+}$  above 5 GPa is dominated by the d–f transition of the  $\text{Eu}^{2+}$  ion. The pressure dependence of the d–f emission deviates the linear relationship, which is different from the result measured by Gatch et al.<sup>14</sup> The difference is perhaps related to the different  $\text{Eu}^{2+}$  concentrations in the samples studied.

Based on the above discussion, the 2.75 eV emission band exhibits the characteristics of STE at pressures below 4 GPa and of d–f emission at pressures above 5 GPa. The transition of the STE peak to the d–f emission takes place in the pressure range of 4–5 GPa. However, discontinuities in the PL profile such as splitting or abnormal broadening were not reduced by the transition process. Instead, in this pressure range, the 2.75 eV emission band shows weak pressure dependence of both emission energy and bandwidth. In addition, the d–f emission band exhibits polynomial rather than linear pressure dependence above 5 GPa, which is a little different from the common pressure behavior of d–f transition.

We suggest that there are two factors—namely, phase transition and coupling between the STE and the 5d electron—affecting the pressure behavior of the 2.75 eV emission at pressures above 4 GPa. When the impurity state is close to the conduction band of the host, a strong coupling effect between the impurity state and the conduction band occurs and induces a nonlinear pressure dependence in the emission band. The special pressure behavior has been observed in GaNAs.<sup>27</sup> Since the nonlinear pressure behavior of the 2.75 eV emission band is somewhat analogous in GaNAs,<sup>27</sup> we propose that the interaction between STE and the impurity-like 5d excited state occurred in  $\text{BaF}_2:\text{Eu}^{2+}$  under higher pressure. In this case, normally the transition from conduction band-like recombination to the impurity-like transition with pressure behaves as a continuous change in the peak shape of the emission band.<sup>27</sup>

The change in pressure coefficient reflects the difference in pressure dependence for the 2.75 eV emission between the cubic phase and the orthorhombic phase. Meanwhile, the phase transformation may have a different influence on the local environment surrounding the original  $\text{Ba}^{2+}$  site and the substitution ion (doped  $\text{Eu}^{2+}$  impurity). Therefore, there would be a distortion on the local crystal field around the  $\text{Eu}^{2+}$  ion because of the phase transition, which is likely also responsible for the nonlinear pressure behavior of d–f emission under higher pressure.

Now we can understand the pressure dependence of the two emissions in  $\text{BaF}_2:\text{Eu}^{2+}$ . When the pressure is below 4 GPa, the ITE and STE recombinations are dominant, and the d–f transitions are absent for the emission spectra. As the pressure increases, (1) the transformation from the cubic to orthorhombic phase occurs at 4 GPa and slows the shift of ITE and STE emissions with pressure; (2) the ITE state moves up, and the 5d excited state moves down. The two states meet in the pressure range of 4.0–4.6 GPa. Meanwhile, the 2.75 eV emission begins to transfer from the STE recombination to the d–f transition of the  $\text{Eu}^{2+}$  ion accompanied by the interaction between the STE and the d electronic state. The d–f transition starts to dominate the 2.75 eV emission at pressures above 5 GPa and shows a typical red-shift upon further compression.

## Conclusion

The pressure dependence of the luminescence from  $\text{BaF}_2:\text{Eu}^{2+}$ ,  $\text{CaF}_2:\text{Eu}^{2+}$ , and  $\text{SrF}_2:\text{Eu}^{2+}$  was investigated. The emissions in  $\text{SrF}_2:\text{Eu}^{2+}$  and  $\text{CaF}_2:\text{Eu}^{2+}$  are from the  $4f^65d^1 \rightarrow 4f^7$  transition of  $\text{Eu}^{2+}$ , and their pressure dependence can be simply explained by the crystal field theory. As for  $\text{BaF}_2:\text{Eu}^{2+}$ , the lowest

d-electron excited state of the Eu<sup>2+</sup> ion is degenerate with the conduction band of BaF<sub>2</sub>. Therefore, the d–f emission is absent at atmospheric pressure in BaF<sub>2</sub>:Eu<sup>2+</sup>. Instead, the emission spectrum of the BaF<sub>2</sub>:Eu<sup>2+</sup> sample at room temperature comprises two emission peaks at 2.20 (563 nm) and 2.75 eV (456 nm). The emission at 2.20 eV originates from the recombination of the ITE while the emission at 2.75 eV is likely related to the STE. Both emissions show a blue-shift in peak position with increasing pressure lower than 4 GPa, which are opposite the typical pressure dependence of the d–f transition of the Eu<sup>2+</sup> ion. The pressure induced emission band shifts are slowed by the transformation from the cubic to orthorhombic phase at 4 GPa. Upon further compression, the 5d excited state of the Eu<sup>2+</sup> ion moves into the band gap of BaF<sub>2</sub> and is lower than the ITE state in the 4–4.6 GPa range. In this case, the self-trapped exciton state can couple with the 5d state by the interaction between the 5d state and the sd-like conduction band. The transition of 2.75 eV emission from the STE-dominated recombination to the d–f emission takes place. Above 5 GPa, the emission from the d–f transition of Eu<sup>2+</sup> ion dominates the 2.75 eV emission band. The pressure-induced change from STE recombination to d–f transition together with the phase transition process from the cubic to orthorhombic phase leads to the nonlinear pressure dependence of the 2.75 eV emission in both peak position and bandwidth.

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