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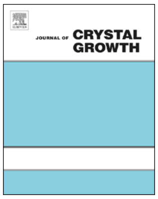

Removal of oxidic impurities for the growth of high purity lead iodide single crystals

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It could be shown that the hydrogen (H_2) treatment of lead iodide (PbI_2) is capable to effectively reduce oxidic impurities contained in the source material used for single crystal growth. Comparative experiments of melting PbI_2 in H_2 and Ar atmosphere as well as thermal analysis (DTA, DSC/TG) of contaminated PbI_2 were carried out to characterise the influence of the H_2 treatment on the resulting material purity. At the same time, a hygroscopic nature of PbI_2 could be disproved, and new results on the controversially discussed thermal behaviour of solid, oxide-polluted PbI_2 are presented. Effective measures for the avoidance of oxidic impurities during source material processing could be derived. Finally, the effectiveness of an H_2 treatment is confirmed by single crystal growth experiments using the Czochralski technique. PbI_2 crystals with improved structural properties and, for the first time, a reproducible predetermination of crystallographic orientation are shown.

1. Introduction

Crystalline lead iodide (PbI_2) is a promising candidate for X- and γ-ray detection. With an average atomic number Z of 62.7, PbI_2 has a high ability to absorb radiation. Because of the high band gap energy of 2.32 eV at 300 K [1], PbI_2 detectors maintain low dark currents and a high signal to noise ratio. The high electrical resistivity of PbI_2 allows the detector to be operated at desirable electric field intensities ≥ 5 kV/cm for a detector thickness in the range of 500 μm [2]. For single crystalline PbI_2 of the basic polytype 2H (CdI_2 structure, space group $P\bar{3}m1$), values $\geq 10^{12}\ \Omega$ cm are described in the literature [2–8].

In comparison to mercuric iodide (HgI_2), which is similar to PbI_2 with respect to its electrical properties and anisotropic (layered) structure, but undergoes a destructive solid–solid phase transformation at 130 °C [9], PbI_2 remains stable up to its melting point (≈ 409 °C) and can therefore be grown directly from the melt. This is usually done by the vertical Bridgman or Bridgman–Stockbarger technique [10,11].

Unfortunately, the charge carrier mobility and lifetime of single crystalline PbI_2 lies 2–3 orders of magnitude below desired values of $\mu_e\tau_e = 10^{-2}\ cm^2\ V^{-1}$ and $\mu_p\tau_p = 10^{-4}\ cm^2\ V^{-1}$ [6], respectively. One of the reasons for the low $\mu\tau$ product is the existence of oxidic impurities in the PbI_2 source material. These react with the fused silica ampoules during melt growth [12] and, similar to other lead halides, the resulting silicates cause nonuniform sticking of the growing crystals to the ampoule walls [13,14]. The strain is released by the formation of structural imperfections or cracking of the ingots, which, in addition to the impurities themselves [15], leads to an increased trapping of charge carriers and deteriorates the electronic properties of the detectors. An improvement of the $\mu\tau$ product is expected if the preparation of high purity material is further improved [16] by reducing major contributors to charge trapping like oxidic impurities and the resulting structural defects.

Contamination with oxidic compounds can be assumed for PbI_2 because part of the source material processing and storage is carried out in air. The reaction

$$PbI_2 + \frac{1}{2}O_2 \rightarrow PbO + I_2 \qquad (1)$$

has an exothermic character (standard free enthalpy of reaction $\Delta_r H^0 = -43.5$ kJ/mol), i.e., the oxidation of PbI_2 already begins at room temperature.

Since oxides usually remain in the melt as insoluble particles, they cannot be removed by zone refining methods. Reduction of lead oxide compounds in PbI_2 has been described only by Eckstein

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et al. [10], who applied a complicated purification process and treated the PbI_2 melt with methylene iodide prior to crystal growth. On the other hand, Palosz confirmed that removal of oxygen from lead oxide compounds by reaction with hydrogen is in general easily done [12]. The reaction

$$\mathrm{PbO} + H_2 \rightarrow \mathrm{Pb} + H_2\mathrm{O} \tag{2}$$

is already occurring at room temperature ($\Delta_r H^0 = -22.8$ kJ/mol [17]), and PbO is reduced to metallic lead. The water can be extracted by subsequent evacuation of the system.

We could show in our investigations that oxidic impurities can be reduced by a melt treatment in a H_2 atmosphere and how their formation during material processing can be avoided in order to achieve high purity source material. It could be demonstrated that the structural properties of PbI_2 crystals are improved by the implementation of the H_2 treatment during crystal growth using the Czochralski method. The latter was recently described to be a valid alternative for the growth of PbI_2 crystals [18], and further results described here prove the reproducible predetermination of crystal orientation.

2. Experimental

The source material for preliminary melting tests, thermal analysis, and Czochralski growth consisted of high purity, undoped PbI_2, synthesised by direct reaction of metallic lead and pure iodine. The resulting PbI_2 was refined by multipass zone melting (ZM) applying 30–38 runs. Details of the methods can be found in [8,11,19,20]. Table 1 summarises all relevant information on the shape and size of the source material used as well as the storage conditions and lists the types of gas under which the material was processed. The gases used were 5 N Ar and 5 N H_2, Pd-diffused H_2 (approximately 7 N), and forming gas (97.6% Ar+2.4(5)% H_2), all from Air Liquide. The impurity levels of forming gas were N_2 (80 ppmv), H_2O (40 ppmv), and O_2 (20 ppmv).

2.1. Preliminary melting tests

Similar amounts of PbI_2 (approximately 3.5 g) originating from the same zone-refined ingot were successively melted in cleaned fused silica ampoules. The ampoules were attached to a vacuum/gas system. After evacuation to 3×10^{-5} mbar, the ampoules were filled with gas to a pressure of 766 mbar (H_2) or 764 mbar (Ar). The lower part of the ampoule was inserted into a resistance furnace, and equal portions of the ampoule were heated (approximately 2 h), twice in each case. After first melting in H_2 atmosphere, the ampoule was evacuated and refilled with fresh H_2, while in the case of Ar no gas exchange was carried out. The temperature was controlled with a type K thermocouple attached to the outer surface of the ampoule about 5 mm above the PbI_2.

Phase analysis of the resulting material was carried out by powder XRD with a STOE STADI-P powder diffractometer in transmission mode using Cu-Kα1 radiation. Phase identification was done with the software package Match! 1.2 using the structure database ICSD (version 2000).

2.2. Thermal analysis

For differential thermal analysis (DTA) a Netzsch DTA 404S was used. Two DTA samples using equal amounts of PbI_2 (0.1 g) were prepared from the clean part of an undoped, zone-refined ingot, which had been stored at air for several months (see Table 1). Thus it is very likely that PbI_2 was partly oxidised to PbO according to Eq. (1). In order to also investigate the influence of the sample surface area on the degree of contamination, e.g., compared to powders, the samples were not ground prior to encapsulation in fused silica ampoules of 35 mm in length and an OD of 6 mm. After evacuation to 1×10^{-4} mbar, the ampoules were sealed under Ar (sample 1) or H_2 (sample 2) at approximately 900 mbar. In both cases, the material did not melt during ampoule preparation. The samples were then stored in darkness and at room temperature for 9 days before the measurements were started. The ampoules were successively heated from room temperature to 500 °C at a rate of 3 K/min. An empty, evacuated ampoule served as reference sample. The ampoule containing PbI_2 in H_2 atmosphere was subsequently measured again for heating (sample 2a) and cooling (sample 2b).

Thermogravimetry (TG) and differential scanning calorimetry (DSC) curves were simultaneously recorded using a Netzsch STA 449C Jupiter. PbI_2 from the same source as for the DTA experiments was ground in an agate mortar and kept in air for 9 days at room temperature. Directly before the actual measurement, a calibration run was carried out using an empty alumina crucible with a loose alumina cover and an open Pt crucible filled with 15.5 mg Al_2O_3 as reference. Then, 17.1 mg of the PbI_2 powder was placed into the open alumina crucible and heated (sample 3a) together with the reference at a rate of 10 K/min. An Ar flow of 15 ml/min was applied. Cooling (sample 3b) at −10 K/min directly followed after heating with a short temperature plateau at 500 °C.

Table 1
Sample parameters and experimental conditions.

Sample	Source material properties	Process gas	Comments
Preliminary melting tests			
A1, B	Grains (mm^3) stored in air for months	H_2 (A1) and Ar (B)	Contaminated by some pieces of lint
A2	Massive (cm^3), 2nd run using sample A1	Fresh H_2 (after evacuation of ampoule)	Contaminated by some pieces of lint
DTA			
1, 2	Grains (mm^3) stored in air for several months, sealed ampoule stored for 9 days before DTA	Ar (1) and H_2 (2)	1st run, only heating recorded
2a, 2b	Massive (mm^3), subsequent measurement using sample 2	H_2 (see sample 2, no exchange of gas)	2nd run, heating (2a)+cooling (2b) recorded
TG/DSC			
3a, 3b	Powder, stored in air for 9 days before TG/DSC	Constant Ar flow	Heating (3a) and cooling (3b) recorded
Czochralski growth			
FZC05	3 bars (cm^3) charged 1.5 h after opening ZM ampoule	Constant flow of Pd-diffused H_2	Growth aborted (crystal torn off at seed)
FZC06	Massive (cm^3), reused from FZC05, in air for 2 days, only seed exchanged	Constant Ar flow	Growth successful
FZC07	3 bars (cm^3) charged 14 h after opening ZM ampoule, doping with metallic Sn	Constant forming gas flow (Ar/H_2 mixture)	Growth aborted (unintentional remelting of crystal)
FZC08	Massive (cm^3), reused from FZC07, in air for 4 days, only seed exchanged, Sn-doped	Constant forming gas flow (Ar/H_2 mixture)	Growth successful