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An Experimental Evidence of some Lead Iodide Polytypes Compatible with the Dielectric Functions Model

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Abstract: The wide-bandgap and highly-resistive lead iodide (PbI_2) crystalline semiconductor has been considered as a promising room-temperature nuclear radiation detector in environmental applications. The PbI_2 single crystals yet grown, however, suffer from problems of phase transformation among its diverse polytypic modifications and formation of polytypes admixture during growth or under post-growth working conditions and from the presence of structural defects and native impurities that normally cause notable deterioration in the performance of devices integrating them. The behaviour of experimental dielectric constant ε_1 of undoped melt-grown 2H-polyttype PbI_2 single crystals with isothermal annealing temperature T_a ($\leq$94°C) may be taken as a sign for the occurrence of a reversible 2H≒12R phase transition in them. However, the effect of reducing the amount of structural native defects and imperfections in such undoped PbI_2 crystals by thermal annealing cannot be entirely excluded. The measured room temperature value of ε_1 at 1 kHz (~6.5 for T_a = 94°C) of these PbI_2 single crystals is compatible with the findings of theoretical dielectric functions model and is consistent with experimental values of ε_1 reported by other workers for melt- and gel-grown PbI_2 single crystals.

Key words: Lead Iodide, polymorphism, nuclear-radiation detector, dielectric constant, loss tangent

INTRODUCTION

Several physical properties of lead iodide (PbI_2) crystalline material were investigated by many researchers (Shah *et al*., 1997; Deich and Roth, 1996; Hermon *et al*., 1998; Shoji *et al*., 1998; He *et al*., 2007; Hayashi *et al*., 2008; Matuchova *et al*., 2005, 2006, 2009a, b, 2010; Hassan and Abdul-Gader Jafar, 2006; Jafar *et al*., 2009; Yadav *et al*., 1980; Dugan and Henisch, 1967; Zallen and Slade, 1975; Jain and Trigunayat, 1996; Choudhary and Trigunayat, 1989; Blonskii *et al*., 1980; Konings *et al*., 1995; Palosz, 1983; Rao and Srivastava, 1978; Salje *et al*., 1987; Palosz *et al*., 1990; Bibik *et al*., 1985) because it is considered as a potential candidate for the use in future solid-state nuclear radiation detectors, which could work efficiently at Room Temperature (RT) or higher (<120°C) without cryogenic external cooling (Shah *et al*., 1997; Deich and Roth, 1996; Hermon *et al*., 1998; Shoji *et al*., 1998). PbI_2 crystalline wafers can be utilized in cost-effective environmental portable devices for detecting uranium traces in drinking water. It has other feasible room-temperature medical and scientific applications, for example, in X-ray medical imaging systems and in laboratory X-ray and γ-ray detectors in the intermediate energy range (1 keV-1 MeV).

The PbI_2 compound typically crystallizes in either the hexagonal (H) or rhombohedral (R) layered-sandwich Bravais lattice structure, with its constituent Pb- and I-atoms being positioned within weakly-bonded identical layers in a translational sequence of the type I-Pb-I−I-Pb-I−.... that are perpendicular to the c-axis (Palosz, 1983; Rao and Srivastava, 1978; Salje *et al*., 1987; Palosz *et al*., 1990; Bibik *et al*., 1985; Shah and Wahab, 2000). In general, lead iodide single crystals can be grown from gel, vapour, or melt (e.g., Bridgman-Stockbarger growth method).

High quality PbI_2 single crystals are very much suitable for exploiting them in the aforementioned electronic devices because high purity and perfectly crystalline PbI_2 has many expedient physical properties such as, among several others, wide bandgap energy (E_g ~2.3 eV at 300 K) and high electrical resistivity (>10^{11} Ωcm), thus giving rise to very low RT leakage current in devices integrating them, large mass density of 6.2 g cm^{-3} (allowing the construction of small, compact portable devices), great stopping power for nuclear radiation (high atomic numbers of its constituent elements: Z_{Pb} = 82, Z_I = 53), good chemical stability (low vapour pressure) and good thermal stability with a high melting point (~ 410°C).

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Unfortunately, even good lead iodide single crystals suffer from the presence of native (residual) impurities, lattice disorder and non-stoichiometry structural defects and imperfections (Shah *et al*., 1997; Deich and Roth, 1996; Hermon *et al*., 1998; Shoji *et al*., 1998; He *et al*., 2007; Hayashi *et al*., 2008; Matuchova *et al*., 2005, 2006, 2009a, b, 2010). Moreover, PbI_2 possesses some awful polytypism features such as the coexistence (admixture) of more than one polytype structure in the same grown crystal or of polytypic phase transformations that may occur during growth processes and post-growth working procedures (Zallen and Slade, 1975; Jain and Trigunayat, 1996; Choudhary and Trigunayat, 1989; Blonskii *et al*., 1980; Konings *et al*., 1995; Palosz, 1983; Rao and Srivastava, 1978; Salje *et al*., 1987; Palosz *et al*., 1990; Bibik *et al*., 1985; Shah and Wahab, 2000). Polytypism phenomenon could be exhibited in a variety of layered crystalline compounds and some solids, which have the same underlying basic lattice structure and chemical composition, but which may have more than one structural phase that differ in the manner of structural stacking of the layers of the different constituent atoms of the solid (Palosz, 1983; Rao and Srivastava, 1978; Salje *et al*., 1987; Palosz *et al*., 1990; Bibik *et al*., 1985; Shah and Wahab, 2000; Raw *et al*., 2004; Saddow and Agarwal, 2004; Adolph *et al*., 1997).

The polytypism phenomenon and effect of coexistence of various polytypes and/or their developing by external agents in materials of technological interest becomes recently important (and controversial) issues. These problems are frequently encountered in pharmaceutical applications (drug manufacturing), where polymorphism in a solid drug would have impact on drug performance, chemical reactivity and patients intake safety (Raw *et al*., 2004). Polytypism effects can also be serious in electrical power applications utilizing very wide bandgap crystalline materials (e.g., SiC (Saddow and Agarwal, 2004)) and in solid-state nuclear radiation detectors using PbI_2 crystals.

Crystalline PbI_2 compound has a large number of different polytypes, which usually have diverse physical properties such as the scheme layer-stacking structure, crystallography patterns, electrical resistivity, dielectric constant and fundamental optical absorption energy-band edges (Zallen and Slade, 1975; Jain and Trigunayat, 1996; Choudhary and Trigunayat, 1989; Blonskii *et al*., 1980; Konings *et al*., 1995; Palosz, 1983; Rao and Srivastava, 1978; Salje *et al*., 1987; Palosz *et al*., 1990; Bibik *et al*., 1985; Shah and Wahab, 2000).

The main common basic types of crystalline PbI_2 polytypic modifications are the 2H, 12R and 4H polytypes, of which the most thermodynamically stable at room temperature, is the hexagonal 2H-polytype form. Pure and highly stoichiometric PbI_2 single crystals produced by the conventional vertical Bridgman-Stockbarger growth method appear to have a 2H-polytype structure (Shah *et al*., 1997; Deich and Roth, 1996; Hermon *et al*., 1998; Shoji *et al*., 1998; He *et al*., 2007; Hayashi *et al*., 2008; Matuchova *et al*., 2005, 2006, 2009a, b, 2010), but other workers have reported that PbI_2 crystals having the 2H polytype structure could be grown from gel or vapour (Konings *et al*., 1995; Palosz, 1983; Rao and Srivastava, 1978; Salje *et al*., 1987; Palosz *et al*., 1990). The rhombohedral 12R PbI_2 polytype structure may be formed as the product of some growth methods (Palosz, 1983; Rao and Srivastava, 1978; Salje *et al*., 1987; Palosz *et al*., 1990) or might be obtained by a suitable heat treatment of PbI_2 crystals having initially the 2H structure at an annealing temperature T_a near 94°C (Salje *et al*., 1987). The hexagonal 4H-polytype PbI_2, which is energetically instable at low temperatures, could be induced by a prolonged isothermal annealing of PbI_2 crystals with an initial 2H-polytype modification at temperatures over a rather wider range 140-200°C (with some disorder at high temperatures) (Zallen and Slade, 1975; Jain and Trigunayat, 1996; Choudhary and Trigunayat, 1989; Blonskii *et al*., 1980; Konings *et al*., 1995; Palosz, 1983; Rao and Srivastava, 1978; Salje *et al*., 1987; Palosz *et al*., 1990). It has been reported (Bibik *et al*., 1985) that laser irradiation of 2H-polytype PbI_2 crystals cannot produce a 2H→4H phase transition but can induce irreversible 4H→2H phase transition.

It deserves noting here that the actual mechanism of polymorphism formation in the crystalline PbI_2 compound is rather complex and the true reason behind the nature of the polytypism phenomenon in this compound is yet unclear. Indeed, there is still a great amount of dispute about the nature of structural phase transformation even among its 2H, 4H and 12R polytypes, which might coexist in the same crystal in different proportions and no clear-cut on the actual temperature around which a particular polytype of these forms would transform to another. Higher order PbI_2 polytypes could also exist in the hexagonal or rhombohedral lattice structures (Konings *et al*., 1995; Palosz, 1983; Rao and Srivastava, 1978; Salje *et al*., 1987; Palosz *et al*., 1990; Bibik *et al*., 1985). The presence of non-stoichiometric and structural defects, imperfections, faults, native and/or extrinsic impurities in PbI_2 crystals may provoke creation or coexistence (admixture) of different polytypic forms.

The dielectric properties have been reported mostly on PbI_2 pressed powder pellets, but not much AC data on PbI_2 single crystals have been published in the literature (Matuchova *et al*., 2009b; Hassan and Abdul-Gader Jafar,

2006; Jafar *et al*., 2009; Yadav *et al*., 1980; Dugan and Henisch, 1967; Salje *et al*., 1987). Salje *et al*. (1987) have used the dielectric constant and loss data of their initially 2H-polytype gel-grown PbI_2 crystals to show that a thermally-induced phase transition of the type 2H→12R had been occurred in these samples at an isothermal annealing temperature around 94°C. Dugan and Henisch (Dugan and Henisch, 1967) have studied the dielectric constant and loss of some gel-grown PbI_2 single crystals (of unspecified polytype form) as a function of AC-signal frequency and the ambient temperature of the samples, which were not subjected to prolonged thermal annealing in priori. The dielectric properties of melt-grown PbI_2 single crystals, the polytype of which was not specified, have been investigated by Yadav *et al*. (1980).

A recent renaissance for studying the AC-properties of PbI_2 single crystals grown by the Bridgman-Stockbarger technique has been embarked on by (Matuchova *et al*., 2009b; Hassan and Jafar, 2006; Jafar *et al*., 2009) to investigate the effect of various *in situ* growth and post-growth experimental factors on some of their AC parameters in an attempt to elucidate the actual conduction and dispersion mechanisms operating in these layered structure crystals. No serious effort has been yet made to relate the dielectric behaviour to the polytype form of PbI_2 single crystals, an issue that is still ambiguous and controversial.

In this work, we present some preliminary experimental results of the 1 kHz and room-temperature parallel-mode capacitance C_p of typical undoped 2H-polytype PbI_2 single crystals that were in prior being subjected to a prolonged post-growth isothermal annealing at various temperatures in the range T_a = 20-94°C. Low-frequency capacitance measurements could give a clue on the occurrence of thermally-induced polytypic phase transformation in PbI_2 single crystals. The obtained dielectric data are compared with experimental dielectric results of other workers and discussed in view of theoretical dielectric functions models (Adolph *et al*., 1997; Ahuja *et al*., 2002).

MATERIALS AND METHODS

The lead iodide single crystals investigated in this work were grown by a vertical Bridgman-Stockbarger technique from undoped polycrystalline PbI_2 ingot synthesized with 10% excess of iodine which has been prepared and purified using the Matuchova preparation procedure (Matuchova *et al*., 2005, 2006, 2009a, b, 2010). According to this method, the starting PbI_2 ingot material was prepared by a 20-days long direct synthesis at 700°C of 6 N lead and 3 N iodine (10% excess). The obtained starting ingot was then subjected to multi-pass purification runs using a horizontal zone-melting (ZM) apparatus. The X-ray diffraction (XRD) studies made on such undoped PbI_2 single crystals revealed a hexagonal 2 H-polytype structural modification.

Thin slices (1 mm thick) were carefully cleaved (by a sharp razor blade) from typical specimens of these PbI_2 single crystals, with the crystal c-axis being perpendicular to the surfaces of these slices. No chemical etching of these slices were attempted in order to reduce the possibility of forming spurious surface structural faults and defects. Then, two metal contacts were applied symmetrically on the opposite sides of such crystalline PbI_2 slices using conductive silver paste.

The room-temperature resistivity of typical samples of these undoped PbI_2 single crystals is somewhat high (>10^9 Ω). The parallel-mode capacitance C_p of some of these highly-resistive crystalline PbI_2 slices has been measured when the applied electric field is parallel to the crystal c-axis, symbolized as (E‖c-axis), using an Agilent LCR meter (model HP 4263B) for an AC-signal of 1 kHz frequency.

The AC-measurements were made at room temperature on both as-grown and previously isothermally-annealed PbI_2 crystalline slices for various annealing temperatures in the range 20-94°C. The measured C_p-values were then used to determine the values of the real part (dielectric constant) ε_1 of the complex relative permittivity, $\varepsilon(j\omega) \equiv \varepsilon_1(\omega) + j\,\varepsilon_2(\omega)$, of the samples studied. The effective dielectric constant of the samples was calculated from the measured C_p-values using the simple relation $\varepsilon_1 = C_p/C_0$, where C_0 is the geometrical (space) capacitance between the electrical electrodes of the sample.

RESULTS AND DISCUSSION

Table 1 depicts the calculated values of the room-temperature dielectric constant of a typical PbI_2 single crystal for various isothermal annealing temperatures. The measured room-temperature 1 kHz dielectric constant ε_1 (E‖c-axis) of these undoped crystalline PbI_2 samples grown by the Bridgman-Stockbarger technique are significantly small at high annealing temperatures.

Table 1: Values of ε_1 (E‖c-axis) measured at 300 K and 1 kHz for as-grown undoped 2H-polytype PbI_2 single crystals isothermally annealed at various temperatures

Annealing temperature (°C)	Dielectric constant ε_1
20	14.0
75	10.0
87	8.0
94	6.5

The room-temperature ε_1-values given in Table 1 are fairly comparable to those reported by Salje *et al.* (1987) at 1 kHz for their gel-grown PbI_2 crystals (of an initial 2H-polytype structure) that were subjected to prolonged thermal annealing at similar temperatures. However, these findings are not in good consistent with the 1 kHz values of ε_1 reported for PbI_2 single crystals grown by a hydrogel growth method (Dugan and Henisch, 1967) or melt-grown PbI_2 single crystals (Yadav *et al.*, 1980), which were not thermally annealed in prior to measurements, but were heated up to elevated temperatures (T<270°C) while taking the data.

The discrepancies in the reported ε_1-values of PbI_2 are likely to arise in part from the nature and purity of the studied crystals, from their perfection and stoichiometry, or from their different structural polytypic modifications, a cause that is not readily affordable to confirm for certain. This may explain why the reported behaviour and changes in the electric and dielectric properties of PbI_2 single crystals under different working conditions were mainly attributed to the presence of impurities, imperfections and native defects in these crystals.

No attempt has been hitherto made to correlate the diminishing trend of the dielectric constant of PbI_2 single crystals upon increasing the thermal annealing (or the ambient) temperature with an interpolytypic phase transformation among its polytype modifications. The reversible first-order polytypic 2H⇆12R phase transition took place when the gel-grown PbI_2 single crystals of Salje *et al.* (1987) were thermally annealed to 94°C has not been assigned to the behaviour of their dielectric constant and loss with annealing temperature.

The samples studied in the present work are undoped PbI_2 single crystals having an initial 2H-polytype structure that were produced using the normal Bridgman-Stockbarger slow-growth freezing method from a synthesized PbI_2 ingot subjected to several prolonged multi-passes in the horizontal ZM-apparatus. The zone-melting procedure would enhance the purification of and reduce the amount of faults and imperfections in the fabricated polycrystalline ingot material, at least over a reasonably large part of the ampoule. We thus believe that the notable monotonic decrease of the measured room-temperature 1 kHz dielectric constant of these undoped PbI_2 crystalline samples with increasing isothermal annealing temperature could be related to a change in the layer-stacking structure of their original 2H-polytype and a first-order reversible polytypic 2H-12R phase transition had been took place for T_a = 94°C. Thermal annealing of PbI_2 single crystals at higher annealing temperatures (T_a <200°C), lattice disorder and additional faults are often created in the crystals and/or structural phase transformations to other polytype modifications are likely to take place in them (Zallen and Slade, 1975; Jain and Trigunayat, 1996; Choudhary and Trigunayat, 1989; Blonskii *et al.*, 1980; Konings *et al.*, 1995; Palosz, 1983; Rao and Srivastava, 1978; Salje *et al.*, 1987; Palosz *et al.*, 1990).

Nonetheless, the effect of reducing the amount of structural native defects and imperfections in our undoped PbI_2 single crystals upon prolonged isothermal annealing at temperatures below 100°C and thus a diminution of the space-charge polarization effects in these crystals cannot be wholly ruled out as a cause for the observed decrease of their dielectric constant upon thermal annealing.

A rigid confirmation of the aforesaid arguments require much more detailed and systematic investigations of the dielectric and optical properties of a variety of as-grown and thermally annealed undoped and doped PbI_2 single crystals.

The experimental values of the room-temperature 1 kHz ε_1 (E‖c-axis) of the undoped crystalline PbI_2 specimens of this work that were thermally annealed for sufficiently long time at fixed temperatures lying between 87-94°C compare well with the values of ε_1 (E‖c-axis) determined from the long-wavelength ellipsometric data at room temperature reported by other workers (Ahuja *et al.*, 2002) for Bridgman-Stockbarger grown PbI_2 single crystals (polytype form was not specified).

The frequency-(energy-) dependent dielectric functions of crystalline samples are usually evaluated numerically by making use of a variety of rigorous theoretical models (Adolph *et al.*, 1997; Ahuja *et al.*, 2002). This can be useful for elucidating the type of structural polytypic modifications in a layered crystalline material as the features of the energy dependence of the dielectric functions remarkably reflect the energy band structure of the crystal that is dependent on the actual polytype structure underlying its direct lattice and on its perfection and purity. Numerical calculations based on these theoretical models are then compared with the pseudodielectric function data, which can be deduced from ellipsometric spectroscopy or transmission and reflectivity measurements over a broad spectral range from the ultraviolet (UV) region through the visible spectrum to deep intermediate infrared (IR) region (Dugan and Henisch, 1967; Blonskii *et al.*, 1980; Adolph *et al.*, 1997; Ahuja *et al.*, 2002), as illustrated, for instance, in Fig. 1a and b, reproduced from the work of Ahuja *et al.* (2002).

Some of the important trends with the crystal structure in the theoretically calculated spectra of the real parts of the dielectric function tensor could be inferred by

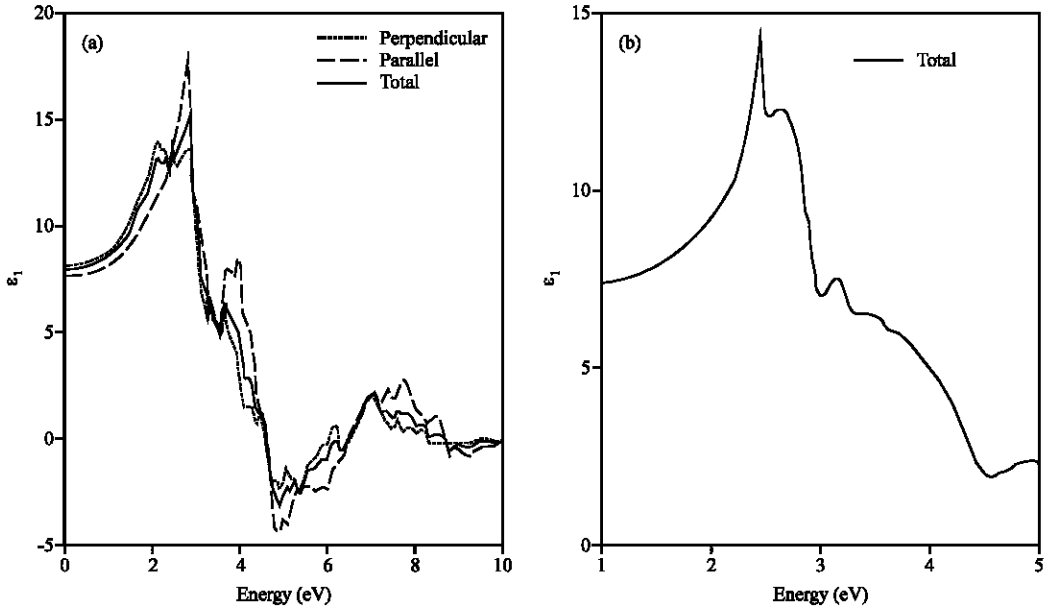

Fig. 1: (a) Photon-energy dependence of the calculated real parts of the dielectric function of a PbI_2 single crystal for different polarization directions of the electromagnetic field relative to the crystal c-axis. (b) Typical experimental ellipsometric data for the total real part of the pseudodielectric function. Both curves are reproduced from Ahuja *et al.* (2002)

discussing its low-frequency limit (i.e., the long-wavelength spectral region) or the dielectric constants ε_1(E∥c-axis) and ε_1(E⊥c-axis) in the low-frequency region (i.e., for $\omega \rightarrow 0$) with the measured dielectric data obtained from normal dielectric (impedance) spectroscopy measurements. In case of crystalline PbI_2, the differences between the values of the measured ε_1(E∥c-axis) and ε_1(E⊥c-axis) for both photon polarization directions relative to the crystal c-axis appear to be insignificant in the long-wavelength spectral region (Dugan and Henisch, 1967; Ahuja *et al.*, 2002). It can be noted that the room-temperature 1 kHz values of ε_1(E∥c-axis) of our samples are also compatible with the long-wavelength findings of ε_1(E∥c-axis) or ε_1(E⊥c-axis) calculated using the so-called full-potential linear muffin-tin orbital (FPLMTO) method with spin-orbit coupling being taken into account (Ahuja *et al.*, 2002).

CONCLUSIONS

We have suggested that the notable decrease of the experimental room-temperature 1 kHz dielectric constant ε_1 of the as-grown 2H-polytype undoped PbI_2 single crystals of this work with increasing isothermal annealing temperature T_a can be taken as an evidence for a trend towards a reversible 2H⇋12R phase transition at $T_a \sim 94$°C, a polytype structure transformation which has been alleged to occur in gel-grown PbI_2 single crystals in the vicinity of this annealing temperature (Salje *et al.*, 1987). The room-temperature 1 kHz ε_1 value of our undoped crystalline PbI_2 samples isothermal annealed at $T_a \sim 94$°C compares well with the measured and calculated long-wavelength values of ε_1 of PbI_2 single crystals of other workers at room temperature (Ahuja *et al.*, 2002).

Normal dielectric (impedance) spectroscopy could be useful in revealing the polytype phase of PbI_2 single crystals grown under different growth conditions and/or to elucidate possible polytypic transformation among its basic 2H, 4H and 12R polytype modifications, which may be induced upon long-period storage, by photon irradiation, or by prolonged isothermal annealing at temperatures below 150°C (Zallen and Slade, 1975; Jain and Trigunayat, 1996; Choudhary and Trigunayat, 1989; Blonskii *et al.*, 1980; Konings *et al.*, 1995; Palosz, 1983; Rao and Srivastava, 1978; Salje *et al.*, 1987; Palosz *et al.*, 1990; Bibik *et al.*, 1985).

Dielectric and impedance measurements are normally feasible to make and may prove to be viable to achieve this purpose compared with other lengthy and dedicated techniques (Zallen and Slade, 1975; Jain and Trigunayat, 1996; Choudhary and Trigunayat, 1989; Blonskii *et al.*, 1980; Konings *et al.*, 1995; Salje *et al.*, 1987; Palosz *et al.*, 1990; Bibik *et al.*, 1985). The viability of the proposed dielectric approach for studying polytypic modifications

f a crystalline sample stems from the fact that the behavior trend of its dielectric functions spectra reflects the integral details of its energy band structure and the underlying crystal lattice. Another privilege of this approach is that one can test its applicability by comparing the measured low-frequency dielectric constant and loss of the crystalline sample with the long-wavelength optical dielectric functions data and with the corresponding numerical values deduced from proper dielectric functions models.

Further detailed dielectric and optical studies are thus required to explore the effect of different external agents on the polytypism phenomenon and possible polytypic phase transformations in PbI_2 single crystals fabricated by the Bridgman-Stockbarger growth method from PbI_2 ingots synthesized under a variety of preparation conditions.

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