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Crystal growth and optical anisotropy of Y:$PbWO_4$ by modified Bridgman method

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Abstract

Large-size yttrium-doped lead tungstate single crystals (Y:$PbWO_4$) of good quality were grown by modified Bridgman method. The growth conditions, such as purity of raw materials, growth orientation and rate, temperature gradient, seed selection and cooling rate of after-growth, were discussed in this paper. Data of crystals along different growth orientations were obtained on the transmittance spectra, and the radio- and photoluminescence emission spectra. Optical anisotropy effects of Y:$PbWO_4$ were observed and studied. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

As a new kind of scintillating medium, $PbWO_4$ has been chosen to construct a homogeneous electromagnetic calorimeter (ECAL) for the Compact Muon Solenoid (CMS) at the Large Hadron Collider (LHC) at CERN for its short radiation length ($X_0 = 0.89\,\text{cm}$), small moliere radius ($R = 2.2\,\text{cm}$), high density ($8.28\,\text{g/cm}^3$), and fast scintillation emission (the mean decay time $\tau \sim 15\,\text{ns}$) [1–6].

$PbWO_4$ crystals occur in nature as tetragonal scheelite type and monoclinic raspite. But the crystal grown in melt has been claimed as a pure scheelite structure (Fig. 1): The space group is C_{4h}^6–$I4_1/a$, with unit cell parameters $a = b = 0.5456(2)\,\text{nm}$, $c = 1.2020(2)\,\text{nm}$, and $z = 4$. As one can see from Fig. 1, the structure of $PbWO_4$ is characterized by the WO_4 tetrahedron and the PbO_8 cube along the *c*-axis. The regular stacking parallel to the *c*-axis of Pb and W atoms forms the crystal skeleton, while O atoms distribute around Pb and W atoms according to corresponding coordinate sites. $PbWO_4$ is grown from a 1:1 stoichiometric mixture of lead oxide (PbO) and tungsten oxide (WO_3) which melts congruently at 1123°C by the Czochralski method and the modified Bridgman method, without a phase transition during cooling. Previous reports

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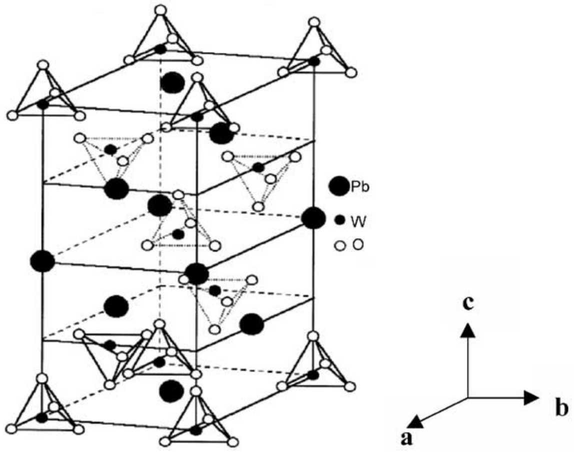

Fig. 1. Structural diagram of unit of scheelite-structured $PbWO_4$ crystal.

[7–10] discussed mainly the problems during crystal growth based on the Czochralski method, and a few were relevant to the modified Bridgman method [11–12]. A better understanding of $PbWO_4$ crystal growth conditions in the modified Bridgman method is necessary, since the method will be used in the mass production for the CMS. In this paper, special attention was paid to the Y:$PbWO_4$ growth conditions including (1) raw materials, (2) growth orientation and rate, (3) temperature gradient, (4) seed selection and (5) cooldown rate after growth. For structurally anisotropic crystal, the seed orientation is important for growth consideration; however, optical anisotropy effects of Y:$PbWO_4$ are also important for the specifications of crystal grown along different directions for the CMS. Therefore, we have more interest here in anisotropy effect on its transmittance, radio- and photoluminescence emission spectra.

2. Experimental procedure

A crystal growth furnace controlled by computer for modified Bridgman method has been designed and constructed by us. The schematic of the furnace and its temperature profiles are shown in Fig. 2. Large-size Y:$PbWO_4$ single crystals for the CMS were grown using the furnace in the open air atmosphere (Fig. 3). Raw materials of 5 N PbO and 4 N WO_3 were weighed according to stoichiometric composition and were loaded into a V-shaped mixer. Y dopant was introduced into the mixer in the form of Y_2O_3. The initial concentration of Y in charge mixture is 150 ppm(at). The typical mixing time is about 2 h. Usually, the charge mixture is pressed into cylindrical rods, but we took another way here that the charge mixture was melted in a platinum crucible at 1210°C, and then they were poured into a parallelepiped platinum crucible with a size of $28 \times 28 \times 400\,mm^3$ for crystal growth. This procedure has many advantages: (1) it facilitates the full chemical reaction between PbO and WO_3; (2) it eliminates the possible contamination during the use of presses; and (3) it is suitable for mass production.

The cooling residue in the growth platinum crucible was analyzed by X-ray diffraction method and only $PbWO_4$ phase was found (Fig. 4).

The size of seed crystal is $25 \times 25 \times 50\,mm^3$ with orientation along [0 0 1] and [1 0 0]. In order to suppress component deviation for evaporation in air atmosphere, the crucible was covered. The lowering rate of crucible was chosen as (1) 0.6 mm/h and (2) 1.0 mm/h. The axial temperature gradient at solid–liquid interface was (1) 20°C/cm, (2) 30°C/cm and (3) 50°C/cm. Samples with dimensions of $25 \times 25 \times 25\,mm^3$ prepared for optical properties measurement were cut from the grown crystals. (0 0 1) and (1 0 0) faces of all samples were determined by X-rays and were optically polished. The study of the optical properties of Y:$PbWO_4$ single crystal was carried out, including transmittance spectra, radio- and photoluminescence emission spectra along different crystal growth orientations.

3. Results and discussion

3.1. Growth conditions

The purity of raw materials is an important factor to control crystal quality. Some impurities, such as Mo, Ca, Na and K, may cause a redistribution of the host matrix defects (lead and oxygen deficiency), which leads to a worsening

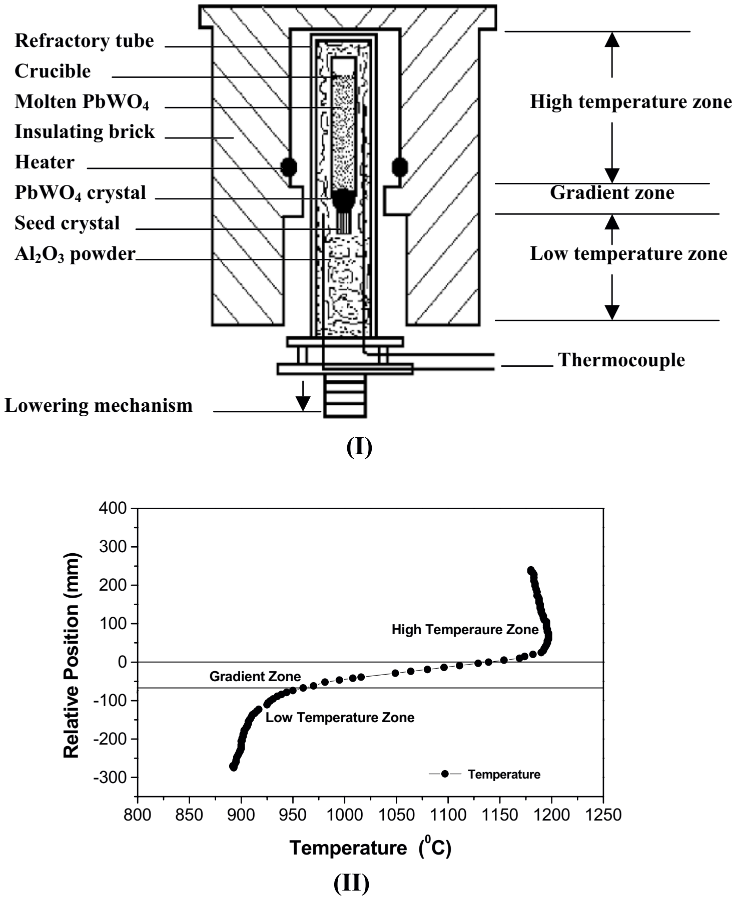

Fig. 2. Schematic (I) and temperature profile (II) of crystal growth furnace.

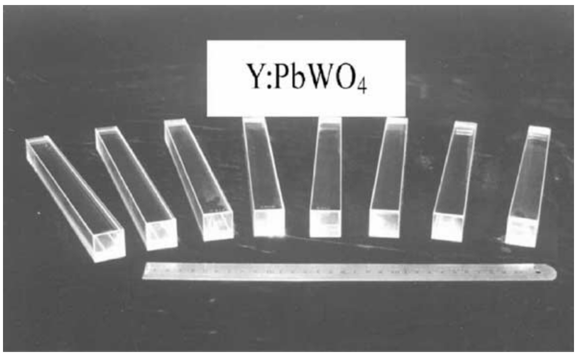

Fig. 3. Full-size Y:$PbWO_4$ crystals (length: 230 mm) for the CMS grown by the modified Bridgman method.

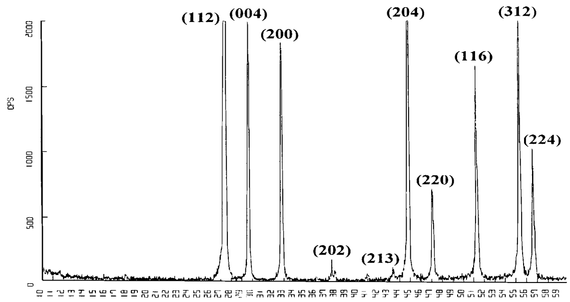

Fig. 4. Pattern of X-ray diffraction of the residue of a melt heated at 1210°C.

of the optical and scintillation properties of Y:$PbWO_4$. For example, Na^{1+} activation in $PbWO_4$ crystal is responsible for the appearance of a red luminescence [13]. Some research work also revealed that the slow decay component of luminescence in $PbWO_4$ is mainly due to the Mo contaminant of raw materials [14]. Therefore, some unwanted impurities must be specified or omitted from raw materials. The main impurities existing in raw materials were analyzed by the glow discharge mass spectroscopy (GDMS) method in CERN. Table 1 shows that the concentration of the impurities mentioned above was <0.5 ppm(wt) in raw materials.

The anisotropy of $PbWO_4$ crystal structure leads to strong consequences in crystal growth conditions by the modified Bridgman method. The growth rate difference between the [1 0 0] and [0 0 1] directions was studied. Under an identical growth rate of 1 mm/h, the cracks appeared easily along crystallographic orientation [1 0 0]. These cracks are parallel to the [1 0 0] direction. On the contrary, few cracks were observed when the crystals were grown along the [0 0 1] direction and they are normal to the [0 0 1] direction. The considerable difference in thermal expansion coefficient along the [1 0 0] ($\alpha_a = 1.28 \times 10^{-5}/°C$) and [0 0 1] ($\alpha_c = 2.95 \times 10^{-5}/°C$) [11] directions mainly accounts for these cracks. When the growth rate was lowered to 0.6 mm/h, it was possible to obtain crack-free crystals along the [1 0 0] orientation. However, from the viewpoint of crack and mass production, the choice of the [0 0 1] direction as the growth direction is preferential in the modified Bridgman method.

One important factor affecting crystal quality in growth process is the temperature gradient. Three different axial temperature gradients during crystal growth were made in our experiments: (1) 50°C/cm, (2) 30°C/cm and (3) 20°C/cm. Experimental results show that 30°C/cm produced the best results, namely large-size Y:$PbWO_4$ crystals without cracks, inclusions and coloration. When the temperature gradient was 50°C/cm, the control of growth rate became very difficult. The actual crystallizing rate exceeded the lowering rate of crucible, and under the conditions, cracks and inclusions were observed in the crystals. When the temperature gradient was decreased to 20°C/cm, the grown crystals showed slight yellow coloration that deteriorated the optical properties of Y:$PbWO_4$ crystals. The initial solid–liquid interface moved up towards the high-temperature zone of the growth furnace gradually with crystal growth. In order to keep solid–liquid interface stable, the temperature of growth furnace had to be increased according to the preset program.

Table 1
The concentration of some impurities in raw materials WO_3 and PbO

Elements	Concentration (ppm(wt))	
	Raw materials	
	WO_3	PbO
Mo	0.2	0.01
Ca	0.4	<0.05
Na	0.1	0.08
K	0.4	0.15

The quality and orientation of seed crystal should be taken into account to improve the quality of crystal. Some defects in the seed crystal are responsible for those in the grown crystal. For example, existing dislocations in the seed crystal will extend into the grown crystal. Some cracks are ascribed to the stresses originating at the inclusions of the seed crystal. Furthermore, the optical uniformity and scintillation properties of crystals are also affected by the orientation of seed crystal.

For Y:$PbWO_4$ crystals the after-growth cooling rate is also very important. If the cooling rate is too high the crystals will crack easily. At the same time, the low cooling rate was also an annealing method that can improve the scintillation properties of Y:$PbWO_4$ crystals. At a cooling rate of 15°C/h, crack-free crystals were obtained.

3.2. *Optical anisotropy effect*

3.2.1. *Transmittance spectra*

Transmittance spectra of Y:$PbWO_4$ along the [1 0 0] and [0 0 1] directions were recorded on a Shimadzu UV-2501PC spectrophotometer and are shown in Fig. 5. The distinct difference between the [1 0 0] and [0 0 1] directions can be seen from the spectra. The [1 0 0] direction has higher transparency, especially at short wavelength, and shorter cut-off edge than the [0 0 1] direction. The anisotropy of transmittance spectra was due to that of the crystal structure. Part of the ideal

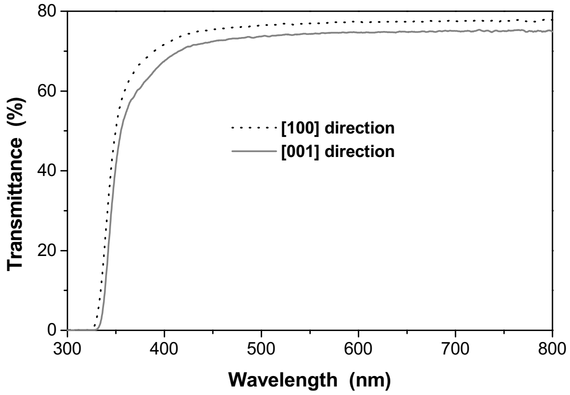

Fig. 5. Transmittance spectra of Y:$PbWO_4$ crystal along the [1 0 0] and [0 0 1] directions.

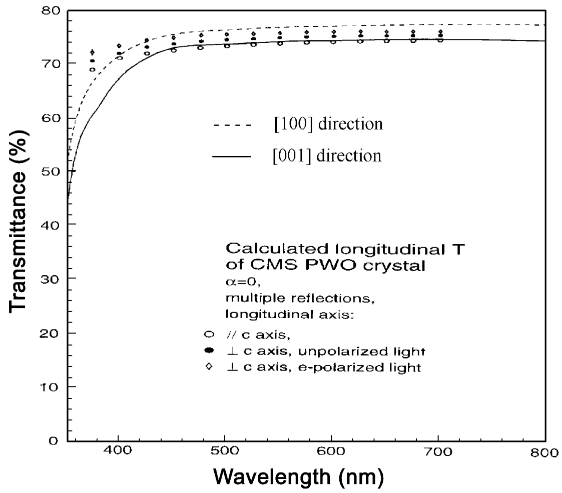

Fig. 6. Comparison between theoretical and experimental transmittance curves of Y:$PbWO_4$ crystal along the [1 0 0] and [0 0 1] directions.

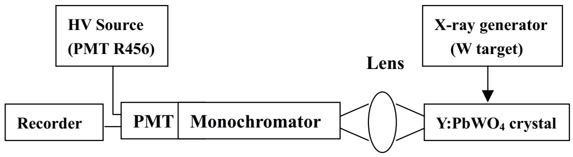

Fig. 7. Scheme of the setup for measuring the radioluminescence emission spectra of Y:$PbWO_4$ crystal.

theoretical transmittance along the [1 0 0] and [0 0 1] directions was calculated as

$$T_s = (1+R)^2 + R^2(1-R)^2 + \ldots = (1-R)/(1+R)$$

with

$$R = (n - n_{air})^2/(n + n_{air})^2,$$

where n and n_{air} are the refractive indices of crystal and air, respectively. Fig. 6 shows the calculated results. Although the theoretical values of transmittance were not fully consistent with the experimental value, the differences existing in the theoretical transmittance curves between the [1 0 0] and [0 0 1] directions are quite similar to the test results in Fig. 5.

3.2.2. Radio- and photoluminescence emission

An accurate knowledge of Y:$PbWO_4$ emission is important. The radioluminescence emission spectra were excited by X-rays. The scheme of the setup is given in Fig. 7. Its working conditions include 80 kV, 4 mA, and W target. The sides of the sample were wrapped with Tyvek and only one side was left unwrapped to let light out. X-rays were injected perpendicularly into the sample. The result was recorded by an x–y recorder. From Fig. 8(I), one can see that there is no significant difference in emission peaks between the [1 0 0] and [0 0 1] directions, both being around 424 nm. This means that there is only "blue" emission, with no obvious "green" emissions being observed. The intensity of emission peak is different for these two directions. The intensity along the [1 0 0] direction is weaker than that of the [0 0 1] direction. The above results demonstrate that the [0 0 1] direction for Y:$PbWO_4$ crystal growth orientation will be preferred for better light yield devices.

It is worth mentioning that the growth orientation of $PbWO_4$ grown by the Czochralski method is not along the [0 0 1] direction actually. The [1 0 0] and [1 0 4] (at an angle of ~19° with the [0 0 1] direction) directions are preferred according to some papers [15,16]. The authors of these papers also think the scintillation properties along the [0 0 1] direction should be better than those along other directions. Unfortunately, the [0 0 1] direction has to be given up because of the peculiarities of thermal field design in the crystallizer for growing a large-size $PbWO_4$ crystal using the

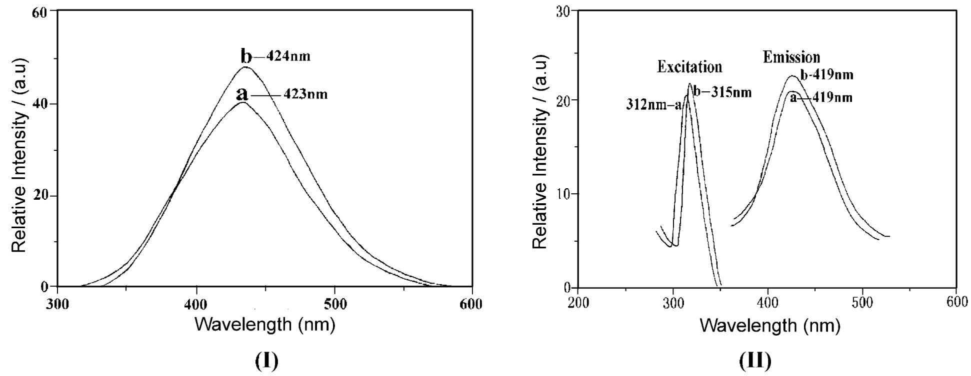

Fig. 8. Radioluminescence emission spectra (I) and photoluminescence emission spectra (II) along (a) [1 0 0] and (b) [0 0 1] directions of $Y:PbWO_4$ crystal.

Czochralski method and cracks caused by the anisotropy of mechanical properties of the crystal. For the modified Bridgman method, the growth orientation of $PbWO_4$ crystal is just the best direction of scintillation properties, namely the [0 0 1] direction, which is regarded as one of the merits of $PbWO_4$ crystal growth using the modified Bridgman method.

Photoluminescence was measured by a fluorescence spectrophotometer (Perkin Elmer, LS50B). The slit width resulted in a resolution of 5 nm for both emission and excitation spectra. The photoluminescence spectra along the [1 0 0] and [0 0 1] directions were shown in Fig. 8(II). The difference in the intensity of emission peak between the [1 0 0] and [0 0 1] directions was also observed. Compared with radioluminescence spectra, the emission peak wavelength of photoluminescence emission spectra shifts about 5 nm toward short wavelength, while there is only "blue" emission.

4. Conclusion

We have discussed the main growth parameters of $Y:PbWO_4$ crystal grown by the modified Bridgman method. The relations between growth rate and growth orientation were studied, the importance of seed crystal was put forward and a reasonable temperature gradient during crystal growth and cooling rate after growth were determined. Under the optimized growth conditions, large-size $Y:PbWO_4$ single crystals without cracks, inclusions and coloration were obtained successfully. The transmittance spectra, radio- and photoluminescence emission spectra along the [1 0 0] and [0 0 1] directions were recorded and compared. The intensity of emission along the [1 0 0] direction is weaker than that of the [0 0 1] direction. However, the former has higher transparency than the latter and this optical anisotropy effect of $PbWO_4$ crystal is attributed to the crystal structure.

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