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Growth of large-size crystal of $PbWO_4$ by vertical Bridgman method with multi-crucibles

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Abstract

In this paper, we report the crystal growth of large-size lead tungstate ($PbWO_4$) crystals by modified vertical Bridgman method with multi-crucibles. The growth conditions were also studied and optimal growth parameters were obtained. The uniformity of grown $PbWO_4$ and the impurities in grown $PbWO_4$ were analyzed by glow discharge mass spectroscopy method. The measurements of lattice parameters and phase analysis were carried out by X-ray diffraction. The scintillation properties of grown $PbWO_4$ crystals were investigated. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently, lead tungstate ($PbWO_4$) has attracted much interest as a promising scintillation crystal for electromagnetic calorimeter due to its physicochemical properties such as high density ($8.3\,g/cm^3$), non-hygroscopicity, low radiation length ($0.89\,cm^{-1}$), a small Moliere radius ($R_m = 2.2\,cm$), high efficiency of detecting ionizing radiations, fast response and sufficient radiation hardness [1,2]. Additionally, its cost is low. Till now, $PbWO_4$ has been grown by the Czochralski or Bridgman method [3,4]. Compared with the Czochralski method, Bridgman method has the following advantages: (1) simple in operation without complicated control system; (2) possibility of using crucibles of large size and multi-crystals in one growth cycle of a furnace; (3) ability to get crack-free uniformity crystals owing to low-temperature gradient; (4) suitable for growing crystal with components evaporation because of the melts enclosed in crucible and components evaporation being prevented; (5) by using different shaped crucible, the crystals with desired shape can be grown and the utilization ratio of the material is high.

In this paper, we grew high-quality large-size $PbWO_4$ crystals by modified vertical Bridgman

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method with multi-crucibles. The growth conditions and the scintillation performances of grown $PbWO_4$ crystals were also investigated. The impurities and phase of $PbWO_4$ crystal were analyzed.

2. Multi-crystal furnace

The multi-crystals furnace is designed based on the Bridgman principle with as many as 28 crucibles being arranged in one furnace as shown schematically in Fig. 1. Fig. 2 shows a schematic of a crucible used for $PbWO_4$ crystal growth by the modified Bridgman method. The horizontal temperature distribution should be kept as uniform as possible. While the vertical temperature distribution can be generally divided into three zones, the high-temperature zone, the gradient zone, and the low-temperature zone, as shown in Fig. 3. In the high-temperature zone, the melt consisting of PbO and WO_3 is allowed to have an ample time for homogenization in the enclosed Platinum crucible. In the gradient zone, the temperature gradient is so controlled that crystal growth proceeds onto the seed with as less defects as possible, and in the low-temperature zone, the grown crystal is allowed to cool to a sufficiently low temperature before the whole growth cycle is completed.

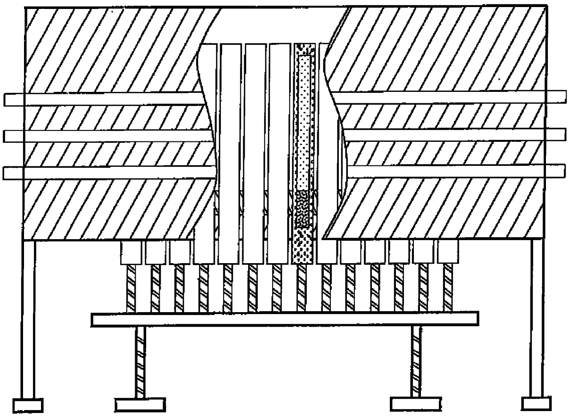

Fig. 1. Scheme of modified vertical Bridgman multi-crystal growth furnace.

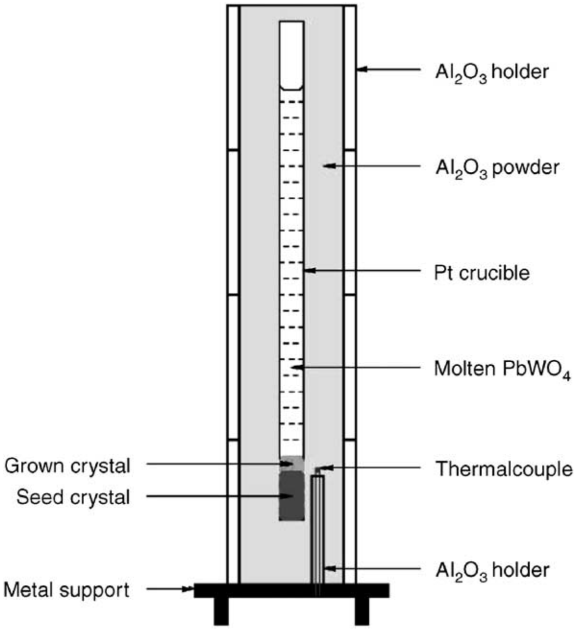

Fig. 2. Crucible configuration of modified Bridgman method.

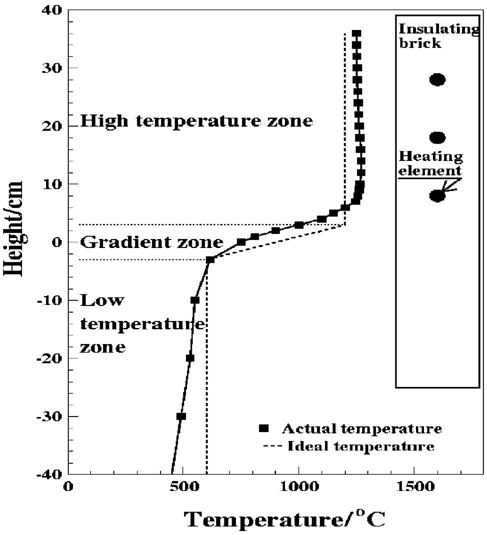

Fig. 3. Vertical temperature distribution of modified Bridgman furnace.

To satisfy these requirements, there are two separate systems that are interwovenly related to one another. One is the temperature measurement and automatic computer control system and another is the mechanical movement system. During crystal growth, the variation of temperature is required to be $< \pm 0.5^\circ$C to stabilize the crystal growth rate and keep the shape of solid-melt boundary. In order to meet with the temperature profile requirements, there is a fine mechanical adjustment system that each crucible can be independently manipulated according to the computer command in response to its need. The whole environment is programmed.

3. Crystal growth

Based on PbO–WO_3 phase diagram [5], $PbWO_4$ is a congruent melting compound with melting point T_m at 1123°C. As-grown crystals produced from high-temperature melting share the scheelite-type structure, which belongs to the space group $I4_{1/a}$ with a tetragonal unit cell. $PbWO_4$ crystals were grown by modified vertical Bridgman method using multi-crystal furnace. The raw materials of 5 N pure PbO and WO_3 were first dried at 200°C for 24 h to remove water, then weighed with an accuracy of 1 mg and mixed uniformly using ball mill coated with polyethylene. The composition of the starting material was chosen to be stoichiometric. In order to suppress Pb^{2+} vacancies and other trapping centers and improve scintillation properties of $PbWO_4$, Y_2O_3 was selected to be dopant and 30–60 ppm(wt) Y^{3+} doping level was introduced [6].

The charge melts at 30°C above the melting point of $PbWO_4$, and was loaded into the 0.2 mm-thick platinum crucible with a size of $34 \times 34 \times 480\,\mathrm{mm}^3$ for crystal growth. The top of the crucible was enclosed by folding it to prevent evaporation and contamination from outside atmosphere, and then embedded with alumina powder and was kept in an alumina crucible holder. Considering the thermal conductivity and the light yield (LY) of $PbWO_4$ crystal in $\langle 0\,0\,1 \rangle$ direction exceeding those in other directions [7], the seed oriented along $\langle 0\,0\,1 \rangle$ with a size of $33.5 \times 33.5 \times 55\,\mathrm{mm}^3$ was used. The optimal growth parameters were found to be as follows: The lowering rate was 0.6–1.2 mm/h. The axial temperature gradient was about 20°C/cm at growth solid-melt boundary to keep boundary flat, as shown in Fig. 3. If the gradient is too low, the growth rate of $PbWO_4$ crystal is less than the lowering rate of crucible, and solid-melt boundary moved to low-temperature zone and formed concave towards the melt. As a result, there are many scattering particles such as impurities and bobbles in grown crystal. On the contrary, if the gradient is too high, $PbWO_4$ growth rate is more than lowering rate of crucible, and then solid-melt boundary moved to high-temperature zone and formed convex towards the melt. With the result that polycrystalline and cloud layer will form and the transparency of $PbWO_4$ crystal will be degraded.

The growth yield has reached about 85% and the size of crystal boule was approximately $34 \times 34 \times 360\,\mathrm{mm}^3$. Since the Bridgman–Stockbargar method is based on a zone-refining principle, the impurities are forced to the tail end of the boule and concentrated there, so the tail end of $PbWO_4$ boule was light yellow. According to inspection, apart from the tail end of 5 cm, the grown $PbWO_4$ was colorless, transparent and defects such as bubbles, scatterings and striations were not recognized. According to compact muon solenoid (CMS) electromagnetic calorimeter requirements, the grown $PbWO_4$ boule was cut and polished to the block which have a front face of $28.6 \times 28.6\,\mathrm{mm}^2$ and a back face of $30 \times 30\,\mathrm{mm}^2$ and a length of 22 mm for end-caps use [8], as shown in Fig. 4.

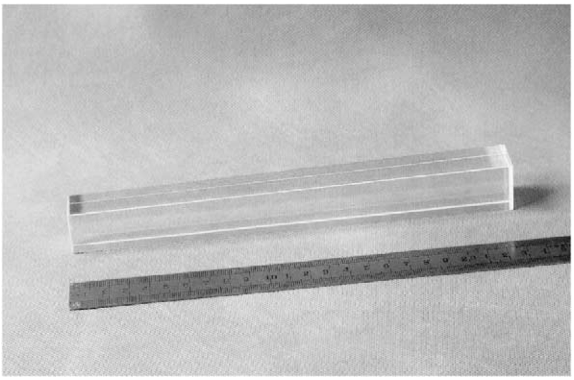

Fig. 4. Block-shaped $PbWO_4$ crystal after being polished.

4. The uniformity

The distribution of Y^{3+} in grown $PbWO_4$ has effects on the uniformity and scintillation properties of $PbWO_4$. The Y^{3+} concentration distributions along the crystal length were determined by glow discharge mass spectroscopy (GDMS). For a typical $PbWO_4$ crystal (1#) with 30 ppm(wt) Y^{3+} doping level, the Y^{3+} concentration distributions in $PbWO_4$ with a length of 26 cm were shown in Fig. 5. It shows that Y^{3+} distributions in $PbWO_4$ crystal are uniform from the seed end to tail end, and indicates that the effective segregation coefficient of Y^{3+} in $PbWO_4$ is less than but close to 1.

5. Impurity analyses and XRD

The impurities in $PbWO_4$ not only affect the crystal quality, but also degrade the optical transmittance properties and light yield and produce radiation damage. Thus, it is crucial to decrease the contents of impurities or eliminate them. The impurities were analyzed by GDMS, the typical results of grown $PbWO_4$ (1#) were shown in Table 1. It indicates that the concentrations of impurity ions such as Mo^{6+}, Fe^{2+}, Na^{+}, K^{+}, etc., were <1 ppm(wt). Generally speaking, the single-valent and divalent cation ions such as Na^{+}, K^{+}, Li^{+}, Ca^{2+}, Fe^{2+}, etc., will cause absorption band at 420 nm and degrade the LY. Mo^{6+} impurity in $PbWO_4$ crystal will create specific electron-capturing defects that have negative influence on $PbWO_4$ scintillation properties and is responsible for slow scintillation component in $PbWO_4$ [9,10]. The contents of impurity ions in $PbWO_4$ crystal can be decreased or eliminated by purifying raw materials and optimizing growth conditions.

The phase analysis and lattice parameters measurement of grown $PbWO_4$ crystals were performed by X-ray diffraction (XRD), Si was used as standard sample. The result of grown $PbWO_4$ crystal (1#) were shown in Fig. 6, and lattice parameters were calculated as follows: $a = b = 0.5461$ nm, $c = 1.2028$ nm and the unit cell volume was $0.35871\ \text{nm}^3$. This result was in agreement with that reported in JCPDS cards [11] and indicated that grown $PbWO_4$ crystal had scheelite-type structure.

6. Scintillation performances

It is the purpose of growing large-size $PbWO_4$ by the modified vertical Bridgman method to satisfy CMS experiment and other detector requirements, thus it is critical for grown $PbWO_4$ crystals to have excellent scintillation properties.

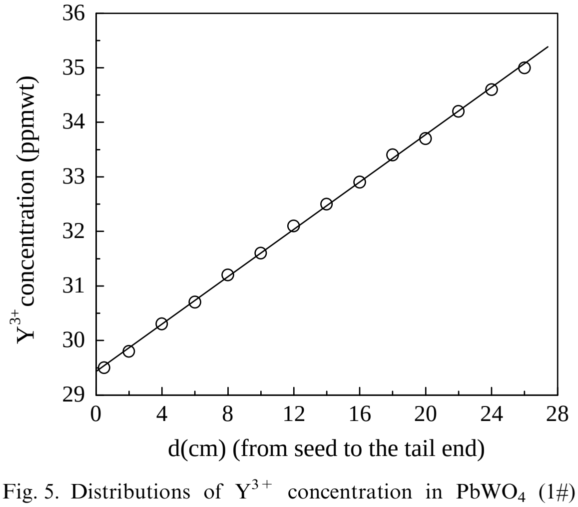

Fig. 5. Distributions of Y^{3+} concentration in $PbWO_4$ (1#) along the growth direction.

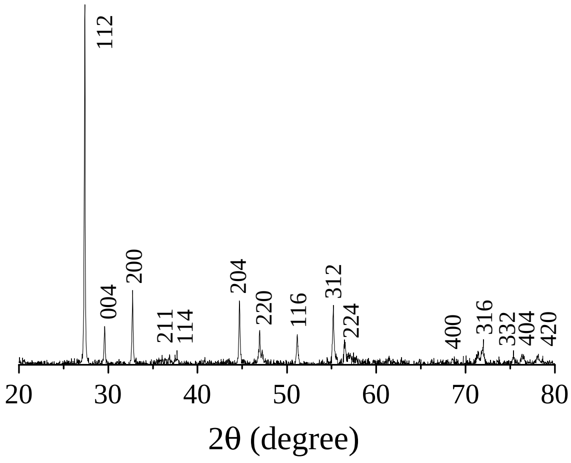

Fig. 6. XRD of $PbWO_4$ crystal (1#) grown by modified vertical Bridgman method.

Table 1
GDMS analyses results of grown $PbWO_4$ (1#)

Element	Concentration (ppm wt)	Element	Concentration (ppm wt)	Element	Concentration (ppm wt)
Li	0.01	Ge	<0.1	Nd	<0.01
Be	<0.005	As	0.46	Sm	<0.01
B	<0.005	Se	<0.01	Eu	<0.05
O	Matrix	Br	<0.01	Gd	<0.005
F	0.02	Rb	<0.01	Tb	<0.005
Na	0.10	Sr	<0.005	Dy	<0.005
Mg	<0.01	Y	32±1	Ho	<0.005
Al	0.01	Zr	<0.01	Er	<0.005
Si	<0.01	Nb	0.4	Tm	<0.01
P	0.02	Mo	0.35±0.5	Yb	<0.005
S	0.03	Ru	<0.005	Lu	<0.005
Cl	<0.01	Rh	<0.05	Hf	<0.01
K	0.13	Pd	<0.05	Ta	<1
Ca	0.03	Ag	0.15	W	Matrix
Sc	<0.05	Cd	<0.5	Re	<0.5
Ti	<0.01	In	Binder	Os	<0.05
V	<0.005	Sn	<0.05	Ir	<0.01
Cr	0.02	Sb	<0.05	Pt	<0.05
Mn	<0.01	Te	<0.05	Au	<0.5
Fe	0.02	I	<0.05	Hg	<5
Co	<0.005	Cs	<0.1	Tl	<0.1
Ni	<0.01	Ba	0.03	Pb	Matrix
Cu	0.20	La	0.62	Bi	<0.5
Zn	<0.01	Ce	0.03	Th	<0.0005
Ga	<0.05	Pr	0.03	U	<0.001

The scintillation properties of $PbWO_4$ can be assessed by optical transmittance and LY and light loss after irradiation.

6.1. Optical transmittance

The crystal boules were cut perpendicular to the growth direction into the dimension of block-shaped with a length of 22 cm and mechanically polished. The longitudinal transmittance of each block was measured using SUIMADZU UV-2501(PC)S spectrometer with a large sample compartment. Typical transmittance spectra of grown $PbWO_4$ crystal (1#) were shown in Fig. 7. The transmittance was close to 30% at 360 nm and >60% at 420 nm, and >65% at 650 nm, after irradiation by ^{60}Co source, the transmittance decreased slightly. For all $PbWO_4$ crystals grown in a furnace, the average transmittance values were >25% at 360 nm, >55% at 420 nm and >65% at 650 nm. These transmittance properties can satisfy the CMS electromagnetic calorimeter requirements [12].

6.2. Light yield (LY)

The LY at room temperature (20°C) for grown $PbWO_4$ was measured using a Hamamatsu photomultiplier tube (R2059PMT) which has a bialkali photocathode and quartz window. A collimated γ-ray source, such as ^{60}Co or ^{137}Cs, was used to excite the sample. The setup for LY measurement is shown in Ref. [13]. The LY of $PbWO_4$ is mainly dependent on the quality of crystal, additionally, it is also related to the size, the shape and the direction of crystal. The measured results of grown $PbWO_4$ crystal (1#) were shown in Table 2. For all $PbWO_4$ crystals grown in a furnace, the average LY values in a gate of 100 ns were excess of 11 photoelectrons/MeV, after irradiation at a dose

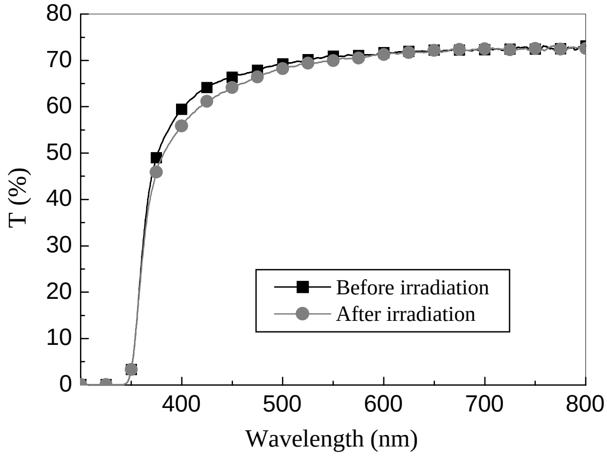

Fig. 7. Longitudinal transmittance of the block (22 cm) cut from grown $PbWO_4$ (1#).

Table 2
Change of LY of grown $PbWO_4$ (1#) before and after irradiation

$PbWO_4$	Irradiation		LY before irradition p.e./MeV (100 ns)	LY after irradition p.e./MeV (100 ns)	Light loss (%)
	Dose rate (rad/h)	Irradiation time (h)			
22 cm	35	70	12.2	11.8	3.3

rate of 35 rad/h, LY values decrease by <5%. These performances of LY and radiation damage can also meet with the CMS experiment requirements [12] and other needs.

7. Conclusion

High-quality large-size lead tungstate single crystal was successfully grown by modified vertical Bridgman method with multi-crucibles. Twenty-eight pieces of $PbWO_4$ crystals can be grown simultaneously in a furnace. The optimal growth parameters were found to be as follows: seed crystal direction $\langle 0\,0\,1 \rangle$, lowering rate 0.6–1.2 mm/h, the axial temperature gradient was about 20°C/cm at growth solid-melt boundary. The crystal boule which was free from crack, inclusions, striations and precipitations had a size of $34 \times 34 \times 360\,\text{mm}^3$, and possessed scheelite-type structure. The growth yield has reached about 85%. The concentrations of impurity ions in grown $PbWO_4$ crystal were <1 ppm (wt). The scintillation properties of grown $PbWO_4$ crystals were as follows: average optical transmittance values were >25% at 360 nm and >55% at 420 nm, average LY values were >11 p.e./MeV, radiation loss is <5%. These parameters indicated that $PbWO_4$ crystals grown by the modified vertical Bridgman method possessed high quality and, therefore, can meet with the CMS experiment and other detector requirements. Owing to the use of crucibles for multi-crystals, this modified vertical Bridgman method is a potential method for mass production of $PbWO_4$ and other crystals.

Acknowledgements

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