Electrical and γ-ray energy spectrum response properties of PbI_2 crystal grown by physical vapor transport*

Sun Hui(孙辉)[1], Zhu Xinghua(朱兴华)[2], Yang Dingyu(杨定宇)[2], He Zhiyu(何知宇)[1], Zhu Shifu(朱世富)[1], and Zhao Beijun(赵北君)[1,†]

[1]Department of Materials Science, Sichuan University, Chengdu 610064, China
[2]School of Optoelectronic Technology, Chengdu University of Information Technology, Chengdu 610225, China

Abstract: Lead iodide single crystal was grown by physical vapor transport method. Two radiation detectors with different configurations were fabricated from the as-grown crystal. The electrical and γ-ray response properties at room temperature of the both detectors were investigated. It is found that the dark resistivity of the detectors are respectively 3×10^{10} Ω·cm for bias electric field parallel to crystal c-axis ($E//c$) and 2×10^{8} Ω·cm for perpendicular to crystal c-axis ($E \perp c$). The energy spectrum response measurement shows that both detectors were sensitive to ^{241}Am 59.5 keV γ-rays, and achieved a good energy resolution of 16.8% for the $E \perp c$-axis configuration detector with a full width at half maximum of 9.996 keV.

Key words: PbI_2 crystal; physical vapor transport; radiation detector; γ-rays energy spectrum
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1. Introduction

PbI_2 crystal is a wide band gap semiconductor ($E_g >$ 2.3 eV) with high atomic number elements ($Z_{Pb} = 82$, $Z_I = 53$) and room temperature resistivity of about 10^{13} Ω·cm and density of 6.2 g/cm^3, which leads to it being regarded as one of the most promising materials for room temperature ionizing radiation detector, γ-ray and X-ray imaging[1, 2]. Several papers have reported PbI_2 crystal grown from melt by the traveling molten zone (TMZ) method[3], zone refining (ZR)[4], the vertical Bridgman method[5, 6], and the PbI_2 platelet by physical vapor transport method[7]. Usually, PbI_2 crystals grown from melt need a ultra-high purity starting material to obtain a γ-ray energy spectrum response[8]. However, the process used to obtain ultra-high material is always time-consuming and complicated. The PbI_2 platelet grown by physical vapor transport is usually small, with thickness less than 250 μm, and because of its small thickness, the platelet is only suitable for low energy X-ray detection except for γ-rays[7]. An ^{241}Am α-particle spectrum response has also been obtained with PbI_2 polycrystalline film detectors[9]. For radiation detection of the platelets and the films, the c-axis of the PbI_2 material is generally arranged perpendicular to the electrode contact surfaces, with an electric field $E//c$-axis.

In this paper, the starting material used for the experiment was synthesized from lead nitrate and potassium iodide without further purification. The crystal was grown on a quartz substrate by using the physical vapor transport method. For the first time, an orange crystal with size of about $24 \times 16 \times 2$ mm^3 was obtained. Two detectors were fabricated from the as-grown crystal: alpha configuration ($E//c$-axis) and beta configuration ($E \perp c$-axis). The dark current, resistivity, and energy spectrum response of ^{241}Am 59.5 keV γ-rays at room temperature of the both detectors were measured. It is found that both detectors are sensitive to the γ-ray photons. An improved energy resolution 16.8% is obtained from the beta configuration with an FWHM of 9.996 keV for 59.5 keV.

2. Experiment

The starting material used for crystal growth was synthesized from lead nitrate (99.5%) and potassium iodide (99.8%). The synthetic PbI_2 was cleaned by distilled water and then dried in vacuum for 24 h at 0.1 Pa. The growth was performed in a quartz ampoule of 3 cm in diameter and 25 cm in length. The ampoule was cleaned with 10% HF–H_2O, rinsed with distilled water, and then out gassed for 24 h at 200 ℃. A quartz substrate was placed at the B zone perpendicular to the ampoule wall and the PbI_2 powder was charged at the A zone of the ampoule, as shown in Fig. 1. The ampoule was sealed at 1.5×10^{-3} Pa and mounted into a horizontal tube furnace. The temperatures of the A zone and B zone were controlled at 440 ℃ and 200 ℃, respectively. After growth, the ampoule was cooled down to room temperature at a rate of 2 ℃/min.

The as-grown crystal is intact with size $24 \times 16 \times 2$ mm^3, as shown in Fig. 2. The color of the crystal is orange and similar to the crystal grown by using the vertical Bridgman method[5]. Lots of reflecting stripes on the crystal's surface (Fig. 2(a)) is usually attributed to the crystal's layer structure. The cleavage face (Fig. 2(b)) is also commonly related to (001) planes[7]. For fabrication and measurements of detectors, two wafers with the size of $2 \times 2 \times 0.5$ mm^3 were cleaved from the green ellipse zone of the crystal. Without mechanical polish or chemical etching, the gold (Au) electrodes were deposited on both sides of the wafers by using the sputtering method to form a

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† Corresponding author. Email: beijun.zhao@tom.com
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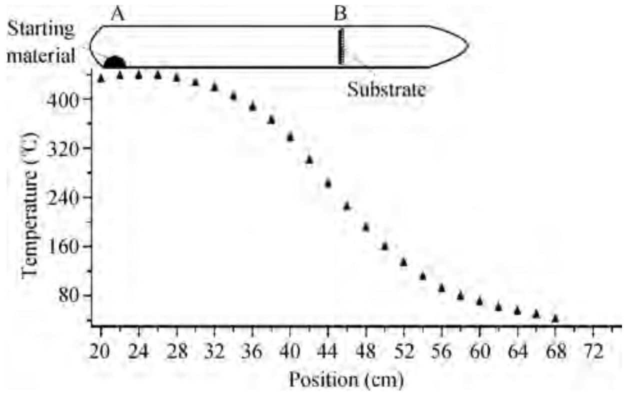

Fig. 1. Arrangement of growth ampoule and the temperature profile of furnace.

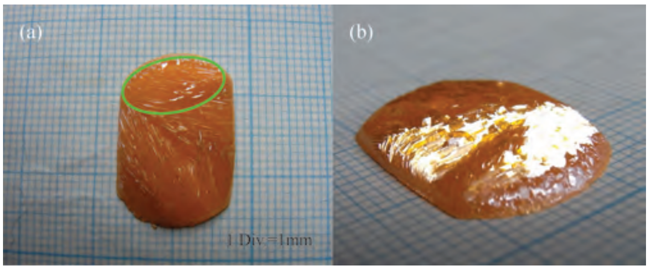

Fig. 2. Photographs of the grown PbI_2 crystal. (a) The grown crystal surface. (b) The cleavage face of the crystal.

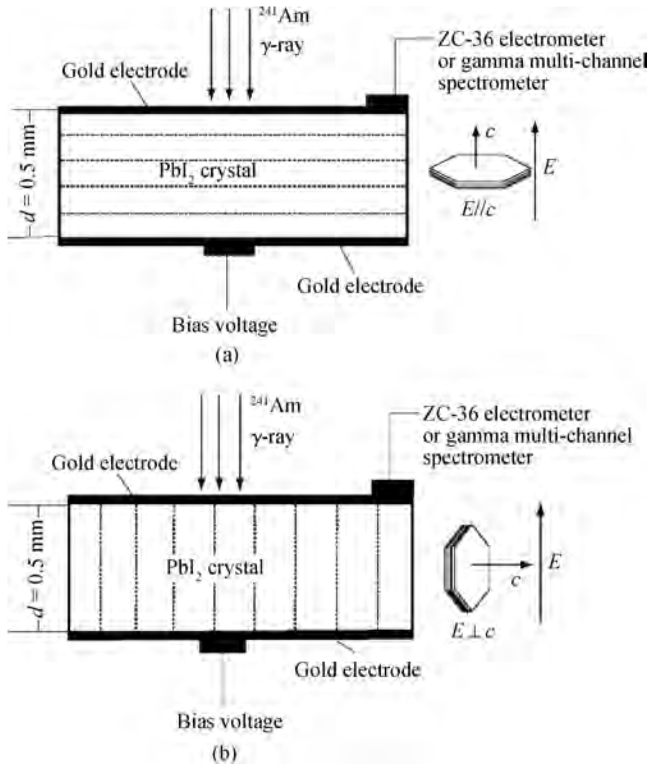

Fig. 3. Schematic diagrams of the PbI_2 detectors fabricated with alpha and beta configuration. (a) Alpha configuration: $E//c$-axis. (b) Beta configuration: $E \perp c$-axis.

Au/PbI_2/Au detector structure. The palladium (Pd) wires of 30 μm in diameter were attached to electrodes surface using graphite conductive adhesive. Then the detectors were packaged in an aluminum cylindrical box. The difference between the both detectors is due to the relative direction between the electric field E and the c-axis of the crystal, i.e., alpha configuration with $E//c$-axis and beta configuration with $E \perp c$-axis, as shown in Fig. 3.

Before the electrical properties measurement, the detectors were kept in a light-tight measuring box for 2 h. The I–V measurements at room temperature were carried out in dark conditions using a ZC-36 electrometer and an adjustable DC high voltage power supply. The dark current versus bias electric field characteristics of the detector were measured before γ-ray radiation.

For γ-ray energy spectrum response measurement, a ^{241}Am source was used as the γ-ray radiation source. The energy of the γ-ray photon is 59.5 keV. The γ-rays from the ^{241}Am source impinging on the PbI_2 crystal generate electron–hole pairs in the crystal. These electric charges were collected by a charge sensitive preamplifier (CSP). The output signal from the CSP was amplified and pulse-shaped with a time constant of 8 μs in the main amplifier. Then the signal was analyzed using a 1024 channel multi-channel analyzer (MCA) connected to a computer.

3. Results and discussion

Figure 4 shows the optical microscopy images of PbI_2 crystal grown by the physical vapor transport method. The hexagonal crystals are clearly visible from the crystal cleavage plane (Fig. 4(a)). Meanwhile, when the observation was carried out on the plane in parallel to the crystal c-axis, a slip between layers generated during the crystal cleavage was also visible (Fig. 4(b)). It is well known that PbI_2 crystal consists of hexagonal crystals with a layered structure. The crystal is composed of Pb–I–Pb covalent bonded layers stacked by Van der Waals force perpendicular to the layer and building (001) faces[9]. Compared to the melt growth system (vertical Bridgman method, ZR and TMZ), this growth mode is more likely to occur in the vapor phase growth system.

The detector dark current density (J) as a function of the bias electric field (E) applied to the detector at room temperature is shown in Fig. 5. The a and b curves represent the measurement results of alpha and beta configuration, respectively. The resistivity can be calculated by the differential form of Ohm's law[10]:

$$J = \sigma E, \quad (1)$$

$$\rho = 1/\sigma, \quad (2)$$

where E is the bias electric field, ρ is the resistivity of the detector, and σ is the conductibility of the detector, which is equal to the slope of the J–E curve.

The dark resistivity at room temperature calculated from a linear fit to the measured data of Fig. 5 is 3×10^{10} Ω·cm for $E//c$-axis and 2×10^8 Ω·cm for $E \perp c$-axis. The dark resistivity along the crystal c-axis is higher than the value perpendicular to the c-axis, which is ascribable to the strongly anisotropy of the PbI_2 crystal structure and the carrier scattering caused by the boundary between layers. The leakage current of the two

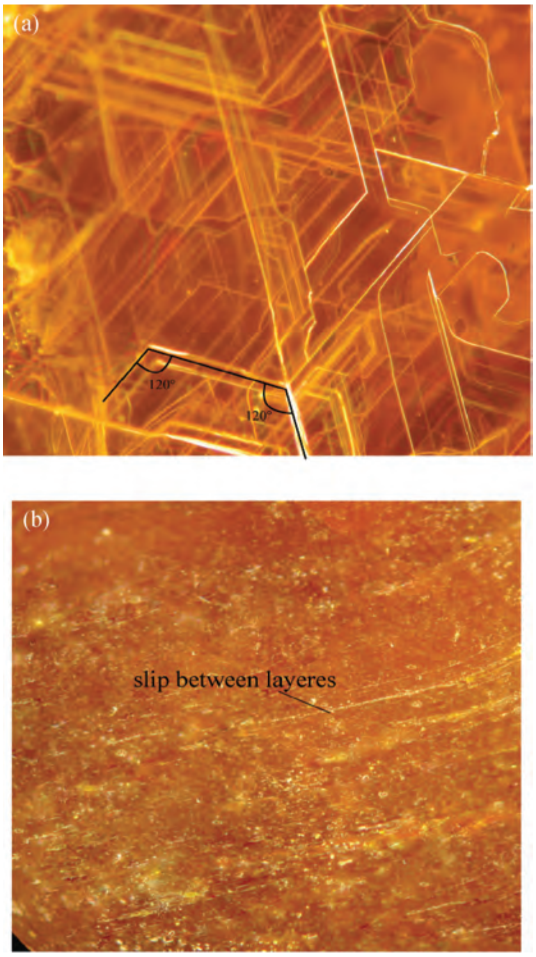

Fig. 4. Optical microscopy images of the as-grown PbI_2 crystal surface (100 × magnification). (a) (001) plane. (b) Plane parallel to crystal c-axis.

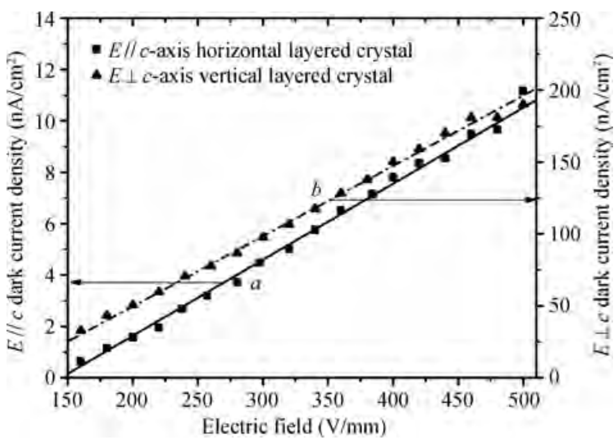

Fig. 5. PbI_2 crystal dark current versus bias electric field at room temperature.

types of detectors is about 8×10^{-10} A and 2×10^{-7} A at bias voltage of 50 V for $E//c$-axis and $E \perp c$-axis, respectively.

Figure 6 presents the pulse-height spectrum of the detectors for the 59.5 keV γ-rays from the ^{241}Am source at room temperature (300 K). The γ-rays impinged on the negative electrode at a bias of 70 V and 50 V for alpha and beta configuration, respectively. The energy spectrum responses for 59.5 keV γ-rays radiation were both obtained by the two detectors. However, the peak broadening of alpha configuration is more serious than that of beta configuration. The best energy resolution for 59.5 keV γ-rays is 16.8% (FWHM = 9.996 keV for 59.5 keV) with beta configuration. In our previous works[6], it was reported that the energy resolution for 59.5 keV ^{241}Am γ-rays is FWHM = 26.7 keV by the detector fabricated from the PbI_2 crystal grown by the vertical Bridgman method. The disparity of the energy resolution can probably be attributed to not fully considering the relative direction between electric field E and the c-axis of the crystal.

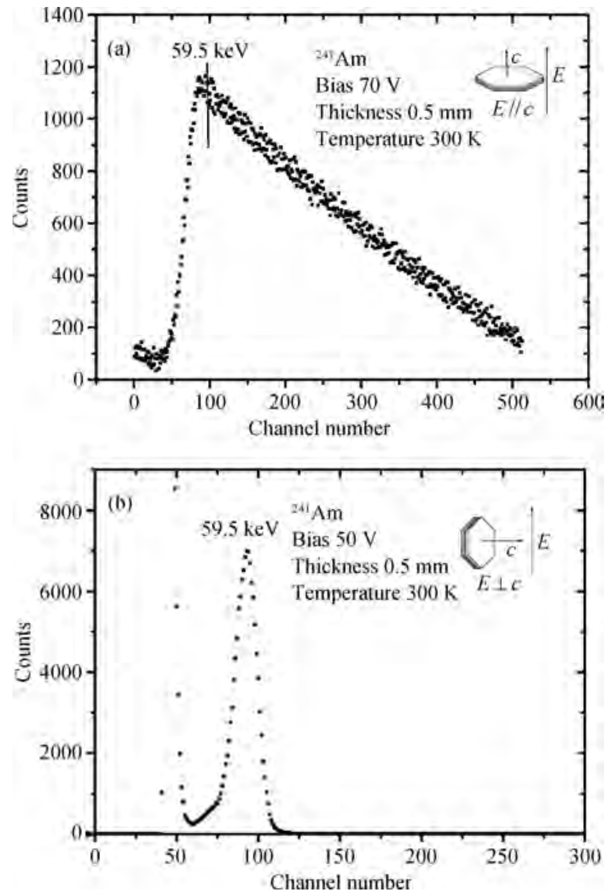

Fig. 6. ^{241}Am, 59.5 keV γ-rays energy spectrum obtained using two configuration PbI_2 detectors.

The major reasons for poor energy resolution or the serious peak-broadening effect in the alpha configuration may be the following ones. Firstly, electron and hole mobility along the c-axis, i.e., perpendicular to the layers, are both relatively low, probably due to the anisotropy of the PbI_2 crystal structure. Secondly, the trapping effect of the crystal defect and impurities on electron and hole transport is more serious in parallel to c-axis crystal than in perpendicular to c-axis crystal. The PbI_2 crystal growth process occurs mostly through building up of Pb–I–Pb layers and layers bonded by weak Van der Waals force, which is weaker than the ionic or covalent bonding. During the crystal growth, impurities easily enter the crystal and damage the Van der Waals bond between layers to form defects, stacking-faults and so on. It is deduced that impurities and defects may be gathered together between layers leading to a remarkable capture of electrons and holes, resulting in poor energy resolution. It can be found that the energy resolution of the alpha configuration detector for ^{241}Am radiation is only 96.46% despite its higher dark resistivity than the beta configuration.

Contrarily, the beta configuration detector can partly avoid the influence of the crystal slippage and boundary between layers. As shown in Fig. 3, the electrodes are parallel to the crystal c-axis, i.e., perpendicular to the slip band or macro-gap between layers in the beta configuration. For this detector structure, the transport channel for electrons and holes is inside the layered crystal and the transport channels still exist even if layers are mechanically separated. It is noteworthy that the alpha configuration is not suitable for detector fabrication due to its ease of mechanical damage i.e., the slippage of layers, result in invalidation of devices.

4. Conclusion

Two different configuration radiation detectors were fabricated from PbI_2 crystals grown by using the physical vapor transport method. The electrical and γ-ray response properties of the detectors at room temperature were investigated. The dark resistivities at room temperature were 3×10^{10} Ω·cm for $E//c$-axis and 2×10^8 Ω·cm for $E \perp c$-axis. The higher resistivity along the crystal c-axis may due to the strong anisotropy of the PbI_2 crystal structure and the carrier scattering caused by the boundary between layers. Photo-peaks for 59.5 keV γ-rays from the ^{241}Am source were clearly observed from both configuration detectors at room temperature. It is found that the beta configuration achieved the best energy resolution of 16.8% with a FWHM of 9.996 keV for 59.5 keV γ-rays, attributing to the weak influence of the boundary between layers and the crystal slippage in this detector.

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