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# Investigations of $Ba_3BP_3O_{12}$:$Eu^{2+}$ single crystal as a scintillator

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ABSTRACT

Single crystals of $Ba_3BP_3O_{12}$:$Eu^{2+}$ with high optical quality have been grown by the top-seeded solution growth (TSSG) method using $BPO_4$–NaF mixture as the flux. $Ba_3BP_3O_{12}$:$Eu^{2+}$ single crystal exhibits wide transparency in the wavelength range from 250 to 700 nm, and shows a broad emission band in the wavelength range of 350–650 nm when excited by X-ray radiation. The overall scintillation efficiency is about 1.8 times of that of BGO crystal under the same conditions. Its room temperature fluorescence decay curve exhibits a single-exponent shape with decay time of about 860 ns. It is worth noting that $Ba_3BP_3O_{12}$:$Eu^{2+}$ single crystal may be of great interest for applications in the field of scintillation materials considering its scintillation properties, as well as the good chemical stability.

## 1. Introduction

Scintillation materials are widely applied in many detector systems in various fields, such as high-energy physics, medical imaging, and safety inspections using transmission methods. Many scientists have been attracted to this field and a large number of scintillation materials have been found. However, the applied commercial scintillation materials, such as NaI:Tl, $BaF_2$, $PbWO_4$, $Bi_4Ge_3O_{12}$, do not always meet the requirements of the detection systems. NaI:Tl shows a relatively long decay time, and heavy hygroscopic as well as non-proportional response [1]. $BaF_2$ has a high afterglow level [2], $PbWO_4$ exhibits a low light yield [3] and $Bi_4Ge_3O_{12}$ has a moderate decay time [4]. Consequently, there is a need to explore and prepare new scintillation materials.

The systematic investigation on borophosphates containing $BO_3$, $BO_4$ and $PO_4$ groups as basic structural units started several decades ago, a remarkable number of borophosphates containing complex anionic partial structures ranging from isolated species, oligomers, rings, chains, layers to three-dimensional frameworks have been reported [5]. Recently, the research in the borophosphates has attracted tremendous attention due to their wide uses as phosphors, non-linear optical and scintillation materials [6–9]. Moreover, many kinds of borophosphate single crystals have been grown using different methods, and their properties have been investigated to explore the applications in the field of nonlinear optics and luminescence materials, such as $BPO_4$ [10], $SrBPO_5$ [8], β-$Zn_3BPO_7$ [11], and $BaBPO_5$ [12].

The compound $Ba_3BP_3O_{12}$ was first prepared and structurally characterized by Kniep et al. [5]. The anion complex consists of linked tetrahedron only. In detail, central “vierer” single chains ($BO_4$ and $PO_4$ in alteration) run parallel to [0 0 1] as shown in Fig. 1(a); the two free vertices of each $BO_4$ tetrahedron are connected with terminal $PO_4$ tetrahedra. In addition, the Ba ions are located in the channels formed by the “vierer” chains (Fig. 1(b)). $Ba_3BP_3O_{12}$ contains wide channels in which the barium ions are located. In 2005, Duan has reported the luminescence properties of $Ba_3BP_3O_{12}$:$Eu^{2+}$ powder, which shows good scintillation properties and is proved to be a potential scintillation material [13]. After that, the preparation of the starting materials and the mechanism of the single crystal growth of $Ba_3BP_3O_{12}$ were investigated by our group [14]. However, there is no report about the $Eu^{2+}$-doped $Ba_3BP_3O_{12}$ single crystal growth and its scintillation properties. In this paper, we present investigations on scintillation properties of $Ba_3BP_3O_{12}$:$Eu^{2+}$ single crystals grown by the top-seeded solution growth (TSSG) method using $BPO_4$–NaF mixture as the flux. And it is interesting to explore the possibility of $Ba_3BP_3O_{12}$:$Eu^{2+}$ single crystals used as scintillators.

## 2. Experimental

### 2.1. $Ba_3BP_3O_{12}$:$Eu^{2+}$ single crystal growth

Microcrystalline samples of $Ba_3BP_3O_{12}$:$Eu^{2+}$ were prepared by using the standard solid-state reaction. A stoichiometric mixture of

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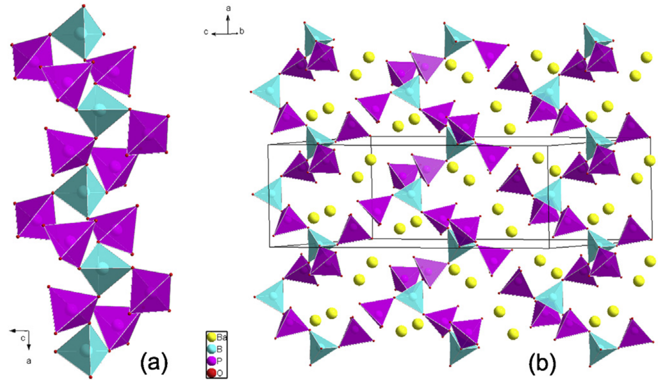

**Fig. 1.** The crystal structure of $Ba_3BP_3O_{12}$: "vierer" single chains with $BO_4$ and $PO_4$ in alteration (a), the location of $Ba^{2+}$ ions in the wide channels in $Ba_3BP_3O_{12}$ (b).

$BaCO_3$, $Eu_2O_3$, $H_3BO_3$ and $NH_4H_2PO_4$ was thoroughly ground, and fired in air at 400 °C for 10 h in a covered alumina crucible, and subsequently fired at 1000 °C for 24 h in a covered alumina crucible under flowing 95% $N_2$–5% $H_2$ atmosphere to obtain the polycrystalline $Ba_3BP_3O_{12}$:$Eu^{2+}$. The concentration of $Eu^{2+}$ is 0.5 mol% of $Ba^{2+}$. The product was checked by X-ray powder diffraction to be single phase $Ba_3BP_3O_{12}$. The appropriate proportion of polycrystalline $Ba_3BP_3O_{12}$:$Eu^{2+}$ and $BPO_4$–NaF were mixed homogeneously for the single crystal growth.

Small single crystals of $Ba_3BP_3O_{12}$:$Eu^{2+}$ grown by the slow-cooling technique were used as the seeds for the growth of big single crystals by top-seeded solution growth method. To grow large and high quality of $Ba_3BP_3O_{12}$:$Eu^{2+}$ single crystals, the main efforts have been focused on the top-seeded solution growth method. The single crystal growth was carried out in a vertical cylindrical furnace ($SX_2$-10-13) equipped with medium frequency induction heating system using a Pt–10% PtRh thermal couple. The temperature of the furnace was controlled by a Euro-Thermal controller. The prepared polycrystalline $Ba_3BP_3O_{12}$:$Eu^{2+}$ and $BPO_4$–NaF as flux were weighed, mixed and put into a platinum crucible. The crucible was heated to about 1100 °C with a rate of 60 °C/h, and then maintained for about 20 h in order to keep the homogeneous convection of the high temperature solution. Then the melt was cooled down to 1065 °C, which is about several centidegrees above the saturation temperature. A $Ba_3BP_3O_{12}$:$Eu^{2+}$ seed crystal attached to a platinum rod was inserted slowly into the crucible with the rotation rate of 20 rpm, and kept in contact with the surface of the solution to make the outer surface of the seed crystal dissolved. Then the temperature of the solution was slowly reduced with a rate of 0.5–1.5 °C/day. Because $Ba_3BP_3O_{12}$:$Eu^{2+}$ crystals suffer a phase decomposition [14], special care should be taken in order to prevent the phase decomposition from $Ba_3BP_3O_{12}$ to $Ba_2P_2O_7$. After the completion of single crystal growth, the single crystal was drawn out of the solution, cooled down to 500 °C, and then maintained at this temperature for 10 h to eliminate the internal stress. Fig. 2 shows the single crystal of $Ba_3BP_3O_{12}$:$Eu^{2+}$ grown by top-seeded solution growth method. A 2 mm thick sample of $Ba_3BP_3O_{12}$:$Eu^{2+}$ single crystal was cut from the as-prepared crystal and polished for optical transmission and scintillation measurements.

### 2.2. Characterization

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 $2\theta$ ranges of all the data sets are from 5° to 100° with a step of 0.005°. The optical transmittance spectrum was recorded at room temperature by spectrophotometer without integrating sphere (Hitachi UV-2800, Japan) in the wavelength range from 250 to 800 nm. The Fourier transform infrared (FT-IR) spectrum of $Ba_3BP_3O_{12}$:$Eu^{2+}$ single crystal was carried out on a Thermo Nicolet Fourier Transform Spectrometer with $\pm 2\ cm^{-1}$ resolution using a KBr pellet method. The X-ray excited luminescence (XEL) of the sample 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 30 kV (peaking voltage) and 4 mA. The fluorescence lifetime was measured at room temperature by exciting the sample with pulsed X-rays (maximal excited energy 30 keV) and detected by a S-1 photo multiplier tube. The time resolution of the X-ray excited fluorescence lifetime is 0.97 ns.

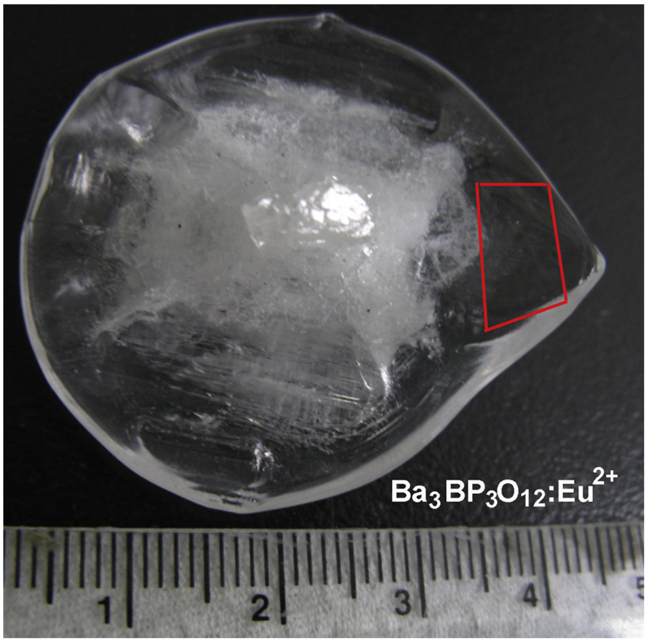

**Fig. 2.** $Ba_3BP_3O_{12}$:$Eu^{2+}$ single crystal grown by top-seeded solution growth method.

## 3. Results and discussion

Fig. 3 shows the powder XRD patterns of undoped and $Eu^{2+}$-doped $Ba_3BP_3O_{12}$ single crystals grown by TSSG method. Both of these two single crystals are $Ba_3BP_3O_{12}$ phase with little difference in the peak position, as shown in the inset of Fig. 3. As we know, the ionic radius of $Eu^{2+}$ ($r = 1.35$ Å, CN = 10) is smaller than that of $Ba^{2+}$ ($r = 1.52$ Å, CN = 10) [15], the unit cell volume of $Ba_3BP_3O_{12}$:$Eu^{2+}$ is expected to shrink compared with undoped $Ba_3BP_3O_{12}$. However, there is no obvious peak shift in the XRD pattern of $Eu^{2+}$-doped $Ba_3BP_3O_{12}$ single crystal compared to that of undoped one, probably due to the low concentration (0.5 mol%) of $Eu^{2+}$.

Fig. 4 shows the FT-IR spectrum of $Ba_3BP_3O_{12}$:$Eu^{2+}$ single crystal. As mentioned above, $Ba_3BP_3O_{12}$ compound contains $BO_4{}^{5-}$ and $PO_4{}^{3-}$ tetrahedra sharing one oxygen atom. In this case, there are two possible group theoretical treatments for the interpretation of the intramolecular modes: one is the vibrations of the tetrahedral $BO_4{}^{5-}$ and $PO_4{}^{3-}$ units separately, and the other is the whole $BPO_7{}^{6-}$ units with some supplement of $BO_4{}^{5-}$ and $PO_4{}^{3-}$ units. Therefore, in the FT-IR spectrum of $Ba_3BP_3O_{12}$:$Eu^{2+}$ single crystal, except the bands which are assigned as the general vibrational modes of $BO_4{}^{5-}$ and $PO_4{}^{3-}$ tetrahedral groups, the remaining bands are in agreement with the vibrational modes of $BPO_7{}^{6-}$ chains. The tentative assignments have been tabulated in Table 1, which is similar to that of $Ba_3BP_3O_{12}$ powder [16].