ELSEVIER

Journal of Alloys and Compounds 255 (1997) 1–4

Journal of ALLOYS AND COMPOUNDS

# High pressure luminescence and pressure induced phase transition for $LiYF_4$:Eu

Liu Shenxin[a,*], Chi Yuanbin[b], Zhao Xuyi[a], Wang Lizhong[b]

[a]Changchun Institute of Physics, Academia Sinica, Changchun 130021, China

[b]State Key Laboratory of Superhard Materials, Jilin University, Changchun 130023, China

Received 20 June 1996; revised 21 October 1996

**Abstract**

We have measured the emission spectra of $LiYF_4$:Eu under high pressure up to 15 GPa at room temperature. On the basis of the spectra we have investigated the dependence of the Stark levels of the $^5D_{0,1}$ and $^7F_{1-4}$ multiplets on pressure. The unsplit level of $^7F_0$ is taken as energy reference. We have also found that an obvious change in the spectra occurs and some spectral lines split into two in the pressure range from 10.0 to 10.5 GPa. This phenomenon shows that a structure phase transition occurs in the $LiYF_4$:Eu and the crystal symmetry lowers in the pressure range.

*Keywords:* High pressure; Luminescence; Phase transition; $LiYF_4$; Eu

## 1. Introduction

As we know, $LiYF_4$ is an excellent host material for laser and up-conversion systems. It crystallizes in the scheelite-type structure and belongs to the space group $C_{4h}^6(I4_1/a)$. In $LiYF_4$ the $Y^{3+}$ ions can be easily replaced by other lanthanide ions, so it has found wide application and attracted more attention in science and technology. The luminescence of the $Eu^{3+}$ ion is a convenient probe in the study of the interaction between central ions and their crystalline environment, which is due to the rather easy interpretation of fluorescence spectra and to some particular features of the energy levels of the ion.

The fluorescence spectrum of $LiYF_4$:Eu has been widely studied [1,2]. In this work we studied the fluorescence spectrum at high pressure up to 15 GPa in order to study the dependence of the energy level scheme on pressure and the pressure induced phase transition of $LiYF_4$:Eu. A structure phase transition is usually accompanied by an abrupt change in the fluorescence spectrum.

## 2. Experimental

The sample used in this work is a polycrystalline powder. It was prepared by a solid state reaction between $YF_3$ and LiF at high temperature and protective atmosphere. The concentration of $Eu^{3+}$ in the sample is nominally 4 mol.%. The sample was routinely analyzed by X-ray powder diffraction.

A gasketed diamond anvil cell was used to generate high pressure. The pressure transmitting medium used was the well-known 4:1 methanol–ethanol mixture. The pressure was calibrated by the ruby $R_1$-line.

The fluorescence was excited by the 457.9 nm line of an argon ion laser and recorded with a Spex-1403 Raman Spectrometer. All spectroscopic measurements were carried out at room temperature.

## 3. Results and discussion

### 3.1. Pressure effects on the emission spectra

The spectral range measured is between 21 600 $cm^{-1}$ and 13 000 $cm^{-1}$. At normal pressure above 50 lines were measured. They originate from the $^5D_{0-2} \rightarrow {}^7F_{0-5}$ transitions and their assignment was performed according to Bihari's work [2]. In the high pressure spectrum measurement only about 30 spectral lines were recorded because the sample in the gasket hole was very small and a part of the light was absorbed by the diamond anvil. They all shift to the red quasilinearly at pressures lower than 10 GPa and their red-shift rates (RSR) are no larger than 6 $cm^{-1}$

*Corresponding author.

0925-8388/97/$17.00 © 1997 Elsevier Science S.A. All rights reserved
*PII* S0925-8388(96)02950-7

$GPa^{-1}$. The peak positions at normal pressure and RSR are given in Table 1. The $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions are the most intense lines and they are still distinct at higher pressure.

The intensity of the spectral lines decreases with increasing pressure, and many lines become too weak to recognize at a pressure higher than 9 GPa. When the pressure is higher than 10 GPa, none of the lines from the transition $^5D_1 \rightarrow {}^7F_J$ can be observed by us. It is worth mentioning that the two spectral lines due to transitions of $^5D_0 \rightarrow {}^7F_1$ ($\Gamma_{3,4}$) and $^5D_0 \rightarrow {}^7F_2$ ($\Gamma_{3,4}$) become wide at a pressure higher than 9 GPa and each of them splits into two lines when the pressure exceeds 10 GPa. This phenomenon manifests the validity of spectrum assignment made by Görller-Walrand et al. and Bihari et al. [1,2]. Terminal states of the two lines are all double degenerate at normal pressure.

### 3.2. Pressure effect on the energy levels

It is a more interesting subject to investigate how the electron states of rare earth ions are affected by their crystalline environment. The study of pressure dependence of energy levels can offer a lot of valuable information about the electron state of rare earth ions. As we know, for a rare earth ion in a crystal its Hamiltonian $H$ can be written as $H = H_F + H_C$. $H_F$ is the free-ion Hamiltonian describing the interaction inside the ion and mainly determines the energy of $^{2S+1}L_J$ multiplets. $H_C$ is the crystal-field Hamiltonian representing the influence of the crystalline environment on the rare earth ion considered and causes the multiplet split. When the crystal is in compression, the interatomic distances reduce, which causes the changes in various interactions. The change in levels with pressure reflects change in interaction between the central ion and the crystalline environment. With the help of the emission spectra measured under pressure we have obtained the relative positions of levels of the rare earth ion at various pressures. The unsplit ground state $^7F_0$ is taken as the energy reference. Because the $^5D_0 \rightarrow {}^7F_0$ transition being electric-dipole forbidden in $LiYF_4$:Eu can not be observed in the emission spectrum, we can not directly determine the energy of the $^5D_0$ level from this transition. However, the $^5D_1 \rightarrow {}^7F_0$ transitions are magnetic-dipole allowed and can be recorded at pressures up to 10 GPa, which gives the energies of the $^5D_1$ multiplet. With the help of the $^5D_1 \rightarrow F_{1,2}$ and $^5D_0 \rightarrow {}^7F_{1,2}$ transitions the energy of $^5D_0$ can be found. The Stark levels of the $^7F_{1-4}$ multiplets can also be obtained from the $^5D_0 \rightarrow {}^7F_J$ (J=1,2,3,4) transitions. The levels determined at pressures up to 10 GPa are given in Fig. 1. At pressures higher than 10 GPa we do not estimate the level positions relative to the $^7F_0$ multiplet, because the emissions from the $^5D_1$ multiplet can be no longer recorded. From the figure we can see that the pressure dependence of levels for $Eu^{3+}$ in $LiYF_4$ is somewhat different from that in LnOX or $Ln_2O_2S$ (Ln≡Y, La or Gd, X≡Cl or Br) [3–6]. For $LiYF_4$:Eu the two levels of $^7F_1$ show a bigger splitting with increasing pressure, whereas for LnOX:Eu and $Ln_2O_2S$:Eu the levels appear close to each other at least at the beginning of pressurization. The situation of the $^5D_1$ multiplet is similar to that of the $^7F_1$ multiplet.

Table 1
The peak positions (in $cm^{-1}$) at normal pressure for spectral lines and their average red-shift rates (RSR) (in $cm^{-1}$ $GPa^{-1}$)

| Spectral line | Assignment | RSR |
|---|---|---|
| 19 040 | $^5D_1(\Gamma_1)-{}^7F_0(\Gamma_1)$ | 2.9 |
| 19 018 | $^5D_1(\Gamma_{3,4})-{}^7F_0(\Gamma_1)$ | 3.2 |
| 18 702 | $^5D_1(\Gamma_1)-{}^7F_1(\Gamma_{3,4})$ | 2.7 |
| 18 681 | $^5D_1(\Gamma_{3,4})-{}^7F_1(\Gamma_{3,4})$ | 3.3 |
| 18 589 | $^5D_1(\Gamma_{3,4})-{}^7F_1(\Gamma_1)$ | 3.7 |
| 18 120 | $^5D_1(\Gamma_{3,4})-{}^7F_2(\Gamma_2)$ | 1.1 |
| 18 056 | $^5D_1(\Gamma_1)-{}^7F_2(\Gamma_{3,4})$ | 0.8 |
| 18 032 | $^5D_1(\Gamma_{3,4})-{}^7F_2(\Gamma_{3,4})$ | 1.0 |
| 17 863 | $^5D_1(\Gamma_{3,4})-{}^7F_2(\Gamma'_2)$ | 5.5 |
| 17 160 | $^5D_1(\Gamma_1)-{}^7F_3(\Gamma_{3,4})$ | 1.8 |
| 17 153 | $^5D_1(\Gamma_{3,4})-{}^7F_3(\Gamma_2)$ | 2.4 |
| 17 138 | $^5D_1(\Gamma_{3,4})-{}^7F_3(\Gamma_{3,4})$ | 2.6 |
| 17 110 | $^5D_1(\Gamma_{3,4})-{}^7F_3(\Gamma_1)$ | 3.1 |
| 17 085 | $^5D_1(\Gamma_1)-{}^7F_3(\Gamma_{3,4})$ | 3.7 |
| 17 063 | $^5D_1(\Gamma_{3,4})-{}^7F_3(\Gamma_{3,4})$ | 3.9 |
| 16 032 | $^5D_1(\Gamma_1)-{}^7F_4(\Gamma_{3,4})$ | 3.8 |
| 16 001 | $^5D_1(\Gamma_{3,4})-{}^7F_4(\Gamma_{3,4})$ | 4.4 |
| 16 931 | $^5D_0(\Gamma_1)-{}^7F_1(\Gamma_{3,4})$ | 2.1 |
| 16 839 | $^5D_0(\Gamma_1)-{}^7F_1(\Gamma_1)$ | 3.2 |
| 16 371 | $^5D_0(\Gamma_1)-{}^7F_2(\Gamma_2)$ | 0.8 |
| 16 285 | $^5D_0(\Gamma_1)-{}^7F_2(\Gamma_{3,4})$ | 0.5 |
| 15 401 | $^5D_0(\Gamma_1)-{}^7F_3(\Gamma_2)$ | 2.3 |
| 15 387 | $^5D_0(\Gamma_1)-{}^7F_3(\Gamma_{3,4})$ | 2.1 |
| 15 359 | $^5D_0(\Gamma_1)-{}^7F_3(\Gamma_1)$ | 2.3 |
| 15 311 | $^5D_0(\Gamma_1)-{}^7F_3(\Gamma_{3,4})$ | 3.5 |
| 14 447 | $^5D_0(\Gamma_1)-{}^7F_4(\Gamma_{3,4})$ | 3.0 |
| 14 361 | $^5D_0(\Gamma_1)-{}^7F_4(\Gamma_2)$ | 5.3 |
| 14 284 | $^5D_0(\Gamma_1)-{}^7F_4(\Gamma_2)$ | 3.7 |
| 14 253 | $^5D_0(\Gamma_1)-{}^7F_4(\Gamma_{3,4})$ | 4.0 |

### 3.3. Pressure induced phase transition

The pressure can reduce the interatomic distances of crystals. When the pressure is higher than a critical value a change in the crystal structure occurs. The structure change brings about a change in physical and chemical properties of the crystal. On the other hand, the abrupt change in properties is often an indicator of a change in crystal structure. In the emission spectra we found that the spectral lines of $^5D_0 \rightarrow {}^7F_1$ ($\Gamma_{3,4}$) and $^5D_0 \rightarrow {}^7F_2$ ($\Gamma_{3,4}$) transitions begin to split at a pressure a little higher than 10 GPa. This change shows that the degeneracy of the terminal states $^7F_1$ ($\Gamma_{3,4}$) and $^7F_2$ ($\Gamma_{3,4}$) has been removed and the crystal symmetry has been lowered. A part of the emission spectra between 17 000 $cm^{-1}$ and 16 200 $cm^{-1}$ at different pressures is given in Fig. 2., from which we can see the obvious change in spectra in the process of pressurization

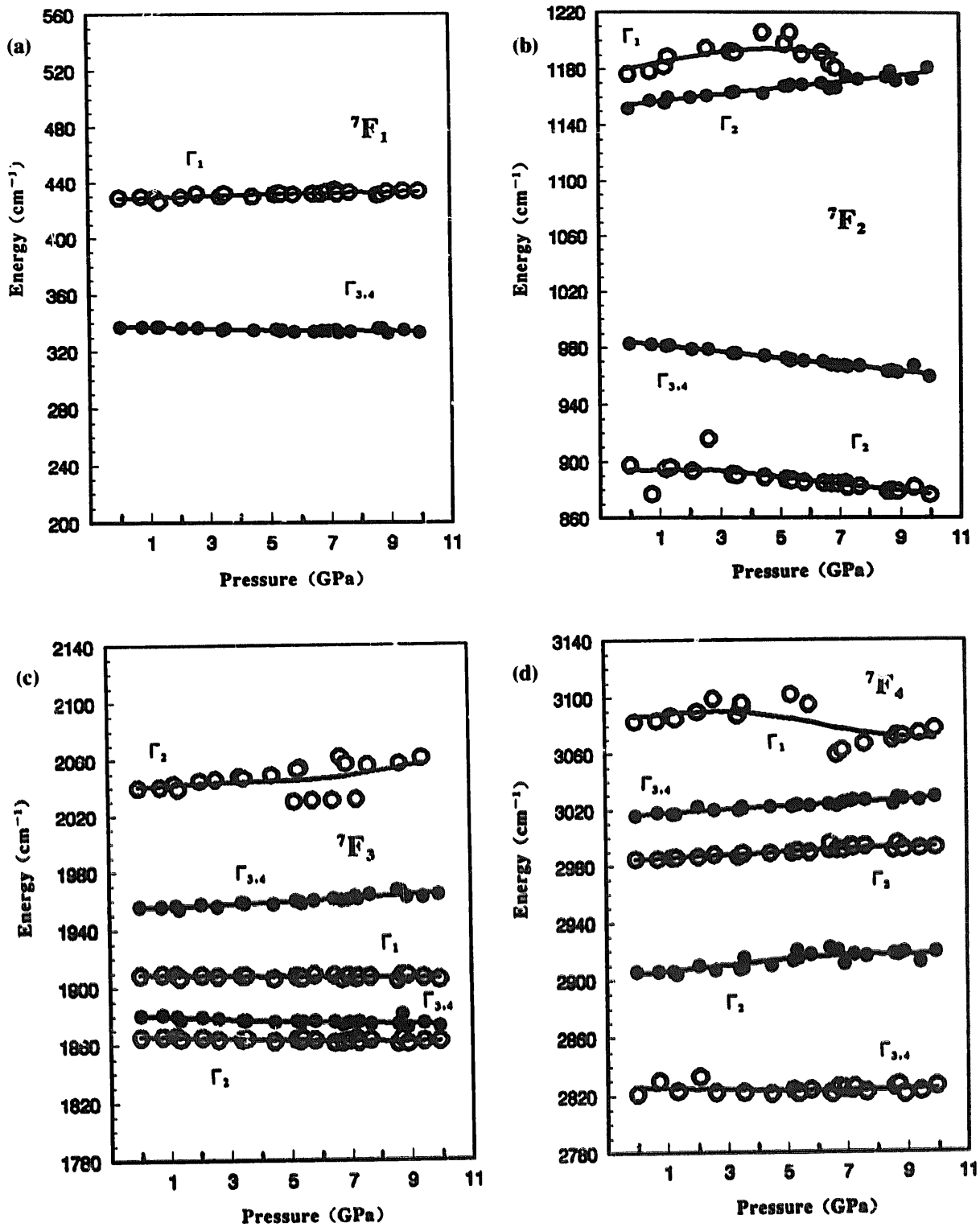


Fig. 1. The positions of Stark levels of $^7F_{1-4}$ and $^5D_{0,1}$. The solid and hollow circles represent experimental points.

and/or depressurization. After depressurization the spectra of $LiYF_4$:Eu return to the original. On the basis of analysis of the spectra we consider that a phase transition occurs near 10.2 GPa. For lack of X-ray diffraction measurements at high pressure the detail of phase transition is unknown, but it is affirmative that the symmetry of the crystal lowers after the phase transition and this phase transition is reversible.

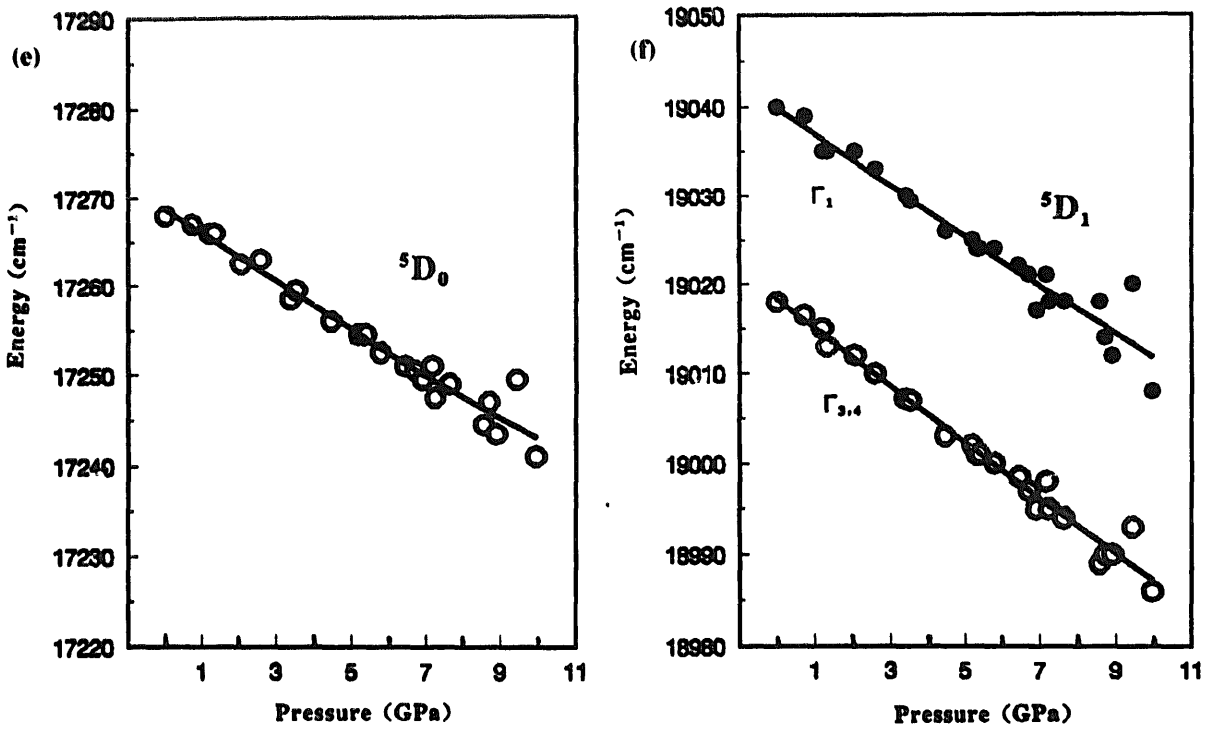


Fig. 1. (*continued*)

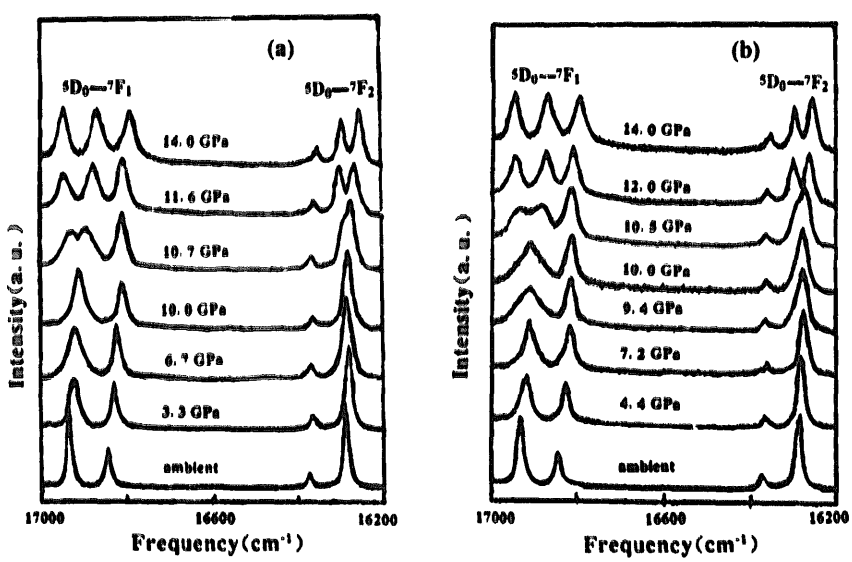


Fig. 2. A part of the emission spectra for $LiYF_4$:Eu at various pressures. (a) Pressurization, (b) depressurization

## Acknowledgments

This work is supported by the National Natural Science Foundation of China.

## References

[1] C. Görller-Walrand, M. Behets, P. Porcher, O.K. Moune-Minn and I. Laursen, *Inorg. Chim. Acta*, *109* (1985) 83.

[2] B. Bihari, K.K. Sharma and L.E. Erickson, *J. Phys.: Condens. Matter*, *2* (1990) 5703.

[3] Liu Shenxin, Chi Yuanbin and Wang Lizhong, *J. Lumin.* *40/41*, (1988) 395.

[4] Chi Yuanbin, Liu Shenxin, Wang Qiuping, Wang Lizhong and Zou Guangtian, *High Pressure Research*, *3* (1990) 150.

[5] Chi Yuanbin, Liu Shenxin, Shen Wufu, Wang Lizhong and Zou Guangtian, *Physica B*, *139/140* (1986) 555.

[6] Wang Qiuping, Lun Lijun, Zhang Dingzheng, Chi Yuanbin and Wang Lizhong, *J. Phys.: Condens. Matter*, *4* (1992) 6941.