

Melt growth of pure and doped lead (II) halide single crystals

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The growth of pure and doped PbX_2 (where $X = Cl, Br$) single crystals is investigated. Special attention was paid to the purification of the polycrystalline source materials. The process was carried out in a controlled atmosphere of gaseous chlorine and bromine, respectively, combined with repeated horizontal zone melting and subsequent vertical Bridgman technique. The influence of the recrystallization rate and number of such recrystallization processes was studied. Pure single crystals of $PbCl_2$ and $PbBr_2$ (up to 15 mm in diameter and 50 mm long), of good optical quality, were grown in sealed glass ampoules by the Bridgman method. The crystals were doped with Tl^+ , using $TlCl$ and $TlBr$, respectively, for luminescence studies.

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1. Introduction

Lead (II) halide single crystals continue to elicit an increasing interest in their luminescent properties [1] and potential applications in acousto-optical devices [2]. Growing large, good quality PbX_2 crystals proved to be a difficult task, due to numerous complications encountered during the various stages of the process. The polycrystalline starting materials are insoluble in water and other organic solvents and readily prone to formation of lead oxides and/or hydroxides, especially at high temperatures.

Extensive studies were dedicated to $PbCl_2$ purification and growth, with good results, including chlorination of the melt [3, 4] followed by directional solidification [3] or Bridgman recrystallization [4].

$PbBr_2$ single crystals' properties and melt growth were studied by Singh et al. [5] and recently by Kaito et al. [6]. Large transparent crystals were grown by the Bridgman-Stockbarger method [5]. The importance of the purification of the source materials, as well as the influence of the growth rate on the quality of the crystals, was pointed out [6].

In this paper we report on the purification and melt growth of PbX_2 single crystals. Special attention was paid to $PbBr_2$.

2. Experimental

2.1 Purification of source materials

The starting materials were commercially available reagents from "Reactivul" Bucuresti (pro analysis) and Merck 99.99% for $PbCl_2$ and Aldrich 99.98% for $PbBr_2$, respectively.

At first, to remove residual water, the material was

loaded in a quartz ampoule 3.4 cm in diameter and 17 cm long, which was heated at about $60^\circ C$, slowly evacuated to 1×10^{-3} Torr and closed under vacuum.

Additional purification was made by distillation in nitrogen atmosphere.

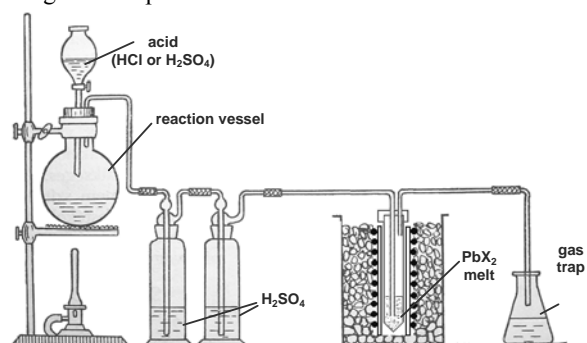


Fig. 1. Experimental setup for halogenation treatment of PbX_2 melt.

The resulted polycrystalline material was further purified by a chlorination/bromination procedure. The Cl_2 gas was obtained as a product of the oxidation of hydrochloric acid with $KMnO_4$. Bromine was obtained from the chemical reaction of KBr , MnO_2 and sulphuric acid. The pure halogen gas was bubbled directly through the melt, after passing through two consecutive H_2SO_4 -filled gas washers. The experimental setup is schematically presented in Fig. 1. The procedure took about 2 hours. Because bromine is still liquid at room temperature, argon was used as inert carrier gas for Br_2 transport. During this period, the melt became homogeneous and clear (yellow in the case of $PbCl_2$ and dark reddish brown in the case of $PbBr_2$) and the black residues formed during the initial melting process disappeared. At this stage, the ampoule was sealed under

halogen atmosphere and the slow freezing of the purified melt took 4 to 8 hours. After melting and solidification, an important decrease in the volume of the resulted crystalline bulk was observed, as compared to the volume of the initial powder material (with a factor of 3). The ampoule was filled with additional quantities of source material and the whole process was repeated for at least 3 times in order to obtain 40–50 g of pure polycrystalline PbCl_2 or PbBr_2 .

The next step of purification was achieved by zone melting technique. The material was placed in a quartz container 10 cm long. This container was closed in a quartz tube (2.4 cm in diameter and 30 cm long), which was mounted in the horizontal zone refiner. The quartz tube was connected to the experimental setup presented in Figure 1 and filled with gaseous Cl_2 or Br_2 . A constant and continuous halogen gas flow was kept in this tube during the entire refining process. A molten zone of ~ 1.5 cm and a translation rate of 10 mm/h were achieved for the initial up to five passes. For the next several passes, both the zone width and the translation rate were reduced to 1 cm (using a narrower electrical heater) and 6 mm/h, respectively. The process was repeated up to 9 times. After each pass, the ingot was extracted from the container and the impure residue was eliminated. Single crystalline blocks were used as seed crystals for subsequent passes. Finally, colorless and transparent samples can be selected from the resulted ingot.

An alternative process applied for purification was the vertical directional solidification of the PbX_2 melt. The previously halogen-treated crystalline material was sealed in a heat-resistant glass ampoule, under gaseous Cl_2/Br_2 atmosphere. The ampoule was lowered through a controlled temperature gradient at a rate of 6 mm/h. About 2/3 of the ingot could be used for subsequent recrystallization. The process was repeated for at least 2 times.

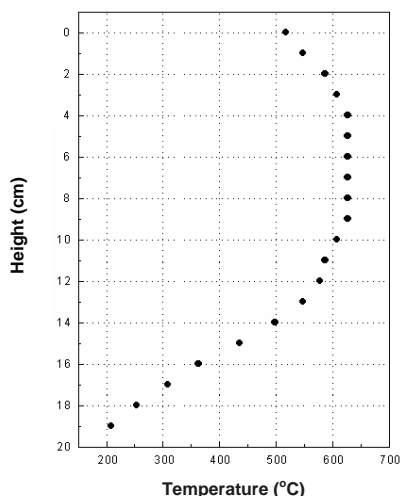


Fig. 2. Temperature distribution in the Bridgman furnace.

2.2 Crystal growth

Single crystals of PbX_2 were grown by vertical

Bridgman method. The purified material was transferred in glass ampoules (1.4–1.6 cm in diameter, 15–16 cm long, pointed end) and sealed under Cl_2/Br_2 controlled atmosphere. The growth ampoule was placed inside a furnace with a temperature distribution as shown in Figure 2. The material was melted in the upper zone of this furnace and was kept at a temperature slightly above the melting temperature for about 2 hours, for homogenization. After thermal equilibrium was achieved, the ampoule was lowered at a rate of 6 mm/h. The growth is initiated at the "cold" pointed end of the ampoule. A complete pass took approx 25 hours. After solidification of the whole crystal, the temperature of the furnace was slowly lowered to room temperature. Growth processes at slower rates (down to 2 mm/h) were performed also, with better results.

PbX_2 crystals doped with Ti^{3+} were grown by the same Bridgman technique. The purified material, together with the required amount of dopant, was loaded and sealed in glass ampoules and the process was carried out as presented above.

3. Results and discussion

Crystal growth of lead (II) halides is strongly influenced by the purity of the starting materials. Special attention has to be paid to the purification of initial PbCl_2 and PbBr_2 in particular. The nitrogen-distilled material was slightly colored, probably due to the resulting PbO formed with oxygen traces in N_2 gas reacting with PbX_2 .

The halogenation of the melt proved to be a necessary step, eliminating most of the unwanted impurities, such as hydroxy- and oxyhalides. The resulted material was yellowish white in the case of PbCl_2 or red-brownish white in the case of PbBr_2 . Some black residues remained and accumulated at the surface of the crystalline bulk, but not in its volume.



Fig. 3. PbBr_2 crystals obtained (from previously halogenated source material) by zone refining in gaseous Br_2 flow – after four passes.

The quality of the ingots obtained after repeated zone refining processes is determined by the recrystallization rate and number of such recrystallization processes. A higher recrystallization rate (i.e. higher rate of translation of the molten zone) produced a better separation and accumulation of the residues at the end of the ingot, hence a higher purity in its first 2/3 part. As a drawback,

formation of internal bubbles and cracks was observed (Fig. 3).

Crystals with no bubble inclusions and fewer cracks resulted for a lower translation rate of the molten zone. This fact, combined with an increase in the number of passes along the ingot, led to better results. Colorless, transparent crystals with large single crystalline blocks ($\sim 1 \text{ cm}^3$) were obtained from previously halogenated material. It is to point out that the controlled Cl_2/Br_2 atmosphere was maintained during each pass. Some cracks in the crystal still appear because the cooling process is too fast.

Larger single crystals, up to 5 cm long and 1.5 cm in diameter, were grown by the Bridgman method.

The quality of the crystals was strongly influenced by the presence of gaseous Cl_2/Br_2 during the growth in the sealed ampoule. An excess of halogen gas proved to be necessary for preventing the formation of any unwanted lead compounds.

Another factor influencing the quality of the crystal was the growth rate. Slower rates improved the transparency and eliminated the macroscopic structural imperfections.

The initial crystals were of lower quality, opaque and colored (light coloration in the first $\frac{1}{4}$ th of the bulk, intense in the last fourth – as considered from the tip of the ampoule). Black residue depositions were formed on the surface of the crystal, especially on top of it. This clearly suggested an undergoing purification process, due to the insufficient previous purification of the starting materials.



Fig. 4. Single crystals of PbX_2 grown by vertical Bridgman method, sealed in gaseous X_2 atmosphere: (a) PbCl_2 ; (b) PbBr_2 .

With deep purified starting materials, the resulted crystals were visibly clear and uniform (Figure 4). The shadowiness observed in Fig. 4 (b), in fact a reddish-brown coloration, is due to layer depositions at the glass-crystal interface only, that is on the interior glass wall and on the exterior surface of the crystal. The excess of

halogen gas was confined in the upper part of the ampoule (visible as a darker zone above the crystal's top end).

4. Conclusions

Growth of good quality single crystals of PbCl_2 and PbBr_2 respectively is determined by the ultra purification of the source materials. This was achieved by:

- distillation in N_2 atmosphere;
- zone refining in continuous halogen gas flow;
- vertical Bridgman method in container sealed under gaseous Cl_2/Br_2 in excess.

It was found that higher recrystallization rates speed up the purification process. Slower passes are necessary to reduce the structural imperfections in the resulted crystals.

Transparent and colorless single crystals, up to 15 mm in diameter and 50 mm long, were obtained by Bridgman technique. Good quality crystals were obtained if:

- a very slow growth rate was used;
- equilibrium conditions were ensured in

the sealed ampoule, with an excess of halogen gas over the melted-solidifying-solid material during the entire recrystallization process.

Lead bromide crystals were more difficult to obtain, mainly because bromine (liquid at room temperature) is, in its gaseous phase, a highly reactive gas, prone to impurity formation; this renders the deep purification of the starting material a more laborious procedure.

Crystals doped with Tl^+ were grown by the same technique for luminescence studies.

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