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An effective method for thallium bromide purification and research on crystal properties

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ABSTRACT

Thallium bromide (TlBr) is a promising candidate for room-temperature X- and gamma-ray detectors in view of its excellent intrinsic features. However, material purity and crystal quality concerns still limit the use of TlBr crystals as detectors. In this work, a combination of hydrothermal recrystallization (HR) and vacuum distillation (VD) methods were applied to purify TlBr salts prior to crystal growth. Trace impurities at the ppb/ppm level were determined by inductively coupled plasma mass spectroscopy (ICP-MS). The results showed that the impurity concentrations of the TlBr salt decreased significantly after HR and VD purification, and high performance of the resultant TlBr crystal in areas such as electrical and optical properties was achieved. The combination of HR and VD methods could fabricate purer material, with an order of magnitude higher resistivity and better optical quality, than HR or VD method used separately. The possible technological considerations affecting the parameters of the crystals are investigated.

1. Introduction

Thallium bromide (TlBr) is a material that shows considerable promise for application in room-temperature radiation detectors due to its wide band gap (2.68 eV), high atomic number (Tl: 81, Br: 35), high density (7.56 g/cm^3), simple cubic crystal structure (CsCl type) and relatively low melting point (460 °C) [1–3]. However, the application of TlBr detectors is limited, due to material purity and fabrication problems, which make it difficult to achieve good-quality crystals.

Purity is a crucial factor that influences the crystal quality and the detector performance. Over the past decades, several studies have been carried out on the purification of TlBr salts [4–11]. In these studies, hydrothermal recrystallization (HR) [4,5], vacuum distillation (VD) [6] and zone refining methods [7–11] were used to purify TlBr salts. It was reported that although there was a strong reduction in impurities after the first pass of refining, after that, the impurity concentrations decreased more slightly, and the values of resistivity in the subsequently grown TlBr crystals were almost unaffected by the number of refining passes [8–10]. Therefore, further investigations have focused on the improvement of the purification techniques [12–14]. It has been indicated that TlBr samples purified by melt methods and from water solutions differ with respect to impurity composition [5,14]. In this work, efforts have been concentrated on the purification of the TlBr material by a combination of HR and VD methods, and the properties of the resulting TlBr crystal have been analyzed.

The purification efficiency was evaluated by inductively coupled plasma mass spectroscopy (ICP-MS). The crystal quality was evaluated by the X-ray diffraction (XRD) method, resistivity measurements at room temperature, transmission spectra and the energy response spectrum.

2. Experimental methods

The production of TlBr crystals suitable for making high-energy radiation detectors consists of synthesis of the initial salt, purification and crystal growth followed by wafer preparation.

2.1. Synthesis of initial salts

The raw $TlNO_3$ (commercial grade, Lida Chemistry Co. Ltd., China) had a quoted purity of 99.9%. The $TlNO_3$ salt was purified by one run of filtration and three runs of recrystallization. The hydrobromic acid (analytical grade, Sinopharm Chemical Reagent Co. Ltd., China) was purified by reduced-pressure distillation.

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The synthesis of the TlBr material used for the study presented in this paper was carried out by the following reaction: $TlNO_3 + HBr = TlBr + HNO_3$, with a stoichiometric ratio of reactants of 1:1. Yellow dendrites of TlBr were formed during the reaction. Then the dendrites were rinsed repeatedly with de-ionized water until the pH value became neutral.

2.2. Purification of TlBr salts

The synthesized TlBr salt, henceforth denoted by P0, cannot immediately be employed for crystal growth because it contains a number of impurities. To remove the impurities, both HR and VD were employed in this work.

The HR purification of the TlBr salts was carried out in a polytetrafluoroethylene (PTFE) cup. First, a large amount of TlBr (80 g in 1000 ml of water) was loaded in an autoclave with a PTFE cup, and the autoclave was put into a two-zone vertical furnace with a steady temperature gradient. Then, a saturated TlBr solution was obtained by heating the furnace to 170 °C and maintaining this temperature for 15 h, after which the top and bottom of the furnace were cooled at the rates of 3 °C/h and 2 °C/h, respectively. Because of the temperature gradient inside the cup, mass transfer of TlBr took place through the solution and dendrites were crystallized at the top of the cup. This powder purified by the HR method will henceforth be denoted by P1.

The VD purification was carried out in a vertical furnace. Fig. 1 shows a sketch of the furnace, including the temperature profile. An ampoule containing TlBr material was first vacuumed to a residual pressure of $1\text{–}4 \times 10^{-4}$ mbar. Next, the ampoule was placed into the working space of the furnace, as shown in Fig. 1. Then, the furnace was heated so that the temperature of the upper section of the ampoule reached 410–420 °C and the temperature of the bottom of the ampoule reached 510–520 °C. These temperature conditions were maintained for 48 h. After that, the furnace was cooled to room temperature. Fig. 2 shows a photograph of the TlBr material after VD purification. Due to the difference in the vapor pressures of TlBr material and other compounds, the final polycrystalline material was sublimated and condensed to the cold (top) section of the ampoule, and the impurity-enriched residual remained at the bottom of the ampoule. The powder purified by the VD method will henceforth be denoted by P2.

The combination of the HR and VD methods in this paper was carried out as follows: the TlBr salt purified by the HR method was dried, fused and distilled. The powder purified by the combination of the HR and VD methods will henceforth be denoted by P3.

2.3. Preparation of TlBr crystals and wafers

The growth process of a TlBr crystal has been described in detail in our early work [15]. TlBr ingots of 8 mm in diameter, grown by the electro-dynamic gradient (EDG) method with a rate of 2–3 mm/h at 520 °C in a two-zone pipe furnace, were sawed into wafers of a thickness of 3 mm along the radial direction using a hacksaw with carborundum daubing, followed by mechanical polishing with abrasives of 1–5 μm in diameter. Next, the surfaces of the wafers were etched in a H_2O_2–HBr mixture for 1.5 min and rinsed in an ethanol solution. The final wafers were clear and had good-quality surfaces. The corresponding wafers, which were fabricated from the P0, P1, P2 and P3 powders, will henceforth be denoted by W0, W1, W2 and W3, respectively.

2.4. Detector fabrication

Gold (Au) electrodes approximately 80 nm thick were deposited by the magnetron sputtering method on two sides of the W0, W1, W2 and W3 wafers. Then copper wires were attached to the electrodes with Aquadag adhesive. The resulting devices were mounted on ceramic substrates for energy spectrum measurement. The as-fabricated devices, which were fabricated from the W0, W1, W2 and W3 wafers, will henceforth be denoted by D0, D1, D2 and D3, respectively.

2.5. Characterization

The purification efficiency was evaluated by measuring the concentrations of trace impurities using ICP-MS (Elan DRC-e, Perkin-Elmer, USA, detector limits of 5 ppb). In order to reduce the interference of the Tl ions with the determination of the trace

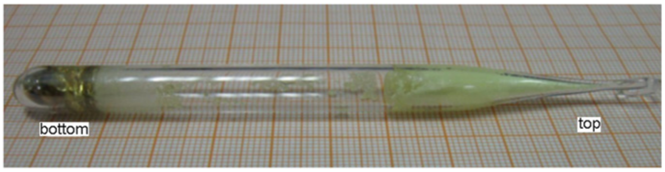

Fig. 2. Photograph of the TlBr powder after VD purification.

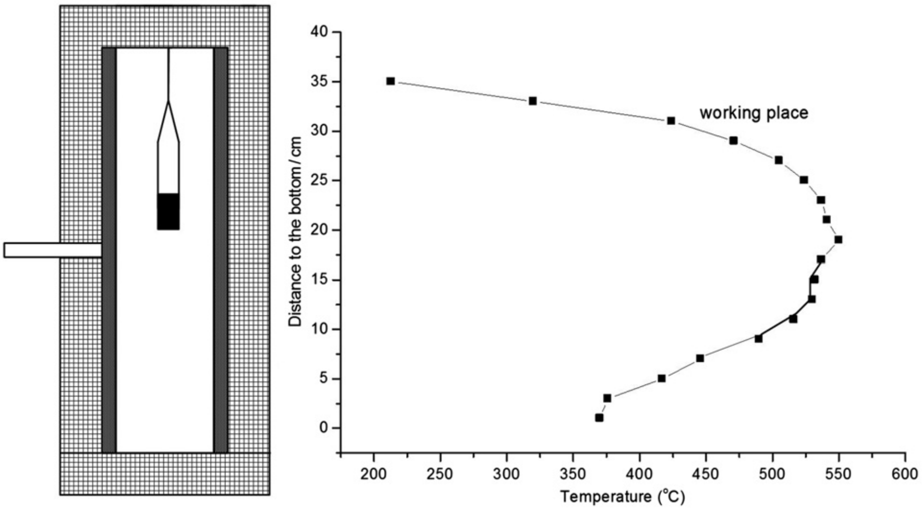

Fig. 1. Sketch of the furnace for VD purification showing the temperature distribution.