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Luminescence properties of efficient X-ray phosphors of $YBa_3B_9O_{18}$, $LuBa_3(BO_3)_3$, α-$YBa_3(BO_3)_3$ and $LuBO_3$

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Abstract

The samples of $YBa_3B_9O_{18}$, $LuBa_3(BO_3)_3$, α-$YBa_3(BO_3)_3$ and $LuBO_3$ powders have been synthesized by the solid-state reaction methods at high temperature and their X-ray excited luminescent properties were investigated. All the studied materials show a broad emission band in the wavelength range of 300–550 nm with the peak centers at about 385 nm for $YBa_3B_9O_{18}$ and $LuBa_3(BO_3)_3$, 415 nm for α-$YBa_3(BO_3)_3$ and 360 nm for $LuBO_3$ powders, respectively. Even though those compounds have the different atomic structures, they have the common structural feature of each yttrium or lutetium ion bonded to six separate BO_3 groups, i.e., octahedral $RE(BO_3)_6$ ($RE =$ Lu or Y) moiety. This octahedral $RE(BO_3)_6$($RE =$ Lu or Y) moiety seems to be an important structural element for efficient X-ray excited luminescence of those compounds, as are the edge-sharing octahedral TaO_6 chains for tantalate emission.

Keywords: Rare-earth and alkaline-earth borates; X-ray excited luminescence; X-ray phosphors; Scintillator

1. Introduction

X-ray phosphors are solid-state inorganic materials used in medical X-ray imaging applications. The role of these phosphors is to reduce the exposure of the patient to X-rays while maintaining the structural features of the X-ray image [1,2]. This is done by amplifying every X-ray photon absorbed by a phosphor screen into hundreds of visible or UV-radiation photons which are then recorded by a detector, such as a piece of photographic film. In addition, the X-ray phosphors with excellent scintillation properties can be grown into large scintillation crystals, which have been widely used in high-energy physics, medical imaging, safety inspection and so on.

Developing an understanding of the relationship between structure and luminescence is of practical, as well as theoretical, importance in the design and synthesis of new phosphor compounds. Knowing what structural features should be incorporated into a material in order to give luminescence at a specific wavelength or region of wavelengths is extremely valuable.

In the past few years, several new rare-earth (*RE*) and alkaline-earth borates such as $RECa_4O(BO_3)_3$, $RE_2CaO(BO_3)_2$, $REBaB_9O_{16}$, $REBa_3B_9O_{18}$ and $REBa_3(BO_3)_3$ have been synthesized [3–8]. *RE* and alkaline-earth borates have attracted so much attention because many of these compounds not only have been explored as new kinds of nonlinear optical materials themselves but also they have been widely used as hosts in preparation of self-frequency-doubling lasers and PDP phosphors [9–13]. However, the X-ray excited luminescence (XEL) of *RE* and alkaline-earth borates themselves have been ignored. In this paper, we reported the XEL of several *RE* and alkaline-earth borates, and explored the relationship between the luminescence and structure of those compounds.

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2. Experimental section

2.1. The sample preparations

All the samples were prepared by solid-state reactions at high temperature. The starting materials were analytical-grade $BaCO_3$, H_3BO_3, Y_2O_3 and Lu_2O_3. Stoichiometric amounts of the reactants were weighed separately on an analytical balance and thoroughly mixed in an agate mortar, and then fired in air at 930, 1150, 1100, 900 °C for 24 h for $YBa_3B_9O_{18}$, $LuBa_3(BO_3)_3$,α-$YBa_3(BO_3)_3$ and $LuBO_3$, respectively, in the covered Pt crucibles. After those steps the temperature was slowly reduced down to room temperature by switching off the furnace.

2.2. Characterizations

The XRD data for phase identification were collected at ambient temperature with a HUBER Imaging Plate Guinier Camera G670 [S](Cu$K\alpha$) 1 radiation, $\lambda = 1.54056\,Å$, Ge monochromator).The 2θ ranges of all the data sets are from 10° to 80° with a step size of 0.005°.

The XEL of the samples was examined under room temperature using an X-ray excited spectrometer (Fluormain), in which an F-30 X-ray tube (W anticathode target) was used as the X-ray source operating at 80 kV (peaking voltage) and 4 mA. The fluorescence lifetimes were measured at room temperature by exciting the samples with pulsed X-ray (maximal excited energy 30 keV) and detected by an S-1 photo multiplier tube. The time resolution of the X-ray excited fluorescence lifetime is 0.97 ns.

3. Results and discussion

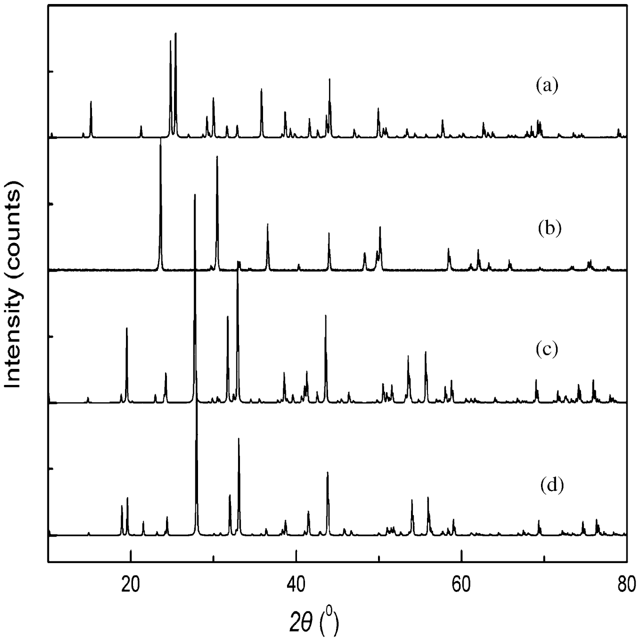

Fig. 1. The X-ray powder diffraction patterns of $YBa_3B_9O_{18}$ (a), $LuBO_3$ (b), α-$YBa_3(BO_3)_3$ (c) and $LuBa_3(BO_3)_3$ (d).

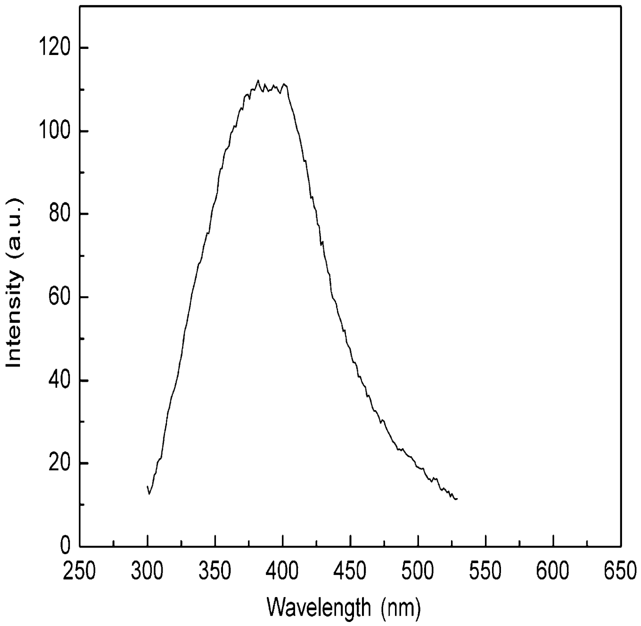

Fig. 2. The XEL spectrum of $YBa_3B_9O_{18}$ powders.

Fig. 1(a)–(d) show the powders X-ray diffraction patterns of $YBa_3B_9O_{18}$, $LuBO_3$ (b), α-$YBa_3(BO_3)_3$ and $LuBa_3(BO_3)_3$, respectively. All samples are showed to pure phases and the powders X-ray diffraction patterns of $LuBa_3(BO_3)_3$,α-$YBa_3(BO_3)_3$ and $LuBO_3$ are in good agreement with the reported powders patterns in PDF2 card numbers 45-0320, 51-1849 and 13-0477, respectively. The powder X-ray diffraction patterns of $YBa_3B_9O_{18}$ is in good agreement with the reported powder patterns by Li [7], which has not been collected in the PDF2 database. For all samples, the observed impurity levels did not significantly affect the X-ray excited emission peak shape or intensity of the samples.

Figs. 2–4 exhibit the XEL spectrum of $YBa_3B_9O_{18}$, $LuBa_3(BO_3)_3$ and α-$YBa_3(BO_3)_3$, respectively. All the studied materials show a broad emission band in the 300–550 nm with the peak center at about 385 nm for $YBa_3B_9O_{18}$ and $LuBa_3(BO_3)_3$, and 415 nm forα-YBa_3 $(BO_3)_3$ compounds, respectively. The room temperature fluorescent decay curve of $YBa_3B_9O_{18}$ exhibits a single-exponent shape with decay time of 27 ns, while the room temperature fluorescent decay profile of $LuBa_3(BO_3)_3$ and α-$YBa_3(BO_3)_3$ powders both exhibit a two-exponent shape with decay time of 86 ns (98%) and 1168 (2%) for the $LuBa_3(BO_3)_3$ powders, 86 ns (98%) and 1048 ns (2%) for the α-$YBa_3(BO_3)_3$ powders, respectively.

Fig. 5 shows the comparisons between the XEL spectra of $YBa_3B_9O_{18}$, $LuBa_3(BO_3)_3$, α-$YBa_3(BO_3)_3$ powders and that of the $Bi_4Ge_3O_{12}$ (BGO) powders under the same measurement conditions. By comparing the integral area of the emission bands for those compounds with that of BGO powders ,it is interesting to note that the light yield of

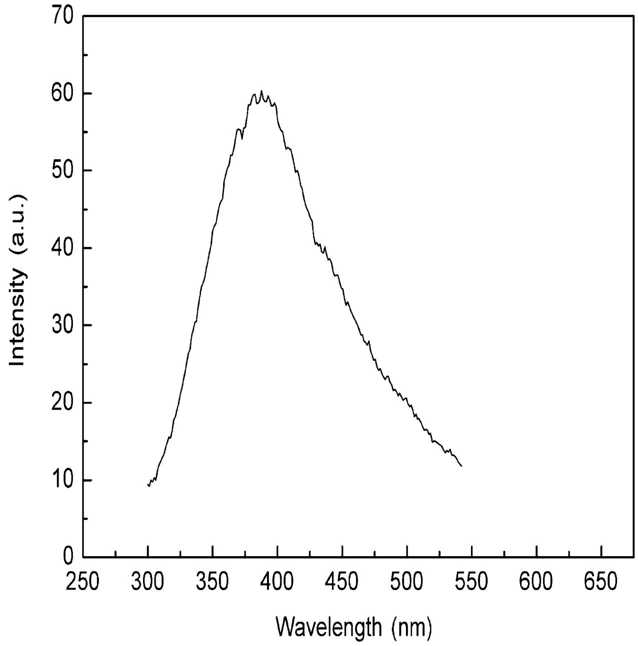

Fig. 3. The XEL spectrum of $LuBa_3(BO_3)_3$ powders.

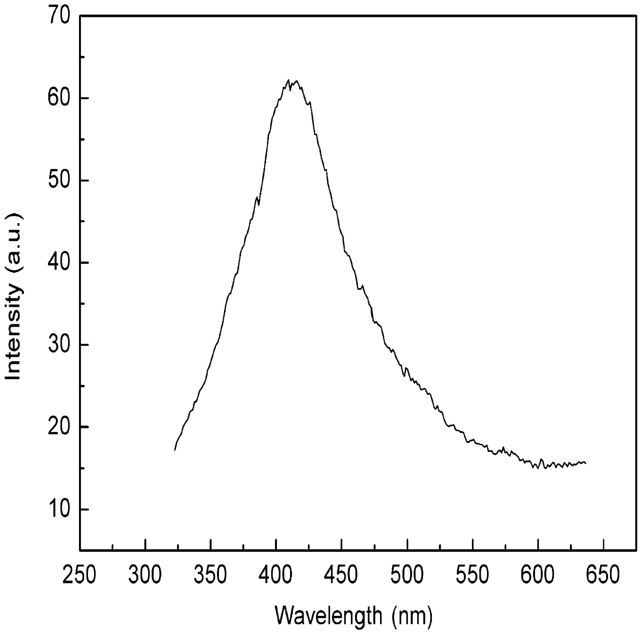

Fig. 4. The XEL spectrum of α-$YBa_3(BO_3)_3$ powders.

$YBa_3B_9O_{18}$ is about 15% as large as that of BGO powders, while the light yield of $LuBa_3(BO_3)_3$ and α-$YBa_3(BO_3)_3$ powders is both about 50% as large as that of BGO powders.

Considering the emission wavelength range, light yield, decay time of $YBa_3B_9O_{18}$, α-$YBa_3(BO_3)_3$ and $LuBa_3(BO_3)_3$ in general, they may have a role to play in the field of X-ray phosphors, scintillators, etc.

Fig. 6 shows the XEL of $LuBO_3$ powders. It shows a broad emission band in the range of 300–500 nm with peak center at 360 nm.

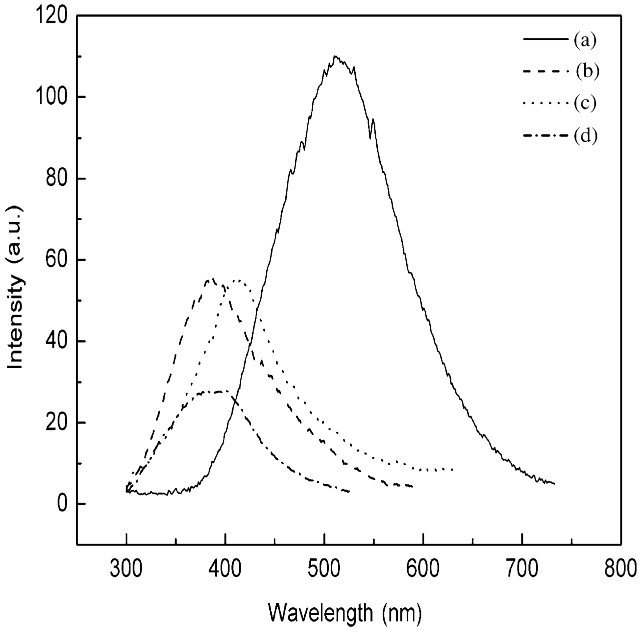

Fig. 5. The comparison between the XEL spectrum of BGO powders (a) and those of $LuBa_3(BO_3)_3$ (b), α-$YBa_3(BO_3)_3$ (c) and $YBa_3B_9O_{18}$ powders (d) under the same measurement conditions.

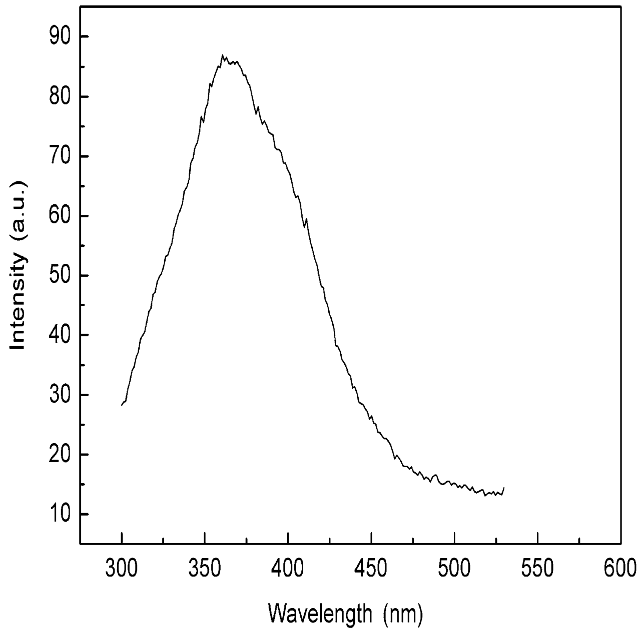

Fig. 6. The XEL spectrum of $LuBO_3$ powders.

In order to investigate the luminescence mechanisms of those compounds, we compared the structures of those compounds. The sample of $YBa_3B_9O_{18}$ was structurally characterized with space group of $P6_3/m$. The fundamental building unit of it is the planar B_3O_6 group. The planar B_3O_6 groups are parallel to each other and distributed layer upon layer along the *c*-axis. Yttrium atoms occupy sites between the B_3O_6 sheets and are bonded to 6 oxygen atoms, each belonging to a different B_3O_6 group. Six vertexes of each YO_6 octahedron interconnect six planar

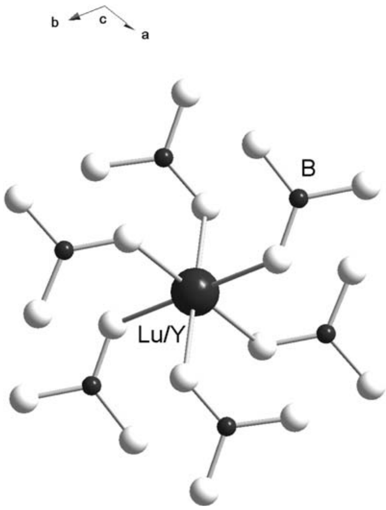

Fig. 7. The $RE(BO_3)_6(RE = \text{Lu or Y})$ unit in the X-ray excited phosphors of $YBa_3B_9O_{18}$, $LuBa_3(BO_3)_3$, α-$YBa_3(BO_3)_3$ and $LuBO_3$ powders.

B_3O_6 groups, and three vertexes of each planar B_3O_6 group interconnect three YO_6 octahedral [7]. In fact, each yttrium atom is bonded to six separate BO_3 groups. The samples of α-$YBa_3(BO_3)_3$ and $LuBa_3(BO_3)_3$ have the similar structure and were structurally characterized with space group of $P6_3cm$. The crystal structures of them consist of isolated BO_3 triangles and *RE* (Y or Lu)-oxygen octahedron and polyhedra of barium–oxygen. All boron atoms are coordinated to three oxygen atoms, which are distributed layer upon layer along the *c*-axis. The *RE* (Y or Lu) atoms are six-coordinated, octahedral polyhedron, which are joined together through BO_3 triangles layer upon layer along *c*-axis [8]. The sample of $LuBO_3$ is structurally characterized with space group of *R*-3*c* H and the main structural feature of it is that each lutetium ion is bonded to six separate BO_3 groups [14].

From the above, we can see that these X-ray phosphors—$YBa_3B_9O_{18}$, $LuBa_3(BO_3)_3$, α-$YBa_3(BO_3)_3$ and $LuBO_3$, have the common structural feature of each yttrium or lutetium ion bonded to six separate BO_3 groups in spite of the different structures, as shown in Fig. 7. This atomic arrangement, i.e., octahedral $RE(BO_3)_6(RE = \text{Lu or Y})$ moiety, seems to be an important structural element for efficient XEL of those compounds, as are the edge-sharing octahedral TaO_6 chains for tantalate emission [15–17], $Zr(PO_4)_6$ moiety for potassium hafnium–zirconium phosphates and barium hafnium–zirconium phosphate [18,19], and octahedral GaO_6 groups for $ZnGa_2O_4$ luminescence [20–22]. The lattice defects may play an important role on the luminescent performances of these materials. As mentioned in the experimental section, these X-ray phosphors—$YBa_3B_9O_{18}$, $LuBa_3(BO_3)_3$, α-$YBa_3(BO_3)_3$ and $LuBO_3$, have been prepared by the solid-state reaction of mixtures of $BaCO_3$, H_3BO_3, and Y_2O_3 or Lu_2O_3 under high temperature. Due to the large difference in chemical characteristics and evaporation pressure of the components, non-equal evaporation during the formation processing of these powder crystals is inevitable and thus results in the formation of lattice defects such as, oxygen-vacancies, cation vacancies and excitons, etc. Further investigations are underway.

4. Conclusions

$YBa_3B_9O_{18}$, $LuBa_3(BO_3)_3$, α-$YBa_3(BO_3)_3$ and $LuBO_3$ powders have been synthesized by the solid-state reaction methods at high temperature and their X-ray excited luminescent properties were investigated. These compounds showed a broad emission band with the peak center at about 385 nm for $YBa_3B_9O_{18}$ and $LuBa_3(BO_3)_3$, 415 nm for α-$YBa_3(BO_3)_3$ and 360 nm for $LuBO_3$ powders, respectively. The light yield of $YBa_3B_9O_{18}$ is about 15% as large as that of BGO powders, while the light yield of $LuBa_3(BO_3)_3$ and α-$YBa_3(BO_3)_3$ powders is both about 50% as large as that of BGO powders under the same measurement conditions. The common structural feature of each yttrium or lutetium ion bonded to six separate BO_3 groups, i.e., the octahedral $RE(BO_3)_6$ ($RE = \text{Lu or Y}$) moiety, seems to be an important structural element for efficient XEL of those compounds, as are the edge-sharing octahedral TaO_6 chains for tantalate emission. Considering the emission wavelength range, light yield, decay time of $YBa_3B_9O_{18}$, α-$YBa_3(BO_3)_3$ and $LuBa_3(BO_3)_3$ in general, they may have a role to play in the field of X-ray phosphors, scintillators, etc.

Acknowledgments

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