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Investigation of thermoluminescence in $Li_2B_4O_7$ phosphors doped with Cu, Ag and Mg

XIONG ZhengYe[1,2†], TANG Qiang[2] & ZHANG ChunXiang[2]

[1] College of Science, Guangdong Ocean University, Zhanjiang 524088, China;
[2] School of Physics Science and Engineering, Sun Yat-sen University, Guangzhou 510275, China

$Li_2B_4O_7$ (LBO):Cu,Ag,Mg phosphors have been prepared by the sintering technique. The roles of the Ag and Mg dopants in the phosphors have been studied using the methods of thermoluminescence (TL) glow curves and TL 3D spectra. The results indicated that proper concentrations of Ag and Mg can enhance the TL of LBO:Cu. It was also indicated that the intensity of TL peak at ~130℃ is reduced with the increasing Ag concentration, and enhanced with the increasing Mg concentration. From the TL 3D spectra, three emission bands (λ_1 = 421 nm, λ_2 = 380 nm, λ_3 = 350 nm) were observed: the intensity of low energy emission band is reduced and that of the high energy is enhanced with the increasing dopant Ag; on the contrary, the intensity of low energy emission band is enhanced and that of the high energy one is reduced with the increasing dopant Mg.

thermoluminescence, spectra, borate lithium

$Li_2B_4O_7$ phosphors with an effective atomic number Z_{eff} = 7.3 are very close to that of biological tissue 7.4, thus attracting much attention[1]. The first TL material based on lithium borate which was introduced in dosimetry was $Li_2B_4O_7$:Mn phosphor with low TL sensitivity caused partly by the emission in the 600 nm region of the spectra, far from the response region of most photomultipliers[2]. The use of copper activator instead of manganese in lithium borate overcomes the drawback of poor TL sensitivity, and TL emission spectra are about 360 nm[3]. However, this phosphor is produced in powder, which is inconvenient for the routine dosimetric use[4].

$Li_2B_4O_7$:Cu,In and $Li_2B_4O_7$:Cu,In,Ag in the form of sintered pellets were prepared at the end of the 20th century. The sintered pellets are tissue equivalent to photon radiation and have a wide linear dose response range with a TL sensitivity which is similar to that of LiF:Mg,Ti, but these TL materials are sensitive to light and the room temperature fading is obvious[1,4]. The TL materials based on $Li_2B_4O_7$ are very promising and attract people to investigate deeply[5,6].

The OSL (Optical stimulated luminescence) characteristic[7] and bleach[8] have been studied and the roles of dopants Ag and Mg in $Li_2B_4O_7$:Cu are discussed in this study.

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†Corresponding author (email: stsxzy@mail.sysu.edu.cn or xiongzhengye@tom.com)
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1 Materials and methods

1.1 Preparation

The dopant Cu (0.02%wt) was added into $Li_2B_4O_7$. After the admixture was made into even compound, the co-dopants Ag and Mg was added into it. The concentration of Ag is 0.01%, 0.02%, 0.05%, 0.1%, 0.2% and 0.5%, and that of Mg is 0.01%, 0.02%, 0.05% and 0.1%. After the admixtures were made into even compounds, the pellets were prepared by a cold pressing method of the even compounds and sintered for 2 h at 800℃.

1.2 TL measurements

The examined phosphors were exposed to ^{137}Cs γ rays at the dose of 60 mGy by FJ417 radiacmeter (manufactured by Beijing Nuclear Instrument Factory). The TL measurements were carried out by the Model 2000 TL Reader with a heating rate of 5℃/s. The TL glow curves of $Li_2B_4O_7$:Cu0.02%, Ag*X*% (*X* = 0, 0.02, 0.1, 0.2) are given in Figure 1(a), and those of $Li_2B_4O_7$:Cu0.02%,Ag0.02%,

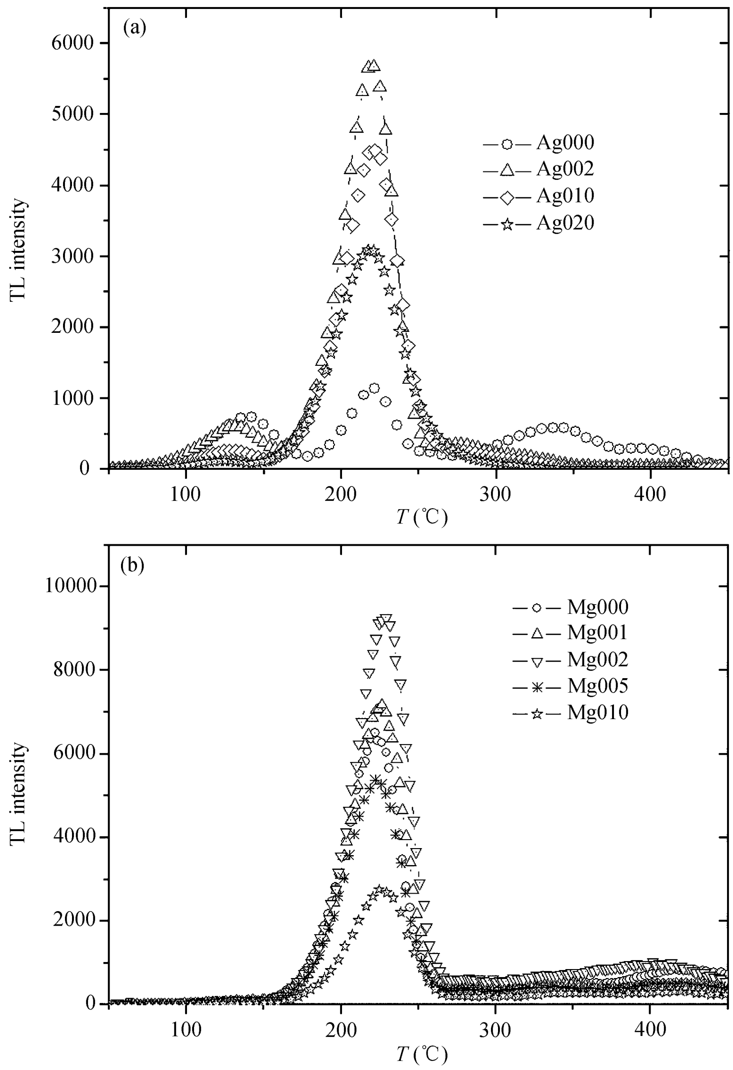


Figure 1 The glow curves of phosphors. (a) $Li_2B_4O_7$:Cu0.02%,Ag*X*%; (b) $Li_2B_4O_7$:Cu0.02%,Ag0.02%,Mg*X*%.

Mg*X*% (X = 0, 0.01, 0.02, 0.05, 0.1) are given in Figure 1(b).

1.3 TL 3D spectra measurements

The phosphors were exposed to ^{90}Sr β rays at the dose of 60 Gy by RISØTL/OSL DA-15B/C Reader. The TL 3D spectra measurements were carried out on the TL 3D spectra Reader[9]. The TL 3D spectra of $Li_2B_4O_7$:Cu0.02%,Ag0.02% phosphor are given in Figure 2, which is similar to that of the other phosphors in this study.

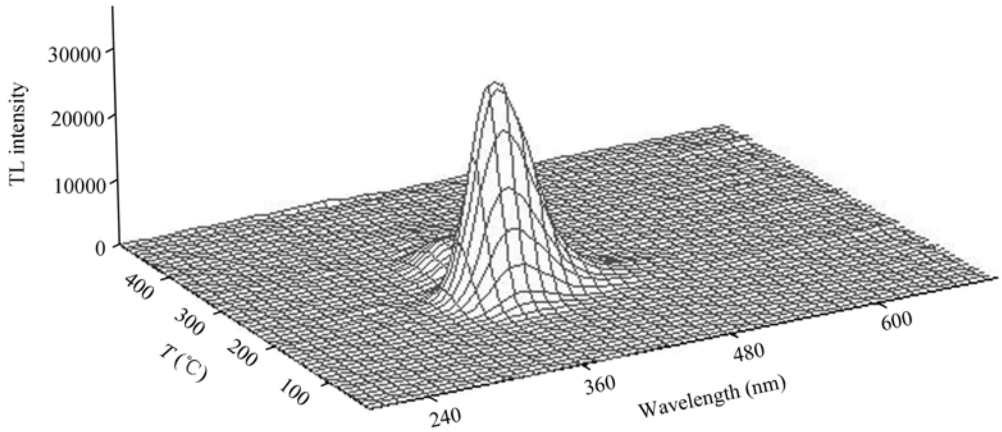


Figure 2 The TL 3D spectra of $Li_2B_4O_7$:Cu0.02%,Ag0.02% phosphor.

2 Results and discussion

2.1 The effect of Ag on the glow curve of $Li_2B_4O_7$:Cu0.02% phosphors

In Figure 1(a), the fact can be seen that the primary glow peak of the phosphors is at about 219℃, and can be enhanced by doping an appropriate quantity of silver. The glow peaks can be fitted using the general order kinetics equation[10]:

$$I(t) = n_0 S \exp(-E/KT)\left[(b-1)(S/\beta)\int_{T_0}^{T}\exp(-E/KT')\mathrm{d}T' + 1\right]^{-b/(b+1)}, \tag{1}$$

where b is the kinetics order, and $1 \leqslant b \leqslant 2$; E is the activation energy of the traps; S is the frequency factor; n_0 is the concentration of the electrons seized by traps at the temperature T_0; β= 5℃/s, is the heating rate. Computer deconvolution can be applied to all the glow curves of phosphors, and then four kinetic parameters can be obtained. The fitted curves of LBO:Cu0.02% and LBO:Cu0.02%, Ag0.05% are given in Figure 3, and these curves are similar to that of other phosphors in this study.

Five glow peaks can be obtained when the glow curve of LBO:Cu0.02% phosphor is deconvolved by eq. (1), and the corresponding temperature values are about 130℃, 219℃, 260℃, 335℃ and 402℃. The intensity of TL peaks above 270℃ is reduced with the increasing Ag concentration. The kinetic parameters of the primary glow peak (~219℃) are listed in Table 1.

The fact can be obtained from Table 1 that the activation energy E and the frequency factor S corresponding to the glow peak at ~219℃ have a decreasing trend with the increasing Ag concentration, and E and S are decreasing with the increasing Ag concentration.

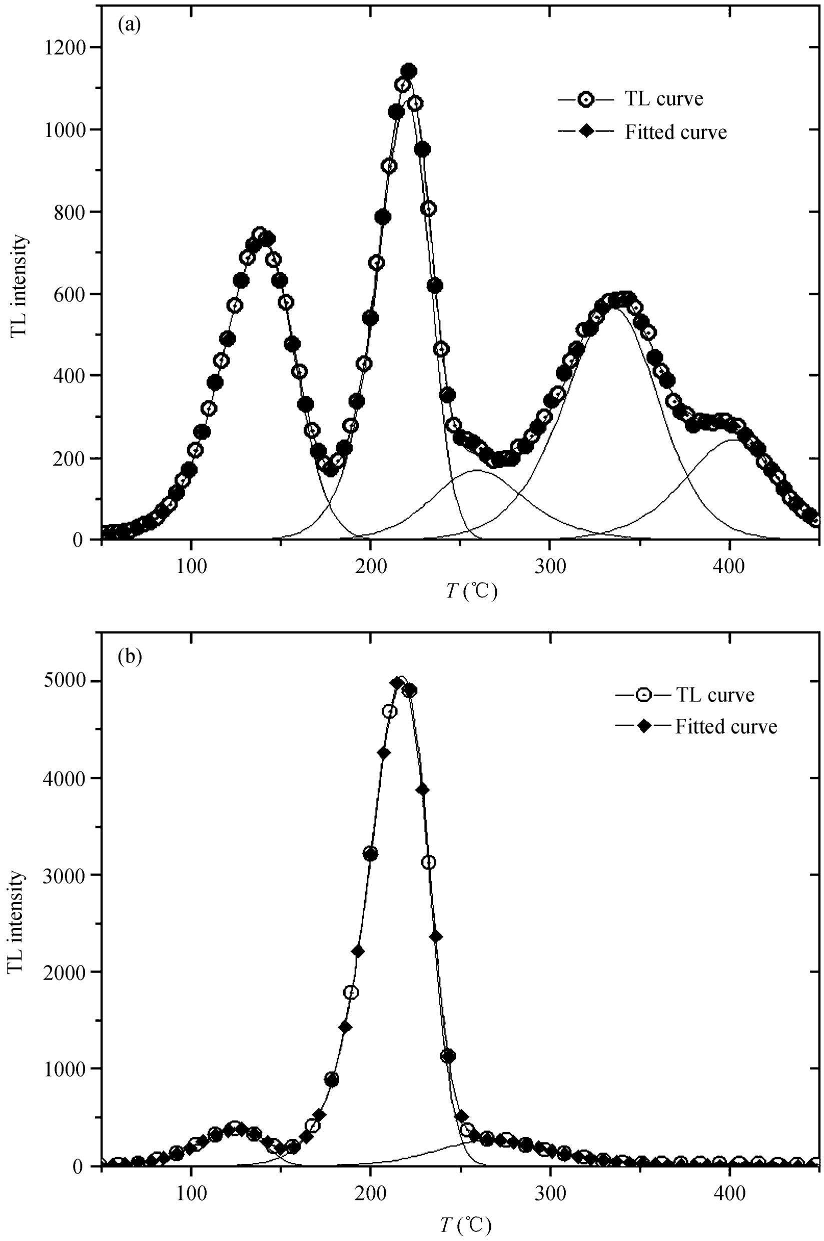


Figure 3 The fitted glow curves of LBO:Cu0.02% and LBO:Cu0.02%,Ag0.05% phosphors. (a) LBO:Cu0.02%; (b) LBO:Cu0.02%,Ag0.05%.

Table 1 The kinetic parameters of LBO:Cu0.02%,Ag*X*% phosphors

Ag (%)	E (eV)	log$S$	n_0	b
0	1.55	15.41	8259.88	1.21
0.01	1.37	13.64	42381.60	1.21
0.02	1.34	13.24	47159.50	1.09
0.05	1.31	12.97	43329.40	1.14
0.1	1.30	12.71	40308.80	1.21
0.2	1.18	11.52	33134.50	1.42
0.5	1.13	11.05	32853.10	1.66

The relation between the glow peak intensity and the concentration of Ag can be shown in Figure 4.

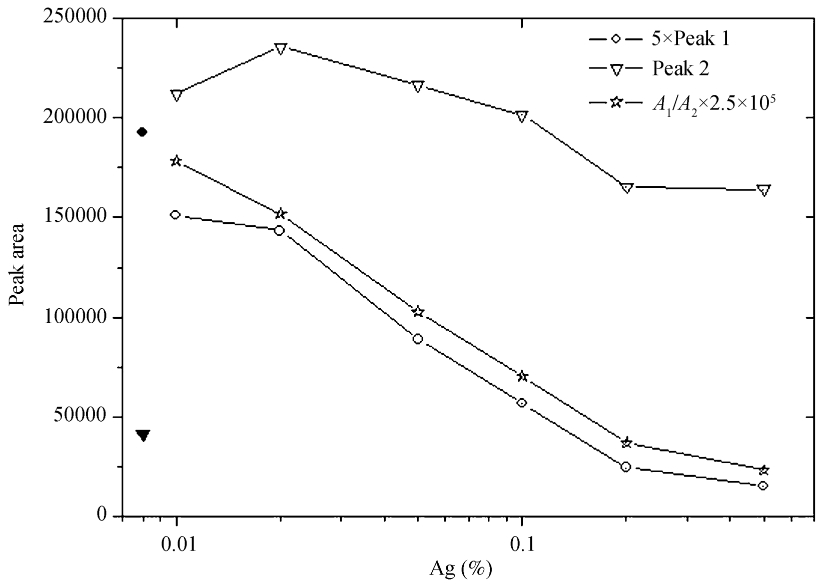


Figure 4 The effect of Ag on the two glow peaks. Peak 1 is the TL peak at ~130℃ and Peak 2 is the TL peak at ~219℃.

The solid points represent the TL glow peaks area of LBO:Cu0.02% phosphor (the concentration of Ag is 0), and the area of glow peak at ~130℃ is magnified about 5 times. The fact can be seen that dopant Ag can enhance the intensity of TL peak at ~219℃ and reduce that at ~130℃, and it is most obvious when the concentration of Ag is about 0.02%. It also gives the relative intensity of TL at ~130℃ (the quotient of the area of TL peak at ~130℃ is divided by that of TL peak at ~219℃, and then the result is magnified 2.5×10^5 times). The fact can be seen that the relative intensity of TL at ~130℃ is reduced with the increasing Ag concentration.

2.2 The effect of Mg on the glow curve of LBO:Cu0.02%,Ag0.02%

Five glow peaks can be obtained when the glow curve deconvolution by eq. (1) was applied to LBO:Cu0.02%,Ag0.02%,Mg*X*% (*X* = 0.01, 0.02, 0.05, 0.1) phosphors. All the kinetic parameters of these phosphors are similar to that of LBO:Cu0.02%, except n_0 related to the TL intensity. The relation between the glow peaks intensity and the concentration of Mg can be shown in Figure 5.

The area of glow peak at ~130℃ is magnified 80 times. The fact can be seen that both TL glow peaks (at ~130℃ and ~219℃) reach the maximum when the concentration of Mg is 0.02%, and the intensity reduces when the concentration of Mg keeps on increasing. It also gives the relative intensity of TL at ~130℃ (the quotient of the area of TL peak at ~130℃ is divided by that of TL peak at ~219℃, and then the result is magnified 1.5×10^7 times). The fact can be seen that the relative intensity of TL at ~130℃ is increased with the increasing Mg concentration.

The $Li_2B_4O_7$ lattice belongs to space group $I4_1cd$, and the measured lattice parameters are $a = b = 0.9479$ nm, $c = 1.028$ nm. Some of lithium atoms are in the tetrahedral lacunas which have little aberrance, and the other lithium atoms are in the oxygenic octahedral lacunas which have much aberrance[11]. When the dopant atoms with large radii come into LBO lattice, the lattice will be distorted. The length of B-O bond in some complexes (BO_3) possibly decreases. The lacunas which

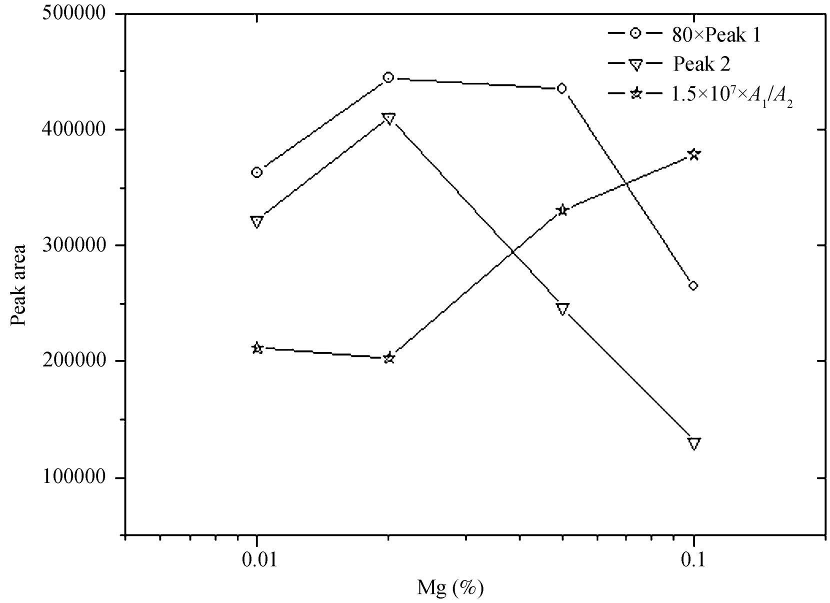


Figure 5 The effect of Mg on the two glow peaks. Peak 1 is the TL peak at ~130℃ and Peak 2 is the TL peak at ~219℃.

contain the dopant atoms are not tetrahedrons or octahedrons any longer, the number of oxygenic atoms which bond with the dopant atom can reach 7 or 8, and the bond distances have a large range[12]. When the dopant Mg atoms come into LBO lattice, the complexes (MgO) and (B_2O_3) possibly come into being, especially the latter, which has some relations with the traps corresponding to the TL glow peak at ~130℃.

2.3 The effect of Ag and Mg on TL 3D spectra

It is shown in sec. 1.3 that the emission spectrum of all the phosphors in this study extends from 300 nm to 500 nm, and has its maximum at approximately 380 nm. When it is figured on wave number, the spectrum can be fitted by 2 or 3 Gauss peaks, and the fitted curves are shown in Figure 6.

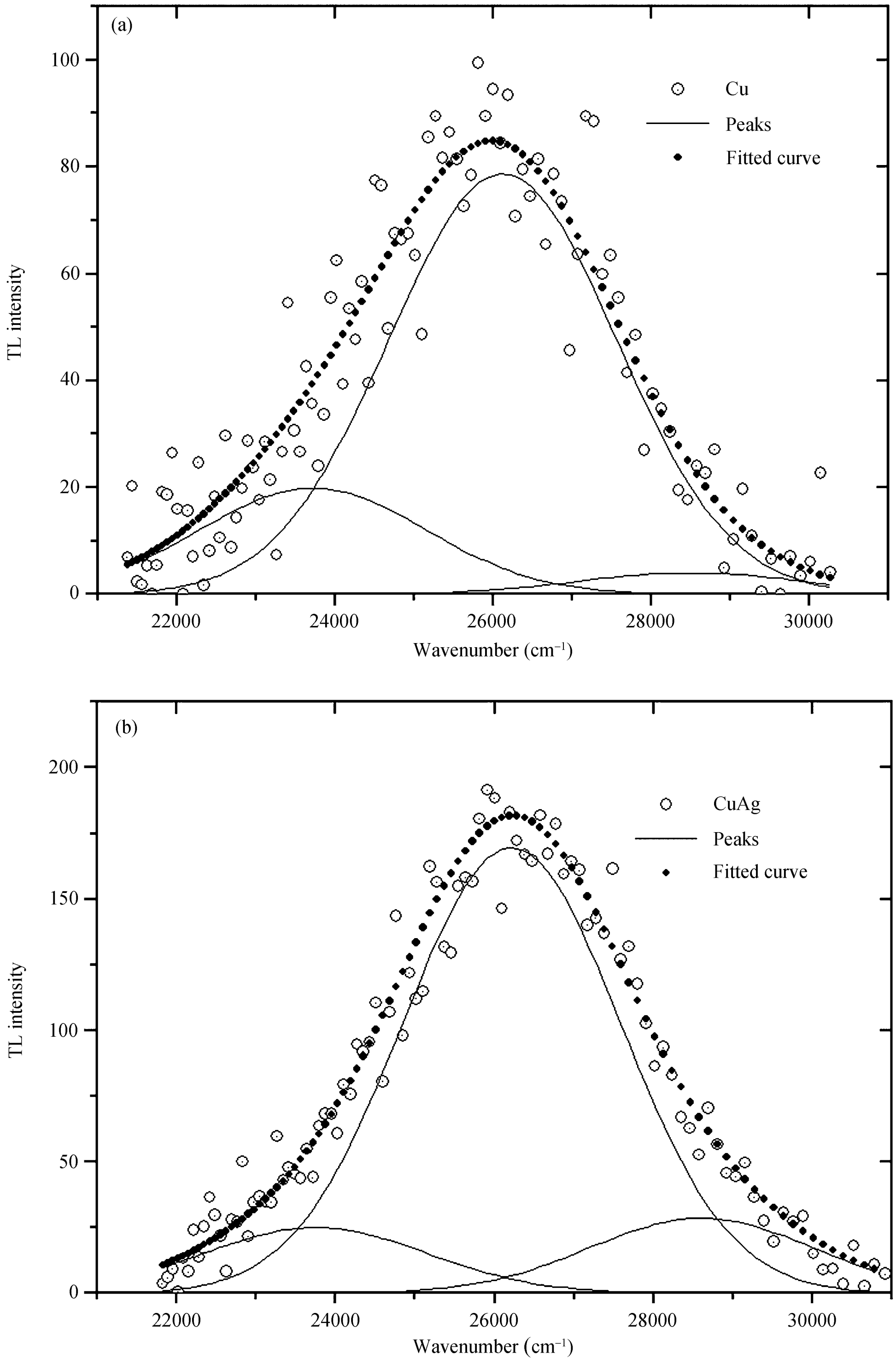
The results show that the emission spectra can be fitted by 3 Gauss peaks ($\tilde{\nu}_1 = 23710$ cm^{-1}, $\lambda_1 =$ 421 nm, $\tilde{\nu}_2 = 26210$ cm^{-1}, $\lambda_2 = 380$ nm, $\tilde{\nu}_3 = 28548$ cm^{-1}, $\lambda_3 = 350$ nm), and the second peak ($\lambda_2 =$ 380 nm) is the maximal one. The relative intensity of the first peak (the quotient of the area of the first peak is divided by that of the second peak) and that of the third peak (the quotient of the third peak is divided by that of the second peak) are shown in Figure 7.

The fact can be found out in Figure 7 that the intensity of low energy emission band is reduced and that of high energy emission band is enhanced with the increasing dopant Ag; on the contrary, the intensity of low energy emission band is enhanced and that of the high energy one is reduced with the increasing dopant Mg. It is known that the peaks showing up in the glow curves of LBO phosphors are related to the relaxation of exited copper Cu+ ions, according to the following mechanisms[13]:

$$\mathrm{Cu^{++}} + \text{electron} \to (\mathrm{Cu^+})^* \to \mathrm{Cu^+} + h\nu. \tag{2}$$

The relaxation has been ascribed to a $3d^9 4s \to 3d^{10}$ transition, and the value of the second peak

($\tilde{\nu}_2$ = 26210 cm^{-1}, λ_2 = 380 nm) agrees satisfactorily with the 381 nm peak corresponding to one of the four wavelengths related to the transition $3d^9 4s \rightarrow 3d^{10}$ ($^1D_2 \rightarrow {}^1S_0$).



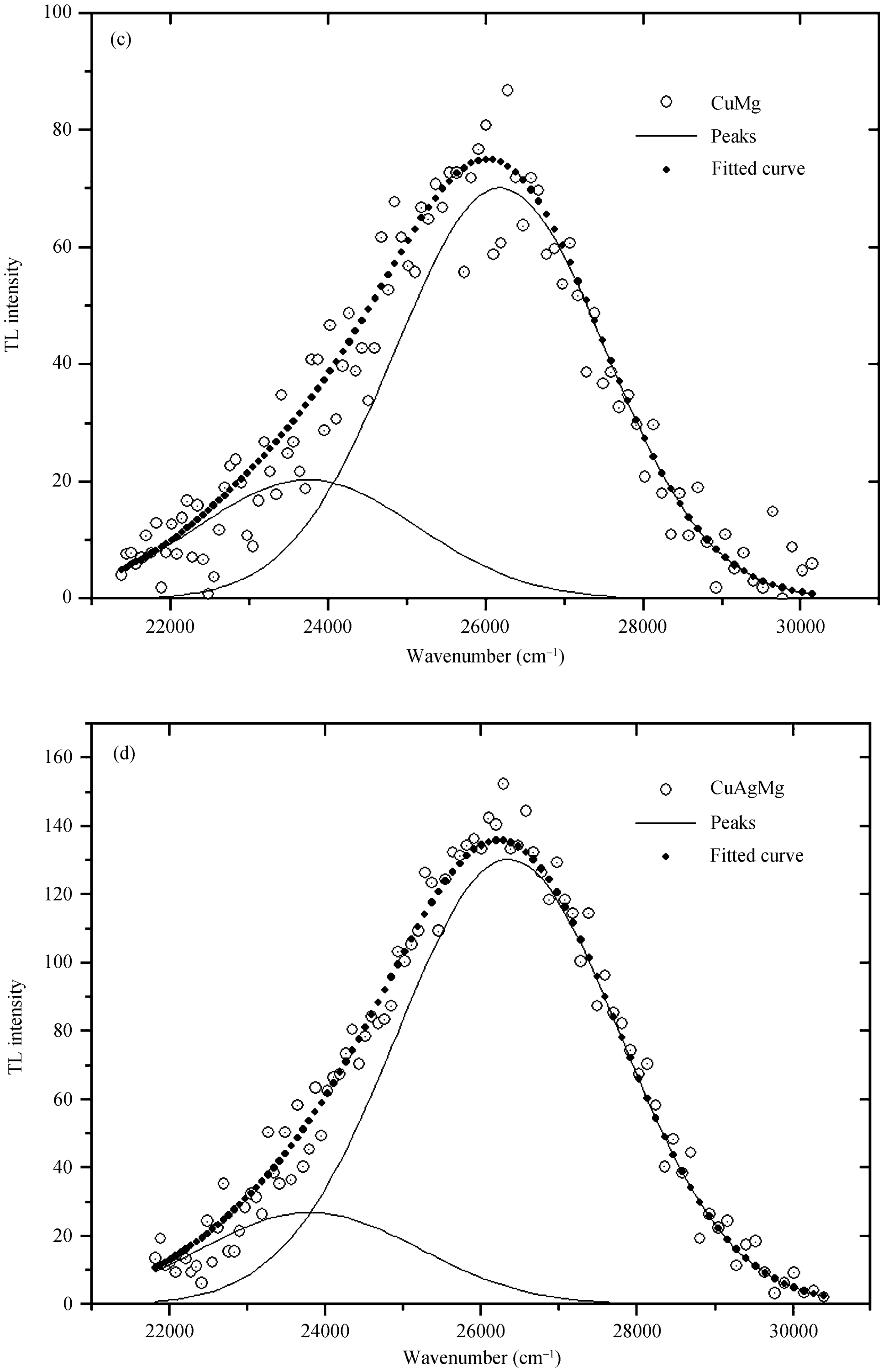


Figure 6 Gauss fitting of the emission spectrum. (a) LBO:Cu0.02%; (b) LBO:Cu0.02%,Ag0.02%; (c) LBO:Cu0.02%,Mg0.02%; (d) LBO:Cu0.02%,Ag0.02%,Mg0.02%.

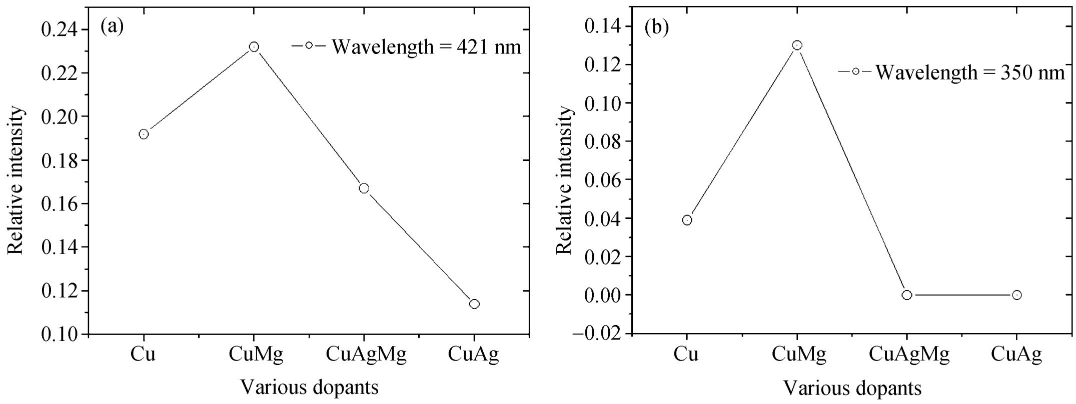


Figure 7 The relative intensity of emission spectra peak of the phosphors doped with different dopants. (a) The first emission band ($\lambda = 421$ nm); (b) the third emission band ($\lambda = 350$ nm).

Copper doped borate glass has a peak at about 448 nm[14], which is similar to the emission spectrum of LiF containing Cu^{++} that has its maximum at approximately 425 nm. The suggested mechanism is

$$Cu^{+} + \text{hole} \rightarrow (Cu^{++})^{*} \rightarrow Cu^{++} + h\nu. \quad (3)$$

Since the complex B_2O_3 is one of the structural patterns of glassy borate whose emission spectrum extends from 400 to 600 nm, it is possible that Cu^{++} ions are involved in the TL processes. As mentioned above, when the dopant Mg atoms come into LBO Lattice, the complexs MgO and B_2O_3 possibly come into being, and enhance the TL emission of Cu^{++} ion. That is to say, the low energy emission band is enhanced.

It was reported that the emission spectrum of lithium borate doped with Cu is nearly at 360 nm[3], and the emission spectrum of LBO:Cu,In is nearly at 420 nm[8]. That can be suggested that the relative intensity of 3 emission bands is changed because of preparation process and some metal-line material, especially the latter.

3 Conclusions

Among the LBO:Cu0.02% phosphors doped with Ag, the activation energy *E* and the frequency factor *S* corresponding to the glow peak at ~219℃ have a decreasing trend with the increasing Ag concentration.

Dopant Ag can enhance the intensity of TL peak at ~219℃ and reduce that of TL peak at ~130℃, which is most obvious when the concentration of Ag is about 0.02%.

Both TL glow peaks (at ~130℃ and ~219℃) reach the maximum when the concentration of Mg is 0.02% in LBO:Cu0.02%,Ag0.02% phosphors, the TL intensity of glow peaks at ~219℃ reduces and the relative intensity of glow peak at ~130℃ keeps on increasing when the concentration of Mg keeps on increasing.

The emission spectra can be fitted by 3 Gauss peaks ($\tilde{\nu}_1$ = 23710 cm^{-1}, λ_1 = 421 nm, $\tilde{\nu}_2$ = 26210 cm^{-1}, λ_2 = 380 nm, $\tilde{\nu}_3$ = 28548 cm^{-1}, λ_3 = 350 nm), and the second peak (λ_2 = 380 nm) is the maximal one. The intensity of low energy emission band is reduced and that of the high energy one is enhanced with the increasing dopant Ag; on the contrary, the intensity of low energy emission band is enhanced and that of the high energy one is reduced with the increasing dopant Mg.

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