

Effect of Er^{3+} concentration on the structural phase transition and rigidity of Er^{3+} doped KYF_4

Ta-Ryeong Park*

Department of Display Engineering, Hoseo University, Asan, Choongnam 31499, Korea

Er^{3+} doped KYF_4 crystals show two structural transitions in the pressure range of 0 to ~70 kbar, as indicated by the abrupt changes of photoluminescence (PL) they exhibit. The crystal with 0.05 at.% Er^{3+} ions ($\text{KY}_{0.9995}\text{Er}_{0.0005}\text{F}_4$) showed a higher first transition pressure (around 40 kbar) and a lower second transition pressure (around 55 kbar) than the crystal with 10 at.% Er^{3+} ions ($\text{KY}_{0.9}\text{Er}_{0.1}\text{F}_4$), which indicates that rigidity reversal between the two crystals occurs at the first transition. This behavior is explained in terms of the pillaring effect where Y^{3+} ions are acting as pillars so that the internal stress on the Er^{3+} ions is alleviated while in the first phase. The Y^{3+} ions and the Er^{3+} ions are differentially compressed until the first transition where the radii of both species become equal. After the first transition, the Y^{3+} ions stop functioning as pillars, leading to an enhanced deformation of the Er^{3+} ions. This effect is evident in the increased pressure-shift rates of the PL in the second phase.

Key words: Photoluminescence, Fluorescence, Radiative process, Structural transition, High pressure, KYF_4 .

Introduction

Er^{3+} doped crystals in various hosts have attracted much interest because of their versatility in optical properties [1-4]. In particular, Er^{3+} doped KYF_4 crystals have photon energy upconversion via energy transfer process between optically excited states of nearby Er^{3+} ions. By this upconversion process, green light is partially upconverted into blue light [5]. Regarding structural aspects, it was reported in a previous publication that $\text{KY}_{0.9}\text{Er}_{0.1}\text{F}_4$ undergoes a structural phase transition at high pressure as marked by the photoluminescence (PL) change it exhibits [6].

It is interesting to see if the transition pressure shifts to a new value when the dopant Er^{3+} concentration changes since Er has a bulk modulus different from that of Y in their pure states. We can expect that as the Er^{3+} concentration decreases the transition pressure also decreases because Er has a larger bulk modulus (44.4 GPa) than Y (41.2 GPa) [7] has. In this paper we present experimental evidences that disagree with this intuitive expectation in one case, in addition to the evidences that show normal behavior in the other case. The unexpected behavior is associated with a secondary phase transformation (around ~40 kbar) which was not reported in Ref. [6]. In the case of the primary phase transition (around ~55 kbar), the experimental data agree with this intuitive expectation.

Experimental Details

Optical excitation of the crystals was obtained by using a diode laser that produced ~406 nm light with ~20 mW of power. In measuring PL, the power was suitably reduced by using neutral density filters to prevent damage in the sample crystals. High pressure was generated by using a commercially available diamond anvil cell with a 4 : 1 mixture of methanol and ethanol as a pressure transmitting medium. Sample chamber was composed of a stainless steel gasket that had a ~0.2 mm diameter hole. A ruby chip was put into the chamber with a sample crystal to monitor the pressure by measuring the peak position of the R_1 PL it produces. The fluorescence from the sample and the ruby chip was collected in a back-scattering geometry. A long pass filter was used to remove the elastically scattered light before the PL entered a 50 cm monochromator. The PL signal from the crystal was dispersed by a 2400 grooves/mm grating and the plasma lines of a mercury lamp were employed as a reference in each measurement of the PL to ensure sub-Angstrom accuracy and reproducibility. The dispersed PL signal was recorded by a thermoelectrically cooled charge-coupled device. The KYF_4 single crystals doped with 10 at.% ($\text{KY}_{0.9}\text{Er}_{0.1}\text{F}_4$) and 0.05 at.% Er^{3+} ions ($\text{KY}_{0.9995}\text{Er}_{0.0005}\text{F}_4$) were measured in this research. The preparation of these crystals is described in Ref. [5] and the references therein.

Results and Discussion

High pressure PL measurements have revealed that while the sample with 10 at.% Er^{3+} has a transition

*Corresponding author:
Tel : +82-41-540-5612
Fax: +82-41-540-5618
E-mail: trpark123@naver.com, trpark@hoseo.edu

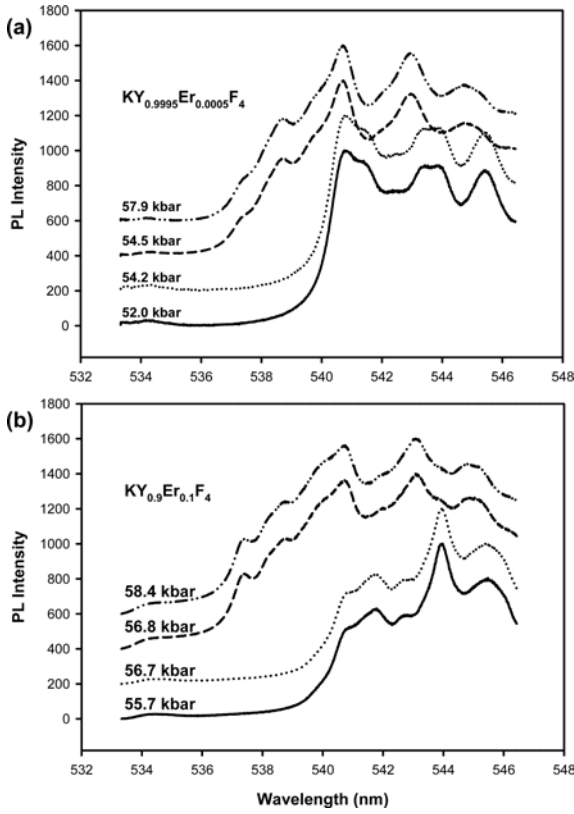


Fig. 1. The spectra around the primary phase transition of (a) $\text{KY}_{0.9995}\text{Er}_{0.0005}\text{F}_4$ and (b) $\text{KY}_{0.9}\text{Er}_{0.1}\text{F}_4$.

pressure in the range between 56.7 and 56.8 kbar, the one with 0.05 at.% Er^{3+} has a corresponding pressure in the range between 54.2 and 54.5 kbar. Fig. 1 shows this behavior in detail. The PL lineshapes shown here correspond to $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ radiative process of Er^{3+} ions [8]. A sudden change in the PL lineshape indicates a structural phase transition which accompanies a change in the symmetry surrounding the Er^{3+} ions. While the structure of new phase is not available, it is reasonable to expect that the crystal with a higher bulk modulus undergoes a structural transition at a higher pressure. The bulk modulus of the doped crystal depends on the Er^{3+} concentration and is supposed to be lower with lower Er^{3+} concentration. (Note that Er has a larger bulk modulus than Y has.) Therefore, the observation shown in Fig. 1 agrees with this expectation. However, there is another transition that behaves in contrast to this expectation.

Fig. 2 shows a transition around 40 kbar, as indicated by the change in the PL lineshapes. The position of PL peak A (inset of Fig. 3) vs. pressure also shows a discontinuous shift around this pressure (Fig. 3). The PL shift rate of peak A in the low pressure range 0–20 kbar is also different from that in the high pressure range 40–53 kbar (Table 1), which is also a good indication that the two phases are different. However, in contrast to the previous case of transition around ~55 kbar, the transition pressure for 10 at.% Er^{3+}

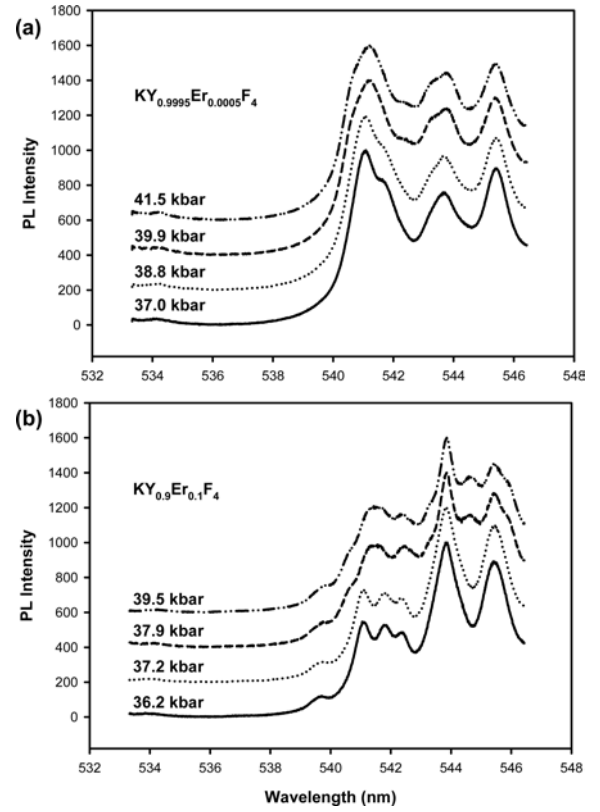


Fig. 2. The spectra around the secondary phase transition of (a) $\text{KY}_{0.9995}\text{Er}_{0.0005}\text{F}_4$ and (b) $\text{KY}_{0.9}\text{Er}_{0.1}\text{F}_4$.

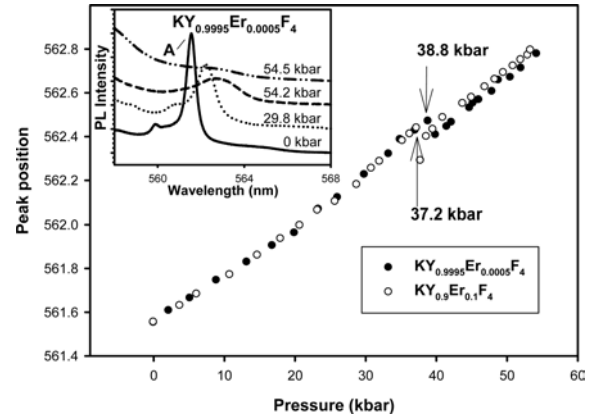


Fig. 3. Pressure dependence of the position of peak A. The inset shows the lineshapes of peak A of $\text{KY}_{0.9995}\text{Er}_{0.0005}\text{F}_4$ at selected pressures.

Table 1. Pressure-shift rates $\frac{d\lambda}{dP}$ of peak A for $\text{KY}_{0.9995}\text{Er}_{0.0005}\text{F}_4$ and $\text{KY}_{0.9}\text{Er}_{0.1}\text{F}_4$ in two pressure ranges in units of nm/kbar. Notice that the pressure-shift rate of $\text{KY}_{0.9995}\text{Er}_{0.0005}\text{F}_4$ is smaller than that of $\text{KY}_{0.9}\text{Er}_{0.1}\text{F}_4$ in the 0–20 kbar range and larger in the range 40–54 kbar.

Er^{3+} concentration	$\frac{d\lambda}{dP}$	
	0–20 kbar	40–54 kbar
0.05 at. %	0.0204 ± 0.0002	0.0257 ± 0.0006
10 at. %	0.0213 ± 0.0003	0.0245 ± 0.0003

sample is lower than that for 0.05 at.% sample (~37.9 kbar vs. ~39.9 kbar), as determined by the discontinuous

change of the peak position A. (More accurately, for 0.05 at.% Er^{3+} crystal, the transition pressure is between 38.8 and 39.9 kbar, and for 10 at.% Er^{3+} crystal, it is between 37.2 and 37.9 kbar.) This behavior can be qualitatively understood in terms of ion size difference between Er^{3+} and Y^{3+} .

Because the atomic radius of Er is slightly smaller than that of Y (175 pm vs. 180 pm [9]), we can suppose that the Y^{3+} ions are playing the role of pillars for the nearby Er^{3+} ions when the Er-doped crystals are pressurized. Then, the rigidity (bulk modulus) of the 0.05 at.% Er^{3+} crystal will be larger than that of the 10 at.% Er^{3+} crystal, since the former has a larger density of pillars available than the latter has, despite the fact that Y is softer than Er. This leads to a higher transition pressure for the 0.05 at.% Er^{3+} crystal than the 10 at.% Er^{3+} crystal.

In the low pressure range of present concern, the Er^{3+} ions are subject to a smaller internal stress than the Y^{3+} ions because of the pillaring effect. The Er^{3+} ions in the 0.05 at.% Er^{3+} sample are under a larger pillaring effect than the 10 at.% Er^{3+} sample. Consequently, the 0.05 at.% Er^{3+} sample will show a smaller pressure-shift rate of PL peak position than the 10 at.% Er^{3+} sample (see the fitted results of Table 1 as evidences for this). The Y^{3+} ions and the Er^{3+} ions are differentially compressed until the first transition pressure (~40 kbar) where the radii of both species become equal. At the pressure range larger than this first transition pressure, the Y^{3+} ions stop functioning as pillars, leading to an enhanced deformation of the Er^{3+} ions. This effect is evident in the increased pressure derivative of the peak position A in the range 40-53 kbar, compared to the one in the 0-20 kbar range (Table 1). In particular, 0.05 at.% Er^{3+} crystal should have lower rigidity than the 10 at.% one in this 40-53 kbar range. This is well represented as a higher pressure-shift rate of PL peak position for 0.05 at.% Er^{3+} crystal than the 10 at.% one in Table 1. Thus, as shown in Table 1, this pressure-shift rate reversal between the two crystals after the first transition is another good evidence for the pillaring effect.

The supposition that the Y^{3+} ions are acting as pillars for the Er^{3+} ions in the first phase until the first transition can be checked with the following reasoning. Suppose that there were no pillaring effect by the Y ions. Then both the Er^{3+} and the Y^{3+} ions would be subject to the same internal pressure, leading to pressure-dependent radii

$$r_i \sim r_{0i} \exp\left(-\frac{P}{3B_i}\right) \quad (1)$$

where r_i and r_{0i} are the radius and the bulk modulus of the ion i ($= \text{Er}^{3+}$ or Y^{3+}) at pressure P , respectively, and is the radius of the ion i at ambient pressure. Here, we assumed that the bulk modulus is pressure independent. From Eq. (1), it is easily seen that the two radii would become equal at ~480 kbar which is significantly

higher than the experimentally measured value of the first transition pressure (~40 kbar). Therefore, this analysis supports the idea that the smaller Er^{3+} ions are under much smaller internal pressure than the Y^{3+} ions until the first transition occurs.

We therefore see that, while in its first phase, the bulk modulus of the Er^{3+} doped crystal does not simply increase with increasing Er^{3+} ion concentration. The 0.05 at.% Er^{3+} crystal has a larger bulk modulus than the 10 at.% Er^{3+} crystal in the low pressure range before the first transition pressure, which is evidenced by the experimental measurements that the former has a higher first transition pressure than the latter. After the first phase transition, the pillaring effect will be absent and the 0.05 at.% Er^{3+} crystal has a smaller bulk modulus than the 10 at.% Er^{3+} crystal has, which is also evident from the lower second phase transition pressure of the former than the latter.

Conclusions

Two Er doped KYF_4 crystals, $\text{KY}_{0.9995}\text{Er}_{0.0005}\text{F}_4$ and $\text{KY}_{0.9}\text{Er}_{0.1}\text{F}_4$, were investigated with PL under high pressure. Structural phase transitions induced by the pressure were recognized by the sudden change in the PL spectra they emit. Two phase transitions were observed in the pressure range 0 to ~70 kbar. The crystal with 0.05 at.% Er^{3+} ions showed a higher first transition pressure around 40 kbar and a lower second transition pressure around 55 kbar than the crystal with 10 at.% Er^{3+} ions. In the first phase below ~40 kbar, the larger and softer Y^{3+} ions are playing the role of pillars that reduces the internal stress on the smaller Er^{3+} ions, leading to a higher bulk modulus for the crystal with 0.05 at.% Er^{3+} ions than the one with 10 at.%. After the first transition, the pillaring effect is removed and the crystal with the 10 at.% Er^{3+} crystal becomes more difficult to compress than the 0.05 at.% Er^{3+} crystal. These behaviors are also supported by the data of Table 1 that shows the reversal of pressure-shift rates between the two crystals at the first transition.

Acknowledgments

This research was supported by the Academic Research fund of Hoseo University in 2012 (20120318).

References

1. T. Riedener, P. Egger, J. Hullinger, and H. U. Gudel, *Phys. Rev. B* 56 (1997) 1800-1808.
2. J. A. Capobianco, F. Vetrone, J.C. Boyer, A. Speghini, and M. Bettinelli, *Optical Mater.* 19 (2002) 259-268.
3. H. Xu, Z. Dai, and Z. Jiang, *Eur. Phys. J. D* 17 (2001) 79-83.
4. S. Georgescu, O. Toma, C. Florea, and C. Naud, *J. Lumin.* 101 (2003) 87-99.
5. T.R. Park, T.Y. Park, S.H. Youn, and N.M. Khaidukov, *J. Lumin.* 106 (2004) 281-289; T.R. Park, *Solid State*

- Commun. 150 (2010) 1378-1381; T.R. Park, Curr. Appl. Phys. 11 (2011) 1201-1204.
6. T.R. Park, J. Kor. Phys. Soc. 60 (2012) 812-815.
7. <https://en.wikipedia.org/wiki/Erbium>. Accessed on November 1, 2015; <https://en.wikipedia.org/wiki/Yttrium>. Accessed on November 1, 2015.
8. M. Bouffard, T. Duvaut, J.P. Jouart, N.M. Khaidukov, M.-F. Joubert, J. Phys.: Condens. Matter 11 (24) (1999) 4775-4782; N.M. Khaidukov, S.K. Lam, D. Lo, V.N. Makhov, N.V. Suetin, Opt. Mater. 19 (2002) 365-376.
9. https://en.wikipedia.org/wiki/Atomic_radius. Accessed on November 1, 2015.