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Frequency dependence of loss tangent of thermally annealed undoped lead iodide crystals in the dark

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Abstract

The effect of isothermal annealing ($T_{\text{an}} \leqslant 120\,^\circ\text{C}$) on the frequency dependence of the loss tangent, $\tan\delta$, of undoped lead iodide (PbI_2) crystals in the dark has been investigated in the range 0.1–15 kHz at different ambient temperatures ($T = 15-120\,^\circ\text{C}$) without and with DC biasing ($V_{\text{DC}} \leqslant 2\,\text{V}$). Thermal annealing of as-grown PbI_2 crystals modified both the magnitude and frequency dependence of their $\tan\delta$. The $\tan\delta - f$ data ($T = 17\,^\circ\text{C}$) of unbiased as-grown crystals were found to fit a $\tan\delta \propto f^{-m}$ dependence, with $m \sim 0.94$ in the range $100\,\text{Hz} < f < 10\,\text{kHz}$. After annealing these crystals at $T_{\text{an}} = 70\,^\circ\text{C}$ for 1 h, the $\tan\delta \propto f^{-m}$ relation was obeyed for unbiased samples at any T over most of the frequency range studied, with the exponent m being reduced to around 0.55; a behavior that was also found for isothermally annealed PbI_2 crystals when were DC biased, but at high ambient temperatures. The $\tan\delta - T$ data ($f = 1\,\text{kHz}$) of the unbiased prolonged annealed ($T_{\text{an}} = 120\,^\circ\text{C}$) PbI_2 crystals exhibited two different thermally activated regimes, with activation energies $E_a \sim 0.23$ and 0.087 eV in the ranges 75–120 °C and 15–75 °C, respectively, which were related to trapping cationic Pb^{+2}-vacancies/hole-impurity levels in the crystal band gap. An interpolytypic phase transformation of the 2H-PbI_2 upon isothermal annealing may not, however, be entirely excluded.

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Keywords: Lead iodide; Loss tangent; Annealing effect; Polytypism; Conduction mechanisms

1. Introduction

Lead iodide (PbI_2) is recently considered as an attractive candidate and a promising material in the fabrication of many industrial and technological applications, such as photocells and indirect/direct radiation detectors for detecting X-rays and low-energy γ-rays (1 keV–1 MeV), as PbI_2 can efficiently operate over a wide temperature range from $-200\,^\circ\text{C}$ up to $130\,^\circ\text{C}$ [1–6]. This is because PbI_2 is an intrinsic wide band-gap compound semiconductor with a high dark resistivity ($E_g \sim 2.3\,\text{eV}$ and $\rho_{\text{dark}} > 10^{11}\,\Omega\,\text{cm}$ at 300 K [7–11]), and therefore giving rise to a very low leakage current at the pA-levels at and/or above room temperature (RT). These specific properties enable one to utilize PbI_2, and similar highly resistive halide compound materials, such as mercuric iodide (HgI_2), in radiation detectors without using the cryogenic liquid nitrogen for cooling, as opposed to most commercially available cryogenically cooled silicon and germanium X-ray detection systems.

PbI_2 has also a small energy necessary for the creation of an electron–hole pair ($E_{\text{e-h}} \sim 5$–$6.6\,\text{eV}$), and thus producing a large number of charge carriers with a high signal-to-noise response [5]. Moreover, PbI_2 has a high mass density ($d \sim 6.2\,\text{g/cm}^3$) and is composed of elements having large atomic numbers ($Z_{\text{Pb}} = 82$ and $Z_{\text{I}} = 53$), and thus should exhibit high photon stopping power (due to its high atomic absorption coefficient). These features allow one to manufacture small, compact portable radiation detectors

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from PbI_2 and HgI_2 compounds with very good volume–efficiency ratio. Compared with HgI_2, PbI_2 solid does not suffer from destructive structural transformations, at least up to its melting point, T_m (402–410 °C, depending on its purity), with a high chemical and environmental stability, and has relatively low vapor pressures, even at high temperatures (200 Pa at 493 °C [12]). HgI_2, however, exhibits at normal pressure a destructive phase transition as its Bravais crystal lattice changes from hexagonal to orthorhombic structures at temperatures around 130 °C and has much higher vapor pressures (200 Pa at 164 °C and >10 kPa at its T_m (256 °C) [12]). These two physical properties render PbI_2 to be a more attractive material than HgI_2 for the fabrication of radiation detectors with better performance stability and less degradation over longer time periods at elevated temperatures up to 130 °C.

Furthermore, in the fabrication of industrial large-area ($>25\,\mathrm{cm}\times 25\,\mathrm{cm}$) digital X-ray medical imaging devices and sensors, in which the X-ray photons are being directly converted into electronic charges, thick polycrystalline films made of highly pure PbI_2 material (e.g., $L\sim 100\,\mu\mathrm{m}$ and 1.56 mm are needed for more than 90% absorption of 20 and 120 keV nuclear radiation, respectively) are nowadays challenging alternative to films made of other wide band-gap energy materials, such as pure amorphous selenium (a-Se), which are already well established in these imaging applications [13]. Similar to PbI_2 layers (films), a pure a-Se film has a very high electrical resistivity ($\rho_{\mathrm{dark}}>10^{12}\,\Omega\,\mathrm{cm}$ at 300 K), as required for a photoconductor to be utilized in the construction of an active matrix radiation system. Compared to PbI_2, however, pure a-Se has a lower band-gap energy (E_g (300 K)$\sim$2.1 eV), a lower atomic number ($Z_{\mathrm{Se}}\sim 34$), much less thermal and ageing/environmental stability due to its rather low glass-transition temperature ($T_{\mathrm{glass}}\sim 40$ °C), a much higher electron–hole pair creation energy ($E_{\mathrm{e-h}}\sim 50$ eV), and much higher operational bias-voltage requirement (0.2–1 V/μm for PbI_2 or HgI_2 but up to 10 V/μm for a-Se) [5], as lower electric-field biasing ensures reduced electrical-breakdown risks.

However, to have an efficient collection of both charge carriers (electrons and holes) in a direct radiation detector/X-ray imaging device employing crystals or amorphous/polycrystalline films of a semiconducting wide band-gap energy material ($\rho_{\mathrm{dark}}>10^{8}\,\Omega\,\mathrm{cm}$ and $1.4\,\mathrm{eV}<E_g<3\,\mathrm{eV}$ [10]), a large charge-carrier mobility and a high mobility (μ)-trapping life-time (τ) product ($\mu\tau$) ($>10^{-4}\,\mathrm{cm}^2/\mathrm{V}$ [10]) of both charge carriers is necessary since absorption of nuclear radiations occurs throughout the material. This implies that crystals or polycrystalline films of ultrahigh pure material deficient in structural defects and trapping centers are needed when used for detection purposes. One of the disadvantages of PbI_2 is the low mobility of its charge carriers and their small $\mu\tau$ even for quality single crystals ($\mu_e\sim 8$–$65\,\mathrm{cm}^2/\mathrm{V\,s}$, $\mu_h\sim 2$–$20\,\mathrm{cm}^2/\mathrm{V\,s}$, $(\mu\tau)_e\sim 2\times 10^{-6}\,\mathrm{cm}^2/\mathrm{V}$, and $(\mu\tau)_h\sim 6\times 10^{-7}\,\mathrm{cm}^2/\mathrm{V}$ [1–6]). Much worse values of μ and $\mu\tau$ of both charge carriers are normally expected in the case of polycrystalline PbI_2 films [14], as the existence of operative structural defects/disorder and trapping centers is generally more probable in polycrystalline film specimens. Therefore, in order to enhance electrical performance and obtain a better charge transport in this material, the trapping life-time characteristics and charges mobility should be improved, probably by growing and synthesizing pure, stoichiometric, and defect-free crystalline and/or polycrystalline PbI_2 specimens.

A second disadvantage of crystalline PbI_2 solid is its layered-sandwich Bravais lattice structure, in which identical two-dimensional layer packets, each of which consists of three monolayers of atoms I–Pb–I, are sandwiched over each other in the sequence I–Pb–I–I–Pb–I–… along the *c*-axis of either a hexagonal closed-packed (HCP) or a rhombohedral closed-packed (RCP) structure [15–22]. The intra-layer chemical bonding between the lead (Pb) layer and the adjacent iodine (I) layers in an individual I–Pb–I layer packet is strongly ionic and/or covalent, whereas the interlayer bonding between the individual layer packets is predominantly due to much weaker van der Waals interactions between the iodine atoms in the adjusting I layers. This layered or "flaky" structural property of PbI_2 crystalline solid does not facilitate crystal handling and renders the cleavage of PbI_2 normal to the *c*-axis very easy. As a consequence, good surfaces parallel to the *c*-axis cannot always be obtained and structural faults or dislocations can easily be created in the crystal.

Another drawback of crystalline PbI_2 that may affect its quality is the contentious polymorphism (or polytype formations) in this layer-structured compound and the possible phase transformation from one polytype modification to another even after purification of the PbI_2 starting material and/or during crystal growth at high temperatures. In principle, PbI_2 can exist in either one of its numerous HCP or RCP crystalline polytypes or as an admixture of two or more of these polytype structures, out of which the complete crystal structure of more than 30 polytypes has been determined [1–7,15–22]. It is traditionally accepted that the HCP or RCP crystal structures of all PbI_2 polytypic modifications are normally formed by structurally identical, yet translationally non-equivalent closed-packed (cp) I–Pb–I layer packets with distinctly different crystallographic orientations, about the *c*-axis, and characteristics, for which the length of the *c*-lattice constant is different, but with the same *a*-lattice constant ($a=0.456$ nm). The most commonly encountered cp structures of PbI_2 polytypic modifications are the three basic hexagonal (H) polytypes (2H, 4H, and 12H) and the rhombohedral (R) polytype modification of the 12R nature, of which the most highly symmetric forms are the 2H and 12R basic polytypes, which, respectively, are the most energetically stable low- and high- temperature polytypic modifications inherent in an absolute minimum of a temperature-dependent free energy, whereas the thermodynamically instable PbI_2 polytype structure at low temperatures is the 4H polytypism form, which has a