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Growth and uniformity improvement of $PbWO_4$ crystal with yttrium doping

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Abstract

Large size single-lead tungstate crystals with yttrium doping were produced at Shanghai Institute of Ceramics by modified Bridgman method along <0 0 1> orientation. Longitudinal transmittance, transverse transmission uniformity, photoluminescence, light output, decay kinetics and light output uniformity of samples with dimension of $30 \times 30 \times 220 mm^3$ were studied. It was found that crystals we made for high-energy physics is highly uniform both in optic and scintillation.

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Keywords: A2. Bridgman technique; A2. Single crystal growth; B2. Scintillator

1. Introduction

Large arrays of scintillating crystals have been assembled for precision measurements of photons and electrons in high energy and nuclear physics. Scintillators used in high energy and nuclear physics should be highly uniform for the experiment to achieve certain resolution. Lead tungstate ($PbWO_4$) crystal was chosen by the compact muon solenoid (CMS) experiment in constructing a precision electromagnetic calorimeter (ECAL) at the large Hadron collider (LHC) [1] because of its high density and fast decay time. And much attention has been paid to the crystal growth for obtaining high-quality crystals for high-energy physics [2–12,16]. It was found that pure $PbWO_4$ has poor optical transmittance and is not radiation hard enough for HEP experiment. And, $PbWO_4$ crystals are so delicate that little change of crystal growth parameters will lead to a great deviation on its scintillating properties. Meanwhile, the tail part of crystal differs from the seed part in both optical and scintillating properties when crystal is long enough [24]. Usually, seed end is better than tail end partially because of contamination elements accumulated in the tail part. Another reason for poor quality of the tail part is the evaporation of PbO [12]. This deviation will surely damage the performance of scintillator, hence the resolution of calorimeter.

Doping during crystal growth is an approach which may compensate structure defects, eliminate

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unwanted impurites and change scintillation properties [7,11,13–16,19,20]. Trivalent (La) doping was first reported by Kobayashi et al. to be effective in improving both transmittance [11] and radiation hardness [16]. Consequent studies found doping with various ions, such as La, Lu, Gd, Y and Nb, at optimized level to be effective in improving transmittance as well as radiation hardness [19,20].

One important technical issue for doping is the uniformity. Since the segregation coefficient of dopant in $PbWO_4$ crystals is usually not equal to one, the dopant tends to distribute not uniformly in the crystal. This would in turn cause bad longitudinal uniformity for large size samples. This bad longitudinal uniformity, if beyond some limit, may affect calorimeter performance. Doping in $PbWO_4$ was extensively studied in SIC. Early attempt of lanthanum (La) doping revealed that it indeed improved transmittance and reduced slow scintillation component, but La-doped $PbWO_4$ crystals suffered from large dose dependence caused by shallow radiation-induced color centers [21]. And, the very large (>2) segregation coefficient of La in $PbWO_4$ crystals also makes it difficult to produce a uniform La distribution in $PbWO_4$ crystals. The segregation coefficient of yttrium in $PbWO_4$ crystals was found to be 0.91 [24]. Thus a rather uniform concentration of yttrium ions in $PbWO_4$ crystal can be achieved by applying adequate technique.

In Shanghai Institute of Ceramics, unique technique of modified vertical Bridgman method was developed for growing bismuth germanate (BGO) single crystals for the L3 experiment. It is an effective method for growth of large dimension scintillation crystals, and we can now produce as much as 28 single $PbWO_4$ crystals at one time by applying this technique. Yttrium-doped single crystals of high uniformity were grown by using raw materials of 50% 5N powders (PbO and WO_3 in stoichiometry of $PbWO_4$) and 50% lead tungstate crystal produced by Bridgman method. We use grown $PbWO_4$ crystal as part of the raw material as it is an effective way to reduce harmful contaminations, such as Na, K and Mo. This paper presents growth technique, optical and scintillating properties of single $PbWO_4$ crystals with yttrium doping.

2. Crystal growth and samples

$PbWO_4$ occurs in nature as tetragonal scheelite type as well as monoclinic raspite. Synthetic $PbWO_4$ crystal, however, either deposited in solution or grown from melt is scheelite only [9,17,18,25]. The space group is $I4_1/a$, and unit cell parameters are $a = b = 0.54619$nm, $c = 1.2049$nm, and $z = 4$ [22]. In this work, crystals were grown along c-axis, $<0\,0\,1>$, as it is hard to grow crack-free large $PbWO_4$ crystals along a-axis. This is mainly because of the great difference in thermal expansion coefficient along axis a, ($1.28 \times 10^{-5}/°C$), and axis c, ($2.95 \times 10^{-5}/°C$) [23].

The crystals were grown in SIC by modified vertical Bridgman method. The raw material consists of 50% 5N powder (PbO and WO_3) and 50% crystallized $PbWO_4$. PbO and WO_3 powders were heated at 200°C for 24 h to remove absorbed water before weighted and well mixed in precise stoichiometry proportion of $PbWO_4$. Crystallized $PbWO_4$ was first ground then cleansed twice in distilled water. Supersonic was applied during cleansing procedure. Again, $PbWO_4$ splinter was heated at 200°C for 24 h to remove the water absorbed. Dry materials were mixed with Y_2O_3 at a concentration of 150 ppm (at) and then melted at 1230°C for ten minutes to ensure complete homogeneity. Melting $PbWO_4$ was poured into 0.2 mm thick platinum crucible with a dimension of $35 \times 35 \times 480\,mm^3$. Seed crystals along axis c, $<0\,0\,1>$, were used. Crucibles were sealed tightly to prevent evaporation, and then loaded into an aluminum holder. A schematic of crucible used in SIC can be found in Ref. [24]. The furnace was controlled by computer, with a temperature fluctuation less than 0.5°C. Temperature gradient at solid–melt interface was set to be 30°C/cm, and lowering rate was 0.8 mm/h. As grown crystals with a dimension of $35 \times 35 \times 300\,mm^3$ were first annealed at 900°C for 10 h before cut and polished to make samples.

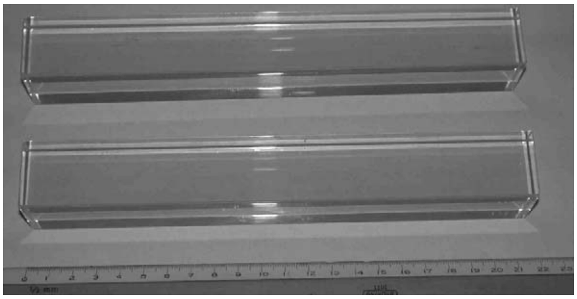

Fig. 1. Large size $PbWO_4$ crystal with a dimension of $30 \times 30 \times 220\,mm^3$ produced at SIC by modified Bridgman method.

In this paper, two samples (see Fig. 1) with a dimension of $30 \times 30 \times 220$ mm^3(named SIC-20301 and SIC-20302, respectively) are investigated. Samples were made $c \perp a \perp b$ and determined by X-ray, that is longitudinal orientated along axis c while transverse-orientated along axis a or b. All samples are transparent, colorless and without visible defects such as cracking, inclusions, scattering centers and growth striation. The crystals were annealed at 200°C for 4 h before optical and scintillation characters were investigated.

3. Experiments and results

3.1. X-ray diffraction

For phrase analysis small block cut from as grown crystal was ground into powder. X-ray diffraction (XRD) spectrum was taken by D/Max-2250 diffractometer with a Cu target running at 40 kV, 50 mA.

X-ray diffraction of as-grown $PbWO_4$ crystal is shown in Fig. 2. As can be seen the crystal we have grown is scheelite type. No other phase was found [22].

3.2. Transmittance

Transmittance spectra were recorded by Shimadzu UV-2501 spectrophotometer. Longitudinal and transverse transmittance for two samples are shown in Fig. 3. As can be seen, transverse transmittance is almost the same as that of

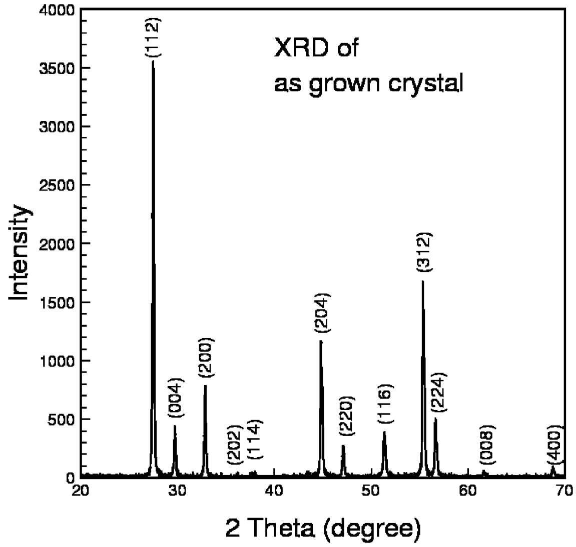

Fig. 2. X-ray diffraction of as-grown $PbWO_4$ crystal.

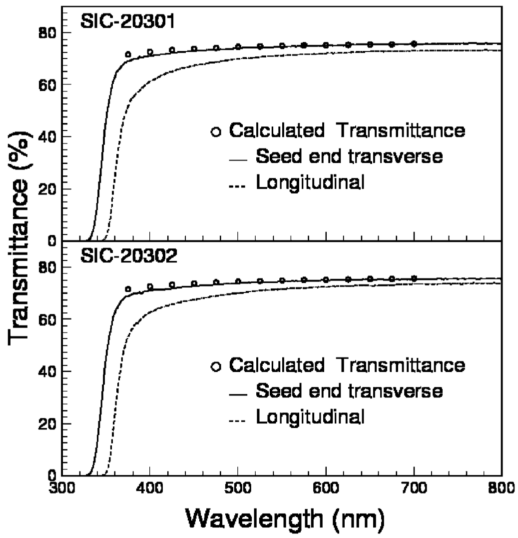

Fig. 3. Longitudinal and transverse transmittance of sample SIC-20301 and SIC-20302.

theoretical limit. It is clear that the pre-exist absorption band within wavelength concerns is very low. To value the optical uniformity, transverse transmittance of five spots evenly distributed along the crystals were recorded. Fig. 4 shows the transverse transmittance at 420 nm normalized to

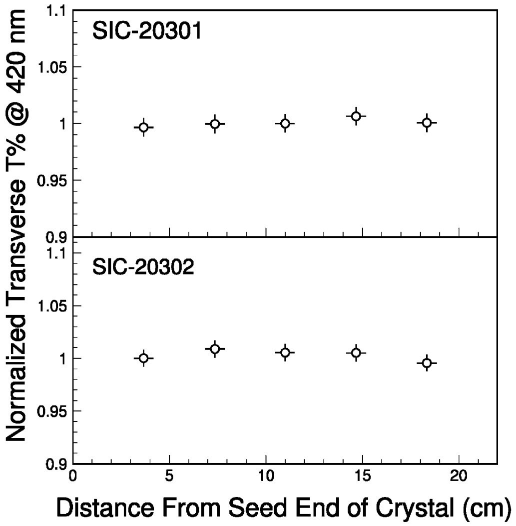

Fig. 4. Normalized transverse transmittance at 420 nm is shown as a function of distance from seed end.

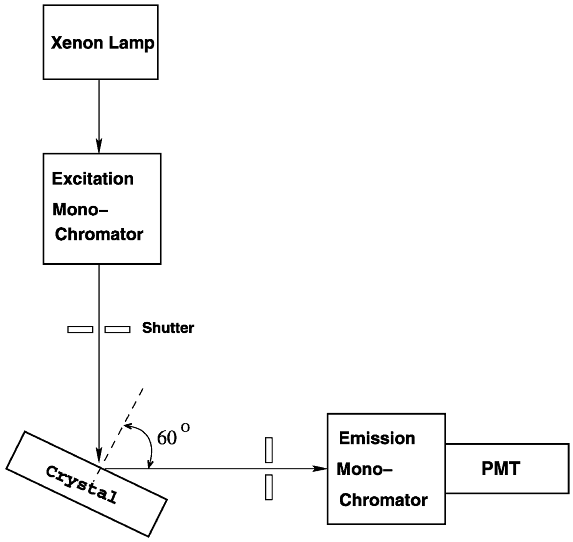

Fig. 5. A schematic of setup used to measure photostimulated luminescence.

that of average value at the same wavelength for the two samples. The deviation of transverse transmittance, as shown in Fig. 4, is within 1.0%.

3.3. Photoluminescence

Scintillating spectra is reported to be affected by contaminations as well as crystal growth conditions [10,27]. For one thing, the change of growth condition shall affect crystallization process, thus intrinsic point defects such as vacancy, interstitial, and dislocation which in turn influence scintillation shall change. For another, cumulation of contaminations may form pre-exist color centers in the crystal, and scintillating mechanism will be influenced if the concentration of contaminations reaches certain level. Studies show that a change in scintillating spectrum usually indicates the change in scintillation mechanism [25,26]. Scintillators for high-energy physics, however, should be uniform in scintillating spectra along the whole crystal.

Photoluminescence (PL) for the two samples were performed by Hitachi F-4500 fluorescence spectrophotometer at room temperature (20°C). A schematic of the measurement setup is shown in Fig. 5. Excitation and emission spectra for both

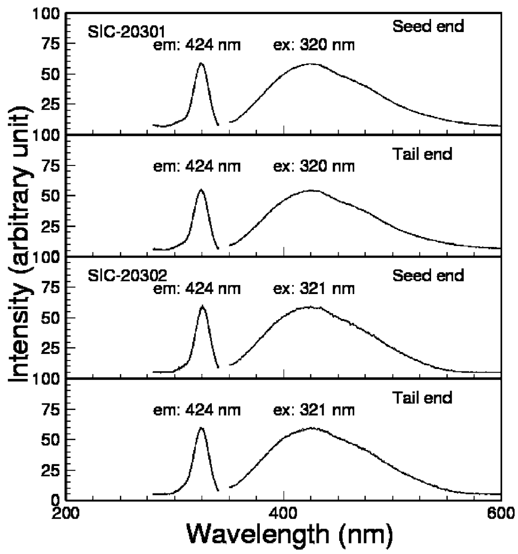

Fig. 6. Emission and excitation spectra are shown as a function of wavelength for SIC-20301 and SIC-20302.

samples were shown in Fig. 6. As can be seen, the emission peaked at 424 nm for both samples with the excitation peaked at 320 and 321 nm for sample 20301 and 20302, respectively. It is clear that PL spectra at two ends for each sample were identical.

3.4. Light output and decay kinetics

Light output measurement were carried out by using R2059 PMT with bialkali cathode. The $PbWO_4$ crystals were coupled to PMT on the seed end with Dow Corning 200 fluid, while all other faces were wrapped with two layers of Tyvek paper to increase the collected light.

Collimated gamma ray from ^{137}Cs source was used to excite the sample. The γ-ray peak was obtained by simple Gaussian fit, and was used to determine light yield by calibration of the single photoelectron peak and quantum efficiency of PMT. Fig. 7 shows distributions of the quantum efficiency of the R2059 PMT and the emission weighted quantum efficiency ($\overline{\mathrm{QE}}$) of samples.

Quantum Efficiency, QE, is a way of expressing cathode sensitivity. It is the ratio of the number of photoelectrons emitted, n_k, to the number of incident photons, n_p:

$$\mathrm{QE} = \frac{n_k}{n_p}. \tag{1}$$

QE is usually specified for monochromatic light and thus wavelength related. $\overline{\mathrm{QE}}$ is calculated by taking into account the scintillation luminescence intensity.

$$\overline{\mathrm{QE}} = \frac{\int \mathrm{QE}(\lambda) Em(\lambda) \mathrm{d}\lambda}{\int Em(\lambda)\, \mathrm{d}\lambda}, \tag{2}$$

where $\mathrm{QE}(\lambda)$ is the quantum efficiency of cathode at certain wavelength (λ), and $Em(\lambda)$ is scintillation intensity at certain wavelength (λ).

The light output in the unit of photon/MeV was obtained by using emission weighted quantum efficiencies, $\overline{\mathrm{QE}}$:

$$\mathrm{photon/MeV} = \frac{\mathrm{photoelectron/MeV}}{\overline{\mathrm{QE}}}. \tag{3}$$

All measurements were carried out at a room temperature of 20°C. For every sample, a total of eight different integration times, ranging from 35 to 4000 ns, were measured and fit to determine the decay time. Fig. 8 shows decay kinetics of the two samples. The result was characterized as

$$\mathrm{L.O} = A_0 + A_1(1 - \mathrm{e}^{-t/\tau_1}), \tag{4}$$

where L.O is the total light output of the sample obtained from the fit, A_0 is the light output of fast component with a decay time of less than 10 ns, and A_1 is the light output with decay time of τ_1. The main decay time is 28.2 and 31.3 ns for SIC-20301 and SIC-20302, respectively.

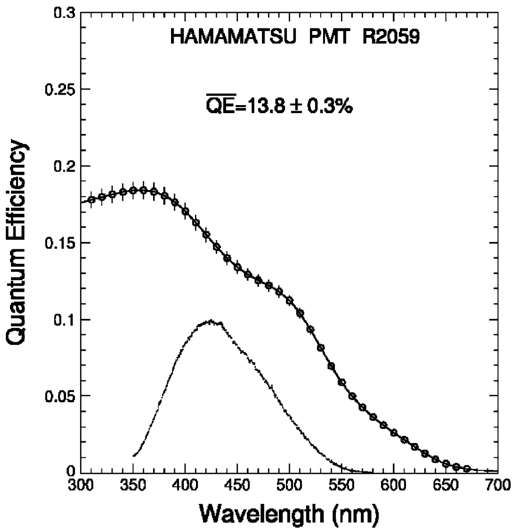

Fig. 7. Quantum efficiency of the R2059 PMT is shown as function of wavelength together with emission spectra.

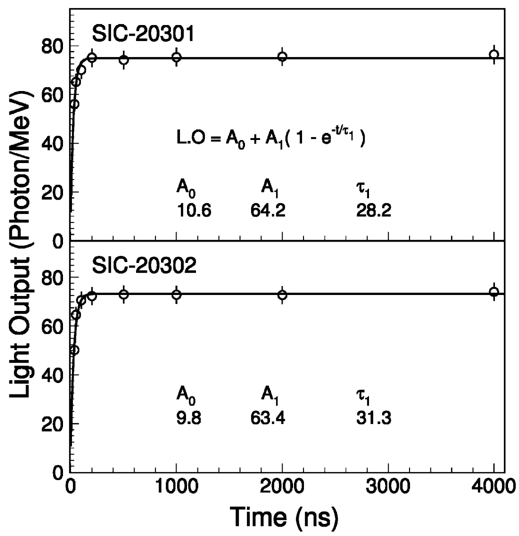

Fig. 8. Decay kinetics of sample SIC-20301 and SIC-20302.

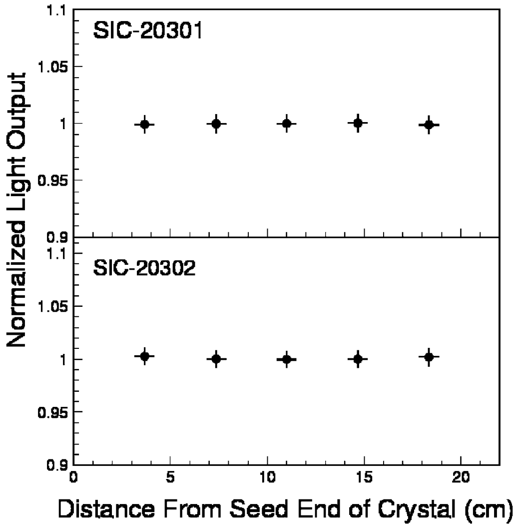

Fig. 9. Normalized light output is shown as a function of distance from seed end for SIC-20301 and SIC-20302.

To evaluate the light output uniformity along the crystal, γ-ray was moved to shoot at five spots evenly distributed along the crystals. And, the pulse high spectra with an integrated time of 200 ns were recorded to determine the light output. The light output, normalized to that of average value, is shown in Fig. 9. The deviation is within 1.0%, indicating a high uniformity in the light output along the crystal.

4. Conclusions

Large-size crack-free $PbWO_4$ single crystals with yttrium doping were grown by modified Bridgman method. Axis *c* was found to be the favorable orientation. The temperature gradient was 30°C/cm at solid–melt interface with a lowing rate of 0.8 mm/h. The concentration of dopant, Y_2O_3, in the melt was 150 ppm (at). To reduce contaminations, crystallized single $PbWO_4$ were used as part of raw material. And, the crystals produced were of high uniformity in photoluminescence, transmittance and light output. The deviation of transmittance as well as light output along crystal is within 1.0%.

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