

## Enhanced luminescence through ion-doping-induced higher energy phonons in $\text{GdTaO}_4:\text{Eu}^{3+}$ phosphor

Bo Liu,<sup>1</sup> Mu Gu,<sup>1,a)</sup> Xiaolin Liu,<sup>1</sup> Kun Han,<sup>1</sup> Shiming Huang,<sup>1</sup> Chen Ni,<sup>1</sup> Guobin Zhang,<sup>2</sup> and Zeming Qi<sup>2</sup>

<sup>1</sup>Laboratory of Waves and Microstructure Materials, Pohl Institute of Solid State Physics, Tongji University, Shanghai 200092, People's Republic of China

<sup>2</sup>National Synchrotron Radiation Laboratory, Hefei 230027, People's Republic of China

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The photoluminescence enhancement effect of Li-, Zn-, or Al-doped  $\text{GdTaO}_4:\text{Eu}^{3+}$  is investigated at 20 and 295 K. The underlying reason of luminescence enhancement by ion doping is revealed, and a mechanism of the enhancement based on the temperature effect is proposed. It can be safely concluded that the photoluminescence enhancement effect originates from temperature enhancement effect, which can be further strengthened by ion-doping-induced higher energy phonons, which are demonstrated by infrared transmittance spectra. This can reasonably explain why the photoluminescence is remarkably enhanced by ion-doping in  $\text{GdTaO}_4:\text{Eu}^{3+}$  phosphor at 295 K rather than at 20 K. © 2009 American Institute of Physics. [DOI: 10.1063/1.3079413]

Trivalent europium ion due to its high emission efficiency is extensively used as activator in luminescent materials in the fields of display and detection.<sup>1,2</sup> In recent years, a promising material of  $\text{GdTaO}_4:\text{Eu}^{3+}$  was proposed and investigated<sup>3</sup> because of its potential applications in x-ray imaging systems and flat panel display devices due to its high luminescence efficiency, high density of 8.84 g/cm<sup>3</sup>, stable chemical properties, strong irradiation hardness, good x-ray absorption, and the red emission of  $\text{Eu}^{3+}$  ion coinciding with the maximum efficiency of charge coupled device detector.<sup>4-6</sup>

It is reported that Li-doping in  $\text{GdTaO}_4:\text{Eu}^{3+}$ ,  $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ ,<sup>8-10</sup> and  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  (Ref. 11) can lead to a great improvement in luminescence brightness. In fact, besides Li ion, doping other ions such as Al or Zn can also significantly enhance the luminescence in  $\text{GdTaO}_4:\text{Eu}^{3+}$ .<sup>7</sup> The enhancement effect by doping ions might commonly be interpreted as the following reasons in the literatures. For example, Li-doping can act as a flux to improve crystallinity and reduce internal reflections caused by rougher surfaces in thin-film samples.<sup>9</sup> It is also proposed that the occupation of  $\text{Gd}^{3+}$  sites by smaller  $\text{Li}^+$  ions could create a number of oxygen vacancies, which may act as a sensitizer for the effective energy transfer.<sup>12</sup> In fact, the enhancement effect is not limited in thin-film samples but also occurs in nanosized phosphors.<sup>13</sup> In addition, the enhancement effect of various doping ions could even be associated with the effective ionic radius of doping ions and the mismatch in electronegativity between doping ions and Gd ion.<sup>7</sup>

However, up to now, the explicit reason for the enhanced luminescence by doping ions is not very clear, though some possible explanations are proposed as mentioned above. In the present letter, we focus on the enhancement effect of Li-, Zn-, or Al-doping, which exhibits the most significant enhancement effect in  $\text{GdTaO}_4:\text{Eu}^{3+}$  photoluminescence (PL). The obvious temperature dependence on the PL for  $\text{GdTaO}_4:\text{Eu}^{3+}$  and Li-, Zn-, or Al-doped  $\text{GdTaO}_4:\text{Eu}^{3+}$  is

found. Based on the luminescence spectra at low temperature and room temperature, combining with the infrared (IR) spectra, a mechanism of enhancement effect by rising temperature and doping ions is proposed.

$\text{GdTaO}_4:\text{Eu}^{3+}$  (8%) and  $\text{Li}^+$  (8%)-,  $\text{Zn}^{2+}$  (8%)-, or  $\text{Al}^{3+}$  (6%)-doped  $\text{GdTaO}_4:\text{Eu}^{3+}$  (8%) phosphors were prepared by solid-state reaction using the raw materials  $\text{Gd}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Al}_2\text{O}_3$  with 99.99% purity. The raw materials were mixed and heated up to 1200 °C from room temperature at a rate of 4 °C/min and kept as such for 3 h. The samples were checked by x-ray analysis. The x-ray diffraction patterns revealed that the samples belong to monoclinic structure with space group of  $P2_1/a$  ( $M'$ -type) from the powder diffraction file.<sup>7</sup> The excitation and emission spectra were measured at the VUV Station of National Synchrotron Radiation Laboratory, Hefei, China. The typical spectral resolution of the primary monochromator (1 m Seya-Namioka) and the secondary monochromator (Spectrapro-275) is 0.4 and 2 nm, respectively. The pressure in the vacuum chamber during the measurements was  $1 \times 10^{-4}$  Pa. The excitation and emission spectra were detected by a Hamamatsu H5920-01 photomultiplier. A 300 nm cutoff filter was used to prevent the incident light entering into the secondary monochromator. The excitation spectra were corrected for the photoflux of the excitation beam using the excitation spectrum of sodium salicylate as standard. The spectra were measured at 20 and 295 K. The IR transmittance spectra for the  $\text{GdTaO}_4:\text{Eu}^{3+}$  and Li-, Zn-, or Al-doped  $\text{GdTaO}_4:\text{Eu}^{3+}$  were measured by a Bruker Tensor 27 Fourier-transform IR spectrometer.

The emission spectra for  $\text{GdTaO}_4:\text{Eu}^{3+}$  and Li-doped  $\text{GdTaO}_4:\text{Eu}^{3+}$  at 20 and 295 K are shown in Fig. 1. The emission lines all belong to the transition of  $\text{Eu}^{3+}$   $^5D_{J(J=0,1,2,3)} \rightarrow ^7F_{J(J=0,1,2,3,4)}$ . As shown in Fig. 2, the excitation spectra of  $\text{GdTaO}_4:\text{Eu}^{3+}$  and Li-, Zn-, or Al-doped  $\text{GdTaO}_4:\text{Eu}^{3+}$  monitoring 612 nm emission from  $\text{Eu}^{3+}$  ( $^5D_0 \rightarrow ^7F_2$ ) at 20 and 295 K comprise several broadbands and some line structures. The common characteristic of their excitation spectra in Fig. 2 can be summarized as following. The two evident groups of line structures cluster-

<sup>a)</sup>Author to whom correspondence should be addressed. Electronic addresses: mgu@tongji.edu.cn and mgu@mail.tongji.edu.cn.

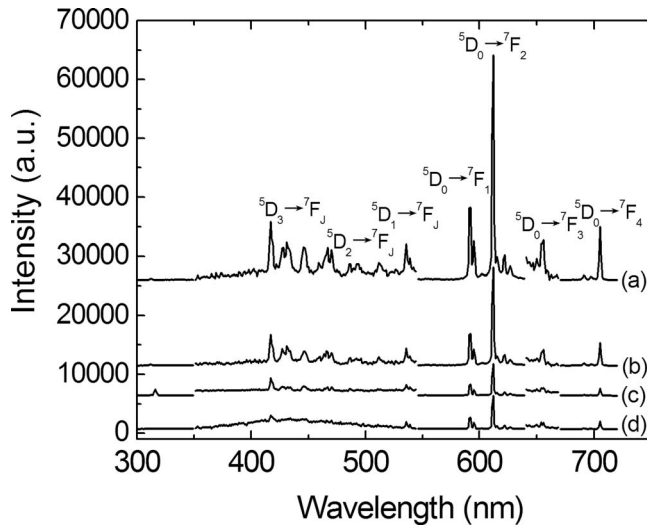


FIG. 1. Emission spectra with the excitation wavelength at 210 nm for Li-doped  $\text{GdTaO}_4:\text{Eu}^{3+}$  at 295 K (a) and at 20 K (d), and  $\text{GdTaO}_4:\text{Eu}^{3+}$  at 295 K (b) and at 20 K (c). The assignment of emission lines is given. The intensities in the ranges of 350–545 and 640–670 nm are magnified by a factor of 15.

ing in the ranges 301–316 and 272–281 nm correspond to the  $4f-4f$  transitions of  $\text{Gd}^{3+}$  from the  $^8S_{7/2}$  ground state to the  $^6P_J$  and  $^6I_J$  excited states, respectively. The weakly line structures in the range 240–260 nm corresponding to the higher energy transitions of  $^8S_{7/2} \rightarrow ^6D_J$  are overlapped with a broadband from 230 to 270 nm, which is characteristic of the charge transfer state (CTS) of  $\text{Eu}^{3+}-\text{O}^{2-}$ . The broadband excitation at 200–230 nm could be ascribed to the CTS of  $\text{TaO}_4$  group. The interband transitions of the  $\text{GdTaO}_4$  host are located at 140–200 nm peaking at 176 nm.

The characteristic emission of  $\text{Eu}^{3+}$  excited through interband,  $\text{TaO}_4$  group CTS,  $\text{Eu}^{3+}-\text{O}^{2-}$  CTS, and characteristic  $\text{Gd}^{3+}$   $4f-4f$  is significantly enhanced when the temperature rises from 20 to 295 K. At low temperature of 20 K, Li-, Zn-, or Al-doping cannot enhance the emission at 612 nm of  $\text{Eu}^{3+}$ , and even an obvious decrease can be found under the

excitation with the wavelength below 220 nm. With the temperature rising to 295 K,  $\text{GdTaO}_4:\text{Eu}^{3+}$  and Li-, Zn-, or Al-doped  $\text{GdTaO}_4:\text{Eu}^{3+}$  all exhibit evident temperature enhancement effect. Furthermore, such temperature enhancement effect shows to be much more remarkable for Li-, Zn-, or Al-doped  $\text{GdTaO}_4:\text{Eu}^{3+}$ , comparing with that of  $\text{GdTaO}_4:\text{Eu}^{3+}$ . For instance, with the excitation of 210 nm, from 20 to 295 K, the emission intensity at 612 nm is magnified by a factor of 2.07 for  $\text{GdTaO}_4:\text{Eu}^{3+}$ , while it is 4.37 for Li-doped  $\text{GdTaO}_4:\text{Eu}^{3+}$ . Thus, it is found that the emission intensity of Li-doped  $\text{GdTaO}_4:\text{Eu}^{3+}$  is stronger than that of  $\text{GdTaO}_4:\text{Eu}^{3+}$  by a factor of 2.03. Therefore, it can be stated that the experimentally observed enhancement effect results from the temperature enhancement effect, and moreover, ion-doping could further magnify such temperature effect. The temperature enhancement effect on the emission of  $\text{Eu}^{3+}$  was also observed in  $\text{YTaO}_4:\text{Eu}^{3+}$  (Ref. 14) and  $\text{GdVO}_4:\text{Eu}^{3+}$ .<sup>15</sup>

The temperature effect can be explained by configurational coordination model shown in Fig. 2 as an inset. Following the excitation to CTS ( $\text{TaO}_4$  CTS or  $\text{Eu}^{3+}-\text{O}^{2-}$  CTS), the energy in CTS can be transferred to  $\text{Eu}^{3+}$ , leading to its excitation of  $^5D_J$  states. Such energy transfer is strongly temperature-dependent since the participation of the vibrational states (phonons) is required in the transfer process. With the rising temperature, the multiphonon-assisted energy transfer process is much more efficient, which can promote the CTS states arriving at the cross between CTS and  $^5D_J$  states and then give rise to the excitation of  $\text{Eu}^{3+} ^5D_J$ .

The rate of multiphonon process with temperature can be governed by<sup>16</sup>

$$W(T) = W(0)(n+1)^p \quad (1)$$

where,  $W(T)$  is the rate at temperature  $T$ ,  $p = \Delta E/h\nu$  is the number of phonons,  $h\nu$  is phonon energy, and  $\Delta E$  is the energy difference between the bottom of CTS parabolic and the cross of CTS and  $\text{Eu}^{3+} ^5D_J$  state parabolic in the configurational coordinate diagram.  $n = [e^{h\nu/kT} - 1]^{-1}$ .  $W(0)$  is the spontaneous rate at 0 K, which can be expressed as

$$W(0) = \beta \exp[-(\Delta E - 2h\nu)\alpha], \quad (2)$$

with  $\alpha$  and  $\beta$  as constants.  $W(0)$  is large for high phonon energy or low  $p$  and temperature-independent.

For a given phonon number  $p$ , the rate of multiphonon-assisted energy process is increased with the rising temperature. This can reasonably explain the enhancement effect on emission intensity with rising temperature. In order to obtain the energy of vibrational modes (phonons), IR transmittance spectra are shown in Fig. 3. The largest phonon energy for the  $\text{GdTaO}_4:\text{Eu}^{3+}$  is about  $800 \text{ cm}^{-1}$ , which is consistent with the report in literature.<sup>17</sup> By Li-, Zn-, or Al-doping some higher energy phonons appear with the highest phonon energy of  $968 \text{ cm}^{-1}$ . Due to the higher phonon energy, less number of phonon ( $p$ ) is required in order to achieve the energy transfer from CTS to  $\text{Eu}^{3+} ^5D_J$  state. Since  $W(0)$  is large for high phonon energy or low  $p$ , the rate of multiphonon-assisted energy process of ion-doped  $\text{GdTaO}_4:\text{Eu}^{3+}$  is expected to be much higher than that of  $\text{GdTaO}_4:\text{Eu}^{3+}$  at given temperature, which in turn leads to a higher multiphonon-assisted energy transfer efficiency and thus a stronger  $\text{Eu}^{3+}$  emission intensity.

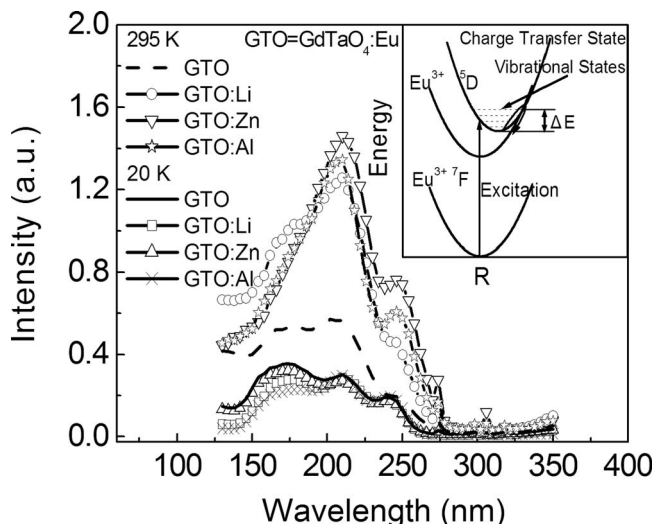


FIG. 2. Excitation spectra with the emission at 612 nm for Li-, Zn-, or Al-doped  $\text{GdTaO}_4:\text{Eu}^{3+}$  at 295 K and at 20 K and  $\text{GdTaO}_4:\text{Eu}^{3+}$  at 295 K and at 20 K. The inset is the configurational coordinate diagram for  $\text{Eu}^{3+}$  in  $\text{GdTaO}_4$ . For the sake of simplification, the multistates for  $^7F_J$  and  $^5D_J$  are ignored.

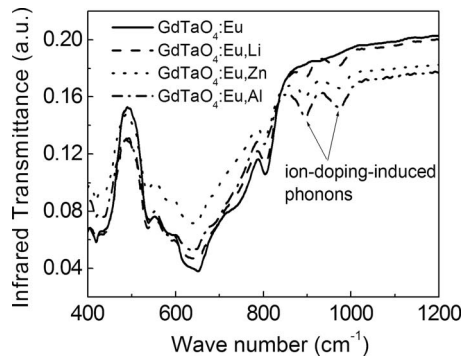


FIG. 3. IR transmittance spectra of  $\text{GdTaO}_4:\text{Eu}^{3+}$  and Li-, Zn-, or Al-doped  $\text{GdTaO}_4:\text{Eu}^{3+}$ .

Concerning the relative intensities of the emission lines from  $\text{Eu}^{3+}$  in Fig. 1, the ratios of emissions from  ${}^5D_0$ ,  ${}^5D_1$ ,  ${}^5D_2$ , and  ${}^5D_3$  under the excitation of 210 nm are 1:0.27:0.04:0.18 and 1:0.23:0.03:0.12 at 20 and 295 K for  $\text{GdTaO}_4:\text{Eu}^{3+}$  and 1:0.20:0.03:0.13 and 1:0.15:0.02:0.11 at 20 and 295 K for Li-doped  $\text{GdTaO}_4:\text{Eu}^{3+}$ . There are similar results for Zn- or Al-doped  $\text{GdTaO}_4:\text{Eu}^{3+}$  spectra that are not shown in Fig. 1. The energy gaps between the  ${}^5D_0$ ,  ${}^5D_1$ ,  ${}^5D_2$ , and  ${}^5D_3$  levels of  $\text{Eu}^{3+}$  ions are around 1416, 2895, and 2429  $\text{cm}^{-1}$ , respectively. Since the phonons are large enough in the samples, these gaps between  ${}^5D_J$  levels can be easily bridged by multiphonon processes, which lead to the nonradiative relaxation from the  ${}^5D_{J(J=1,2,3)}$  to the  ${}^5D_0$  levels. At higher temperature or with higher energy phonons, such multiphonon processes are enhanced. Therefore, the ratio of  ${}^5D_0 \rightarrow {}^7F_J$  to  ${}^5D_{J(J=1,2,3)} \rightarrow {}^7F_J$  emissions is increased with the rising temperature or higher energy phonons.

The ion-doping-induced phonons could be the local vibrational modes, which may be associated with some defects caused by doping ions. However, from the fact that the energies of ion-doping-induced phonons are nearly identical (about 896 and 968  $\text{cm}^{-1}$ ) for Li, Zn, or Al doping samples, the local vibrational modes might be not directly involved with the doping ion itself. The explicit origination is not clear now.

In conclusion, the PL enhancement effect essentially is a consequence of temperature effect, which exhibits enhanced emission as temperature rises. Such temperature effect is

governed by the multiphonon-assisted energy transfer from CTS to  $\text{Eu}^{3+} {}^5D_J$  states. Some vibrational modes with higher energy phonons induced by ion-doping remarkably increase the rate of multiphonon-assisted energy transfer and thus significantly enhance the PL intensity of ion-doped  $\text{GdTaO}_4:\text{Eu}^{3+}$  at 295 K compared with  $\text{GdTaO}_4:\text{Eu}^{3+}$ . The higher energy phonons are demonstrated by the measurement of IR transmittance spectra. Therefore, it is concluded that PL enhancement effect comes from temperature effect, which can be strengthened by ion-doping-induced higher energy phonons.

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