Peculiarities of growing PbWO$_4$ scintillator crystals for application in high-energy physics

S. Burachas$^a$, V. Martynov$^a$, V. Ryzhikov$^a$, G. Tamulaitis$^{b,*}$, H.H. Gutbrod$^c$, V.I. Manko$^d$

$^a$Institute of Single Crystals, 60 Lenin Ave., Kharkov 31001, Ukraine
$^b$Institute of Materials Science and Applied Research, Vilnius University, 24 Naugarduko, Vilnius 2006, Lithuania
$^c$Subatech, Ecole des Mines de Nantes, Laboratoire de Physique Subatomique et des Technologies Associées, 4 rue Alfred Kastler, F-44070 Nantes Cedex 03, France
$^d$Kurchatov National Center, Kurchatov sq. 1, Moscow 123182, Russian Federation

Received 28 January 1997; accepted 10 June 1997

Abstract

Results on investigation of radiative and optical properties of PbWO$_4$ and optimization of the Czochralski method in order to grow single crystals suitable for application in high-energy physics are presented. Special attention is paid to crystal anisotropy, the thermal conditions of the crystal growth enabling to avoid deviations from stoichiometric composition and inclusions of abnormal phases, as well as to the role of atmosphere during the crystal growth and annealing. It has been shown that the consideration of these peculiarities enables us to reliably fabricate 230 mm long scintillators with quantum yield of 11–14 phe/MeV and without a slow component of luminescence decay. © 1998 Elsevier Science B.V. All rights reserved.

PACS: 81.10.Fq; 29.40.Mc; 78.55. – m

Keywords: Czochralski method; PbWO$_4$; Scintillator crystals

1. Introduction

Application of PbWO$_4$ (PWO) single crystals in scintillator detectors of electromagnetic calorimeters raises specific requirements for fabrication of this material. The single crystals have to be large, homogeneous, radiation hard, and to have fast luminescence decay. Understanding of the mechanisms of luminescence in the PWO, the peculiarities of the crystallographic structure of the crystal, and the physical properties of the system PbO–WO$_3$ are necessary for the choice of optimal conditions and regimes of crystallization.

The luminescence spectrum of the PWO usually consists of several overlapped bands. The band peaked at 2.9–3 eV seems to be of intrinsic origin and is usually attributed to the recombination at regular $WO_4^{2–}$ molecular ions [1–3]. A weak luminescence component observed at the
The high-energy slope of this band was interpreted to be also of intrinsic origin [3]. The luminescence in the green region strongly depends on growth conditions. The recent results led to a conclusion that this luminescence is caused by structural defects such as isolated WO$_3$ groups or WO$_3$ + F complexes [2, 4]. The decay is dominated by the component of 2–3 ns decay time at RT. However, a slow component decaying with characteristic time of the order of some microseconds or more is observed [5–8]. This component severely limits the possibilities of application of the PWO in scintillator detectors expected to operate at a high rate. It has been recently established that the luminescence decay is slower at longer wavelength [5, 7]; however, investigation of the origin of the slow component is still at an initial stage of investigation [7].

The aim of this work is a detailed study of principal aspects of fabrication of the PWO scintillator crystals by Czochralski method to meet the requirements for application in high-energy physics. Attention is paid to the relation between the growth parameters and scintillation characteristics obtained.

2. Experimental procedure

The PWO scintillator crystals were grown by Czochralski method. Our crystallizer was designed by taking into account growth peculiarities of the oxide crystals of constant diameter [9–11]. The analysis was based on balance equation describing dissipation of the power consumed for heating of the melt $W(t)$ [12]:

$$\frac{dQ}{dt} = W(t) - W_c(t) - W_s(t) - W_b(t) - W_w(t),$$  \hspace{1cm} (1)

where the left-hand side of the equation describes the change rate of the heat content of the melt while the time-dependent terms $W_c$, $W_s$, $W_b$ and $W_w$ indicate power dissipated, correspondingly, through the crystal, the free surface of the melt, the bottom and the walls of the crucible. In accordance with calculations of the dissipated power (see Ref. [12] for details) and our recent experimental investigations, we modified the structure of our crystallizer to optimize thermal insulation of the crucible, its positioning in the inductor, sizes of the crucible and the inductor. A proper temperature distribution along the growth axis to ensure the optimal heat conductivity through the crystal was also achieved by modifying the design of components of the crystallizer. The power consumed by the heater was chosen as the main integral parameter indicating correctness of the crystallizer design. The power under automated maintaining of the constant diameter of the growing crystal must have monotonically increasing character when the process of growth proceeds.

The fabrication of the PWO scintillator crystals consists of two major steps, i.e. growing of the crystal and annealing of as-grown boule, semi-finished product, and the scintillation block after the mechanical treatment is completed. We would like to especially emphasize the importance of the second stage. To maintain the necessary content and pressure of the atmosphere during the processes of crystal growth and annealing we designed a special device. The device ensured homogeneous thermal field in the annealing zone and hermetic sealing of the annealing chamber. The oxygen content in the chamber was measured by using a gas analyzer “Zircon”. We found that the oxygen content in the atmosphere of the chamber increases in the process of annealing. This increase is caused by desorption from heat-insulating ceramics, especially in the early stages of heating. Some amount of oxygen can be contained in inert gas when the chamber is filled up with inert gas. Anyway, even in the early stage of heating process when the temperature is increased to $\sim$300°C, the oxygen content in the chamber can easily exceed the desirable value. In order to keep the oxygen content low enough, a special device was designed in the annealing chamber to bind the oxygen into solid chemical compounds (oxides). By monitoring the oxidation reaction, we were able to reliably maintain the oxygen content in the limits not exceeding the critical value during the whole annealing process.

The luminescence of the PWO was studied under selective excitation of the blue emission band. The fourth harmonic of the YAG : Nd$^{3+}$ laser radiation with quantum energy of 4.66 eV and pulse duration of 10 ns was utilized. The spectra without delay
were measured by using a box-car integrator, while the spectrum of the slow component was recorded by utilizing the more sensitive photon-counting technique.

3. Experimental results and discussion

3.1. Radiative properties of PWO

In order to reveal whether the slow luminescence decay of PWO is caused by a radiative recombination at a specific center or it is inherent for the centers responsible for the blue and green luminescence bands, we selectively excited the center of the blue component, preferable in PWO scintillators [13], and measured the luminescence spectra synchronously with excitation as well as with delay of several microseconds. The spectra are presented in Fig. 1 illustrating stability of the band shape in the decay process. So the slow component seems to be caused by recombination at the same radiative center which is responsible for the blue luminescence at initial stages of luminescence decay. As it is discussed elsewhere [14], the same conclusion can be applied to the green luminescence, however, the relative intensity of the slow component in the green region is higher and its decay proceeds slower, in agreement with Refs. [7, 15]. So, it seems to be rather plausible to interpret the slow component by reexcitation of trapped carriers back to the radiative centers responsible for the luminescence in the blue and green regions of the spectrum. The trapping process takes place at initial stages of excitation relaxation and determines kinetics of the fast luminescence decay at elevated temperatures. The strong temperature dependence of the luminescence decay rate confirms a natural conclusion that the trapping of the photoexcited carriers is thermally activated over a certain barrier. Since the slow decay component of the blue luminescence band of intrinsic origin is weaker than that in the green region, it is desirable, from the point of view of kinetic characteristics, to fabricate scintillation crystals with dominating blue band in their luminescence spectrum.

However, the green component contributes to the total light yield of the crystal [7]. So new ways to increase the quantum yield in crystals with dominating blue component of its luminescence is highly desirable to compensate the contribution of the green component. Diminishing of reabsorption of the emitted light by increasing the crystal transparency can be pointed out as one of the major opportunities to increase the effective quantum yield, which mean to suppress especially 420 nm band ascribed to O⁻ centers [16].

3.2. The growth of PWO

State diagram of the system PbO–WO₃ reveals existence of two congruently melting compounds: Pb₂WO₅ with melting point \( T_m \) at 899°C and PbWO₄ with \( T_m = 1123°C \) [17]. The high-temperature tetragonal \( \beta \)-modification of the PbWO₄ transfers to a low-temperature monoclinic \( \alpha \)-modification at temperature of 887°C. So inclusions of \( \alpha \)-modification and Pb₂WO₅ have to be carefully avoided when homogeneous monocrystals of \( \beta \)-modification of the PbWO₄ are grown. We observed that the \( \alpha \)-modification occurs when the melt is sustained in a supercooled state for a long time. X-ray analysis of the melt crystallized from the supercooled state indicated the presence of \~2% of the \( \alpha \)-modification of the PbWO₄. Consequently, a special attention has to be paid to the
conditions of heat removal from the front of crystal growth in order to grow homogeneous high-quality crystals.

It is worth noting that the homogeneity of the crystal might be disturbed also by deviations from stoichiometry when the melt is superheated. Consequently, the melt temperature optimal for the growth of the PWO, like that of the BGO [9], is limited both from below (to avoid supercooling that increases the probability of formation of inclusions of the \(x\)-modification of PbWO\(_4\) and the Pb\(_2\)WO\(_5\)) and from above (because of superheating that causes deviation from stoichiometry). The appropriate temperature range is determined by choosing optimal thermal conditions of growth by means of optimization of growth regimes and special design of the crystallizer.

Furthermore, the tetragonal crystal system of the PbWO\(_4\) causes anisotropy of its crystallochemical and physical properties. We measured the thermal conductivity of the crystal in different crystallographic directions and found out that the thermal conductivity in [0 0 1] exceeds that in directions [1 0 0] and [1 0 1] by 10%. Consequently, the [0 0 1] direction is more preferable as a growth direction because of higher rate of heat removal from the crystallization front. Moreover, the light yield in such crystals is by 5–10% higher than that in the crystals grown in other directions [18].

Unfortunately, the anisotropy of mechanical properties of the PWO works not in favor of the crystals grown in [0 0 1] direction. Cleavage planes, thoroughly investigated in PWO crystals in Ref. [19], are of crucial importance for mechanical processing of the boules. When the crystal is grown in [0 0 1] direction, the cleavage plane (0 0 1), being perpendicular to the growing axis, plays highly destructive role during the mechanical processing and easily cause ruptures of the crystal, especially if large blocks have to be fabricated. We did not succeeded to reliably fabricate scintillation blocks of necessary size from boules grown in [0 0 1]. The cleavage plains (1 0 1) and (1 1 2), important for mechanical treatment of crystals grown in [1 0 0] direction, are not so destructive, and large crystal blocks can be fabricated from such boules, though their scintillator properties are slightly worse than that of crystals grown in [0 0 1]. So we came to the conclusion that the [1 0 4] direction forming an angle of \(\sim 19^\circ\) with [0 0 1] is an optimal choice combining high quantum yield and thermal conductivity with passable mechanical properties.

Irrespective of the growth direction, growth of screw-shaped crystals was observed. We elucidated that it was caused by misalignment between the growth axis and the axis of temperature distribution in the melt. The screwing effect is considerably enhanced by increasing the rate of crystal rotation as well as by excessive thermal screening of the crystal.

The modified structure of the crystallizer allowed us to fabricate homogeneous, highly transparent crystals with diameter of 34 mm and length of up to 300 mm at the pulling rate of 4–6 mm/h and rotation rate of 15–30 rpm which were found to be optimal. The crystal diameter was controlled by weighting the crystal. The duration of the technological process of crystal fabrication of 65–75 h consisted of 53–60 h of crystal growth and 12–15 h of annealing in the growth chamber.

Some of the crystals in the early experiments had slightly yellow color though the purity of the row materials, technique of melt preparation and thermal conditions of the growth were identical for both colorless and yellow crystals. The yellow color of the crystal is caused by the absorption band peaked at 430 nm. The band is due to excess oxygen, in accordance with results of a detailed study of this band in Ref. [16]. Furthermore, the ratio of intensities of the green luminescence and the blue one was different in different samples. The detailed analysis of this phenomenon led us to a conclusion that the atmosphere during the crystal growth and its subsequent thermal treatment is of crucial importance for the optical and radiative properties of the PWO. It was also observed that the intentionally chosen content and pressure of the atmosphere in the process of preparing the mixture of row materials and the melt also contribute to the shift of the luminescence band towards the blue region.

We also carried out a detailed study of correlation between annealing conditions and the luminescent properties of the PWO and established...
optimal regimes of thermal treatment of semi-finished and finished scintillation crystals enabling to increase the light yield by 15–30% in comparison with that of as-grown crystals without deviation from the initial luminescence spectrum.

3.3. Optimized crystals

The discussed study of the conditions of the PWO growth allowed us to fabricate homogeneous crystals with good scintillation properties. Typical examples of the boule and block-shaped crystals before and after polishing are presented in Fig. 2. The transmission spectrum of a PWO crystal fabricated in optimized conditions is compared with the spectrum of an ordinary crystal in Fig. 3. The luminescence spectra of the optimized crystals are dominated by the blue component of radiation so that the fraction of the slow decaying luminescence be considerably diminished. Nine crystals shaped as $22 \times 22 \times 200$ mm$^3$ blocks for the program ALICE and six 230 mm long crystals tapered from $23.8 \times 23.8$ mm$^2$ at the large end to $20.4 \times 20.4$ mm$^2$ at the small end for the program CMS at CERN were fabricated in summer, 1996 at the Institute of Single Crystals in Kharkov, Ukraine, by utilizing the discussed optimization of the processes of growth and annealing. The six scintillators for CMS were comparatively studied at CERN and PSI together with crystals fabricated in Bogoroditsk, Russia, and at Shanghai Institute of Ceramics in China. The investigation at PSI evidenced that all our crystals studied had identical decay characteristics without slow component [20].

Together with the luminescence characteristics of the PWO, its radiation hardness is also of crucial importance for application in high-energy physics. The comparison from this point of view of the crystals provided for the CMS project was recently discussed by Lecoq [21]. Taking the added width of less than 0.3% at 50 GeV excitation, as given by APD measurements, as criterion for “good crystal”, 4 from our 6 samples meet the requirement. This conclusion might be treated as a high merit in comparison with 1 out of 4 crystals from SIC and 11 out of 24 crystals from Bogoroditsk found to satisfy the criterion.

4. Conclusions

In conclusion, the optimization of the conditions of growth and thermal treatment allowed us to fabricate highly homogeneous and transparent PWO scintillation crystals with fast initial luminescence decay and minimized slow component. Their quantum yield equals 11–14 phe/MeV. The detailed study of the growth and annealing conditions enabled us to achieve good reproducibility of optimized scintillation properties of the PWO crystals.
Acknowledgements

We would like to thank Dr. P. Lecoq and Dr. D. Renker for interesting and inspiring discussions and comparative analysis of scintillation properties of our crystals and L. Nagornaya for measuring radiation hardness and light yield as well as for discussions on some technological aspects of crystal fabrication. This work was partially supported by INTAS under contract INTAS-93-2773 and by the program of the Ukrainian State Committee for Science and Technology “High Energy Physics”.

References