JOURNAL OF MATERIALS SCIENCE **40** (2005) 3725–3728

The structure and luminescence characteristics of LaOBr: $Tb^{3+}(Dy^{3+})$

JINGHAI YANG
Institute of Condensed State Physics, Jilin Normal University, Siping 136000, People's Republic of China; College of Materials Science and Engineering, Jinlin University, Changchun, 130023, People's Republic of China
E-mail: jhyang@jlnu.edu.cn

JIE GONG, HOUGANG FAN, LILI YANG
Institute of Condensed State Physics, Jilin Normal University, Siping 136000, People's Republic of China

The rare earth luminescence materials LaOBr:$Tb^{3+}(Dy^{3+})$ were synthesized at high temperature (HT) and treated by high pressure (HP), and the structure and luminescence characteristics of the samples were studied. The results show that the co-doping with Dy^{3+} may make the luminescence strength increase greatly and energy transfer takes place between Tb^{3+} and Dy^{3+} cations. The XRD results show that no obviously structural change occurs after the HP and HT treatment.

1. Introduction

Because of the special electronic properties of rare earth elements, the luminescent materials activated by rare earth ions have rich and varied luminescence characteristics [1, 2]. LaOBr: $Tb^{3+}$is a good phosphor applicable to cathodoluminescence and X-ray induced intensifiers [3, 4], but its applicable range has been limited owing to its chemical stability and price. In order to improve the luminescence properties, Holsa *et al.* [5] utilized the principle of energy transfer and sensitized LaOBr:Tb^{3+} with co-doping Ce^{3+}. The results of our experiment show that Ce^{3+}, as a sensitizer, can sensitize Tb^{3+} only when it is excited at certain wavelength. When Ce^{3+} is selectively excited at 365 nm, the Ce^{3+} can sensitize Tb^{3+} and the energy is transferred from Ce^{3+} to Tb^{3+} in principle, when Tb^{3+} is selectively excited at 250 nm, Ce^{3+} centers can quench the transition from $^5D_3$ and $^5D_4$ in Tb^{3+} ions, the energy is transferred from $^5D_3$ levels of Tb^{3+} to Ce^{3+} principally. The experiment result also shows that Ce^{3+} seriously quenches the cathodoluminescence of Tb^{3+} in LaOBr: Tb^{3+}. According to the characteristics of the energy levels of the phosphor, we co-doped Tb^{3+} in the phosphor with Dy^{3+} and found that the brightness of cathodoluminescence is increased by more than 40% in comparison with the phosphor without co-doping Dy^{3+} and the price is also lowered at the same time.

2. Experimental details

The starting materials used are NH_4Br, KBr of analytical purity and rare earth oxide La_2O_3, Tb_4O_7, Dy_2O_3 of 99.99% purity. In order to purify and thoroughly mix the rare earth oxides, they were dissolved in nitric acid, then diluted and filtered. The rare earth oxalates were formed by the addition of oxalic acid to above nitrate solution, after being washed with deionized water. By baking the oxalates at 900°C for 0.5 h, the rare earth oxides were formed after heat decomposition. The appropriate stoichiometric proportions of $La_{(1-x-y)}Tb_yDy_xOBr$ ($y = 0, 0.0075$ and $x = 0, 0.001, 0.003, 0.006, 0.01, 0.03$) were determined, and the mixed samples were prepared by sintering at 950°C for 10 h under carbon atmosphere.

The high temperature, high pressure experiments were carried out using a 500×10^3 kg bulk-type high pressure apparatus. The magnitude of the pressure generated inside the cell was calibrated by electrical changes on the basis of the phase transformations of Bi (2.55, 2.69 and 7.7 GPa) and Ba (5.5 GPa) [2]. The temperature of the samples was controlled by the supplied electric powder through the carbon heater, and calibrated by inserting a Pt 30t% Rh-Pt 6t% Rh thermocouple into the cell. The treated mixture was put into the sample chamber at the press [2], in the range of 2.5–3.0 GPa and 800–950°C, pressure was first applied at the rate of 1.0 GPa min^{-1}, then the temperature was increased at a rate of 200°C min^{-1}; After maintaining the desired high temperature and high-pressure conditions for 20 min, the samples were quenched to room temperature prior to the release of applied pressure, and then the pressure was released.

The X-ray diffraction spectra of above samples were determined with Rigaku D/max RA Cu rotating anode X-ray diffractometer, NaCl was used as an internal standard, and cell parameters were refined by the least square method. The emission and excitation spectra were determined using a M-4 spectrometer and MPF-4 fluorphotometer with a xenon lamp of 150 W, the cathodoluminescent spectra were determined using a Y-2 spectrometer, with voltage 10 kV, and beam current density 1 μA/cm^2, the thickness of sample was 1 mm and the vacuum 0.0133 Pa. The spectra were measured with a photomultiplier in connection with a monochromator and the brightness was measured with a photocell calibrated to the sensitivity of human eyes by means of a filter.

3. Results and discussion

3.1. Structure of LaOBr:Tb^{3+}(Dy^{3+})

XRD analysis shows that the LaOBr:Tb^{3+}(Dy^{3+}) samples have a tetragonal structure, the lattice parameters are $a = b = 0.4155$ nm and $c = 0.7390$ nm, the space group is D^7_{4n}, as given in Fig. 1a. There are two La^{3+} ions, two Br^{1-} and two O^{2-} ions in every lattice cell. The Tb^{3+} and Dy^{3+} may be substituted for La^{3+} sites to form the luminescence center. For the Tb^{3+} center, it has four possible first neighbors of Tb^{3+} or Dy^{3+}, the estimated bond length is 0.3960 nm, it has four second, four third, four fourth and eight fifth neighbors with the bond length of 0.416, 0.557, 0.559 and 0.709 nm respectively.

After HP(3.0 Gpa) and HT(950°C) treatment, the crystal structure of all samples is still tetragonal, the lattice parameters change slightly and changes of the relative intensities of lines in the XRD spectra occur. The lattice parameters of the samples synthesized at atmosphere press and treated by high pressure are given in Table I, and the XRD spectra are displayed in Fig. 1b.

3.2. Emission spectra of LaOBr:Tb^{3+}(Dy^{3+}) excited by cathode ray

The emission spectra of LaOBr:Tb^{3+}(Dy^{3+}) with different concentrations of Dy^{3+} excited by cathode ray were determined; the spectra of LaOBr:Tb$^{3+}_{0.0075}$ with co-doping 0 and 0.01 mol excited by cathode ray were given in Fig. 2. It can be seen from Fig. 2a, two groups of peak in the neighborhood of 417 and 438 nm are corresponding to the transitions of $^5D_3 \sim {}^7F_5$ and $^5D_3 \sim {}^7F_4$ of Tb^{3+}, the peak group at 490 nm comes from the transitions of $^5D_3 \sim {}^7F_1$ and $^5D_4 \sim {}^7F_6$, and the peak group at 545 nm the transition of $^5D_4 \sim {}^7F_5$. Comparing Fig. 2a with Fig. 2b, it can be found that co-doping Dy^{3+} makes the emission from $^5D_3$ decrease, and that from $^5D_4$ enhance obviously, specially the emission of $^5D_4 \sim {}^7F_5$ at 545 nm increases by about 40%. Also in Fig. 2b, a new sharp peak was found at 570 nm, it comes from the transition of $^4F_{9/2} \sim {}^6H_{13/2}$ of Dy^{3+}. It is obvious that co-doping Dy^{3+} makes the emission at violet-blue wavelength weaken and the emission at 545 nm enhance greatly, which is sensitive to human eyes, so makes the total brightness of the phosphor increase.

The luminescence intensity and brightness of LaOBr:Tb$^{3+}_{0.0075}$ co-doping with Dy^{3+} of different concentrations excited by cathode ray are given in Table II.

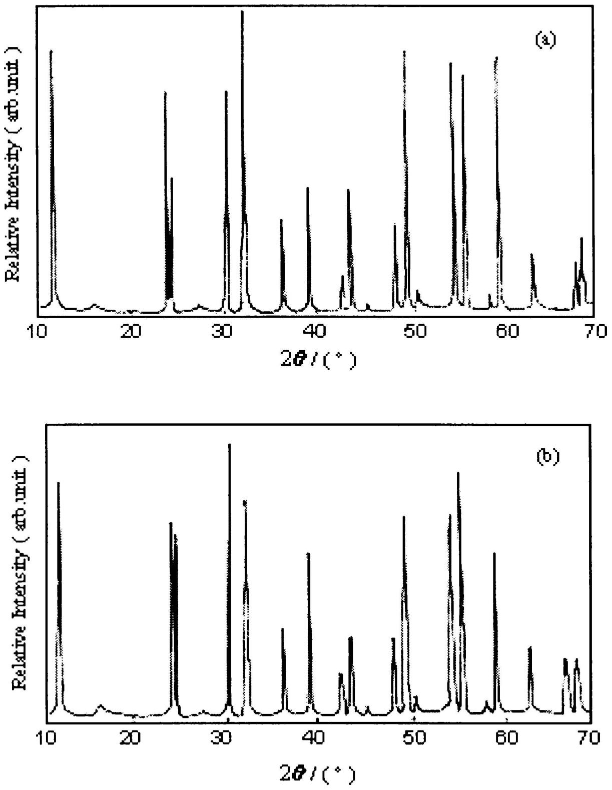

Figure 1 XRD pattern of LaOBr:Tb^{3+} (Dy^{3+}). (a) Sintering at high temperature. (b) Treated by HP & HT.

TABLE I The lattice parameters of LaOBr:Tb^{3+}, Dy^{3+} synthesized at high temperature and treated by high pressure (HP) and high temperature (HT)

Synthesis method	$a = b$/(nm)	c/(nm)
Sintering at HT	0.4155	0.7390
Treated by HP & HT	0.4068	0.7275

3.3. Emission spectra excited by ultraviolet light

The emission spectra of LaOBr:Tb$^{3+}_{0.0075}$ co-doping with 0 and 0.01 moles Dy^{3+} excited by 254 nm ultraviolet light are shown in Fig. 3. From the Fig. 3, one can see that doping Dy^{3+} makes the luminescence of $^5D_4$ of Tb^{3+} ions enhance and the luminescence of $^5D_3$ decrease, which is similar to the results excited by cathode ray, but the luminescence from Dy^{3+} is not observed.

3.4. Luminescence decay

The decay of photoluminescence of the phosphors was measured at 265 nm excitation wave length, the luminescence lifetimes of $^5D_3 \sim {}^7F_5$ and $^5D_4 \sim {}^7F_5$ of Tb^{3+} are given in Table III. The decay time changes

TABLE II Luminescence intensity and brightness of $^5D_3 \sim {}^7F_5$, $^5D_4 \sim {}^7F_5$ of LaOBr:Tb$^{3+}_{0.0075}$ (Dy$_x{}^{3+}$)

	Intensity/a.u.		
Concentration of Dy^{3+}(mol)	$^5D_3 \sim {}^7F_5$	$^5D_4 \sim {}^7F_5$	Brightness/a.u.
0	0.30	0.48	330
0.001	0.25	0.51	355
0.003	0.16	0.52	370
0.006	0.10	0.53	460
0.01	0.06	0.64	470
0.03	0.015	0.32	105
0.08	0.00	0.11	70

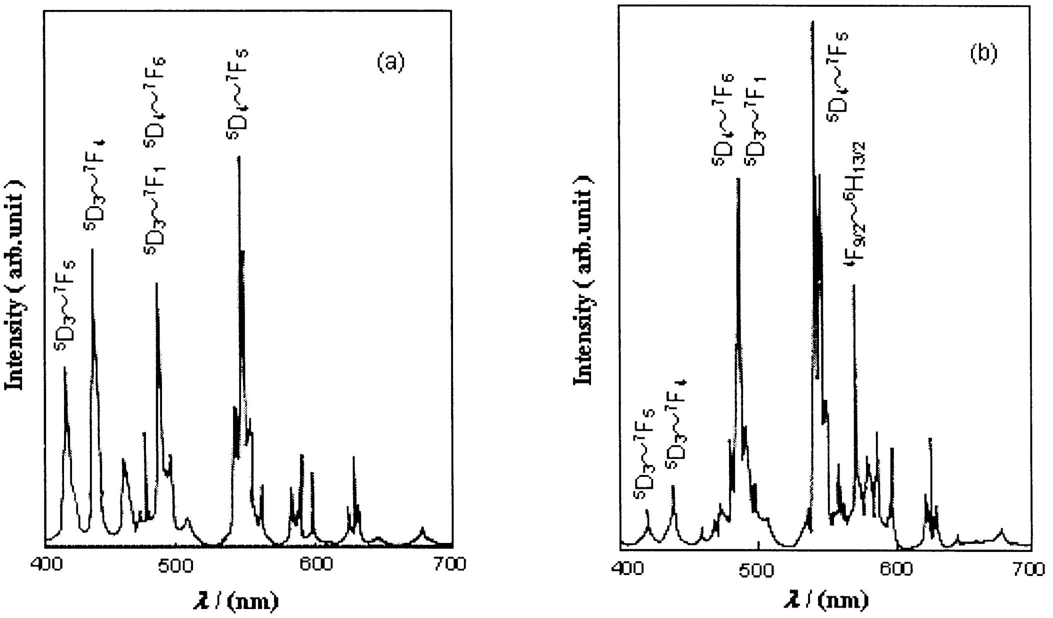

Figure 2 Emission spectra of LaOBr:$Tb^{3+}_{0.0075}$ (Dy^{3+}_x) excited by cathode ray at (a) $x = 0$, (b) $x = 0.01$.

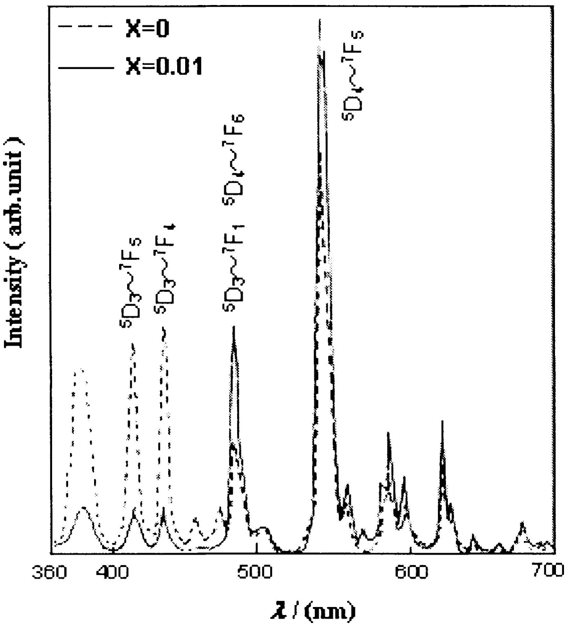

Figure 3 Emission spectrum of LaOBr:$Tb^{3+}_{0.0075}$ (Dy^{3+}_x) excited by ultraviolet light (245 nm).

very quickly in the neighborhood of concentration 0.01 mol of Dy^{3+} for $^5D_3$ lines of Tb^{3+} ions. A similar behavior occurs for $^5D_4$ lines of Tb^{3+} ions around the concentration 0.03 mole of Dy^{3+}. The same trend appears in cathodoluminescence, the concentration quenching takes place in the region of Dy^{3+} concentration from 0.01 to 0.03 mol.

TABLE III Decay time of LaOBr:$Tb^{3+}_{0.0075}$ (Dy^{3+}_x) under 265 nm laser excitation

	Decay time(μs)	
Concentration of Dy^{3+} (mol)	$^5D_3\sim{}^7F_5$	$^5D_4\sim{}^7F_5$
0	230	1280
0.001	221	1250
0.003	176	1240
0.006	166	1200
0.01	71	1200
0.03	10	720
0.08	7.2	500

3.5. Mechanism of energy transfer between Tb^{3+} and Dy^{3+}

An enhancement in brightness is clearly demonstrated following the doping with Dy^{3+}. There are two explanations which are commonly applied to account for such an observation. One is that Dy^{3+} plays the role of sensitizer; another the luminescence of Dy^{3+} itself makes the total brightness increase. Analysis of the emission and excitation spectra of different samples shows that the possibility of Dy^{3+} acting as sensitizer is very small, for the brightness of Dy^{3+} is only the one thirtieth of that of Tb^{3+}, and no excitation spectrum of Dy^{3+} has been found in the spectra of $^5D_4$ of Tb^{3+}, so the main reason of the enhancement of brightness is not Dy^{3+} sensitizing Tb^{3+}.

The photoluminescence of Dy^{3+} itself is also not responsible for the large increment of brightness. As from Fig. 3, the luminescence Dy^{3+} excited by ultraviolet light is only the one thirtieth of that of Tb^{3+}, and there is a sharp peak indeed at 570 nm excited by cathode ray, but according to its width and intensity, it can not make the brightness increase by 40%.

The real reason of the large enhancement of the brightness is that cross relaxation interaction between Dy^{3+} and Tb^{3+} results in resonance energy transfer. From the spectra one can discover that co-doping with Dy^{3+} makes the luminescence region of Tb^{3+} change. When no doping of Dy^{3+}, the luminous range of Tb^{3+} is from ultraviolet 380 nm to green light, and the co-doping of Dy^{3+} makes luminescence in the region of ultraviolet and blue light ($^5D_3\sim{}^7F_J$) weaken, the excitation energy of $^5D_3$ is effectively transferred to the emission of $^5D_4\sim{}^7F_J$, this function has the same effect with the increasing of Tb^{3+} concentration, which

TABLE IV Mean square deviations s of decay time for different l

Dy^{3+}(mol)	l 6	8	10
0	0.019	0.033	0.043
0.001	0.010	0.020	0.031
0.003	0.033	0.038	0.051
0.006	0.020	0.035	0.052
0.01	0.033	0.059	0.081

can be reasonably explained with Hoshina's theory of cross relaxation [6].

The energy level interval of $^6H_{11/2} \sim {}^6H_{15/2}$ of Dy^{3+} is the same as that of $^5D_3 \sim {}^5D_4$ Tb^{3+}, both being 5800 cm^{-1}. The increasing of the concentration of Tb^{3+} and Dy^{3+} ions results in the increase of the interaction of ions, which makes the electrons of Dy^{3+} on the ground state ($^6H_{15/2}$) transmit to the second excitation state ($^6H_{11/2}$), at the same time, the electrons of Tb^{3+} on $^5D_3$ energy state transmit to the $^5D_4$ state, which results in the enhancement of the luminescence of $^5D_4$.

The results of luminescence decay also confirm the conclusion of cross relaxation interaction. As the concentration of Dy^{3+} and Tb^{3+} are not large, according to the theorem of Wigner-Echart [7], the expression for dependence of luminescence intensity on time is given as

$$I(t) = I_0 \exp\left\{-(t/\tau_0) - (C/C_0)\Gamma(1 - 3/l)(t/\tau_0)^{(3/l)}\right\} \quad (1)$$

where I_0 is the intensity at $t = o$, τ_0 is the decay time of Tb^{3+} photoluminescence without doping of Dy^{3+}, Γ is Gamma function, C the concentration of accepter ions, C_0 the critical concentration defined as $C_0^{-1} = 4\pi R_0^3/3$, R_0 is critical distance. The value of l may be 6,8 or 10 according to the type of multipole interaction between the acting ions, $l = 6$ represents the interaction between electric dipole and electric dipole, $l = 8$, electric dipole-electric quadrupole and $l = 10$ electric quadrupole-electric quadrupole.

In order to find out the value of l, the experimental results of luminescence decay are compared with that obtained from formula (1), and for different l the mean square deviation s is calculated and given in Table IV.

From Table IV, it can be seen that $l = 6$ provides the best agreement between the experimental data and the theoretical value. Therefore, energy transfer between Dy^{3+} and Tb^{3+} ions is mainly due to electric dipole-electric dipole interactions.

C_0 value can be obtained by fitting the experimental data, for $R_0^3 = 3/(4\pi C_0)$, R_0 can be easily obtained. The calculation shows that critical distance R_0 equals to 1 nm, when the concentration of Dy^{3+} is 0.01 mol. The R_0 has different values from 0.96 to 1.06 nm as the concentration of Dy^{3+} ions changes.

4. Conclusions

(1) The luminescence of LaOBr:Tb^{3+} can be enhanced by 40% by co-doping with Dy^{3+}, and the optimum concentration of Dy^{3+} is 0.01 mole.

(2) The energy transfer between Tb^{3+} and Dy^{3+} is in the form of cross relaxation interaction, which is of a character of electric dipole-electric dipole interaction.

(3) The cross relaxation of Tb^{3+} and Dy^{3+} transforms the light in the region of violet-blue into that of green, which is more sensitive to human eyes.

(4) The critical distance of cross relaxation is determined as about 1 nm.

Acknowledgement

This work was supported by the science and technology Bureau of Jilin province of China (Item No. 20020615) and the overseas-back scholar program of Ministry of Personnel of China.

References

1. HONGJIAN LIU, YIFENG WANG, JINGHAI YANG and WEHUI SU, *J. Alloy Comp.* **191** (1993) 1.
2. JINGHAI YANG, YIFENG WANG, HONGJIAN LIU and WENHUI SU, Chin. *J. High Pres. Phys.* **3**(3) (1989) 1983.
3. CHUAOSU SHI, *Chin. J. Rare Earth* (3) (1982) 17.
4. G. BLASSE, *Recl. Trav. Chim. Phys-bas* **105** (1986) 143.
5. J. HOLSA, M. LEAKELA and L. NIMISTA, *J. Solid State Chem.* **37** (1981) 267.
6. T. HOSHINA, *Jpn. J. Appl. Phys.* **6**(10) (1967) 1203.
7. G. H. DIEKE, "Spectra and Energy Level of Rare Earth Ions in Crystals" (John Wiley, New York, 1968).

Received 22 March 2004
and accepted 10 February 2005