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Doping impact on the electro-optical properties of a TlBr crystal

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Abstract

TlBr doped with In and Pb was synthesized and grown using a vertical Bridgman method. The segregation coefficients of both dopants in TlBr were calculated using the different experimental optical and electrical characteristics of $(TlBr)_{0.973}$–$(InBr)_{0.027}$ and $(TlBr)_{0.972}$–$(PbBr_2)_{0.078}$ crystals. The solubility of In and Pb in the liquid phase is higher than their solubility in solid TlBr: $k_s(In) = 1.06$ and $k_s(Pb) = 1.3$–1.6. Doping with both impurities leads to degradation of the electrical, optical, and detector properties of TlBr.

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1. Introduction

Over the past six decades, considerable effort has been expended in developing TlBr crystals for use as radiation detectors (see, for instance, Refs. [1–3]). The interest in TlBr is due to its high average atomic number, high density, and wide band gap. One of the major problems of TlBr crystals is their mechanical softness, which leads to easy plastic deformation, even during handling of samples. As a result, any promising physical properties of "perfectly chemically pure" crystals can be killed by unsuitable mechanical treatment during sample preparation. It is possible to increase crystal hardness by doping crystals with impurities that can "lock" dislocations in place. However, while these impurities can improve some properties, these same impurities can degrade others. Therefore, selection of appropriate impurities, that not only make crystals mechanically harder but also maintain the good spectroscopic properties of TlBr, is an important scientific and applied task.

In the current work we use In^{1+} and Pb^{2+} ions, in the form of InBr and $PbBr_2$, respectively, as dopants. Indium was selected because it is in the same column of the periodic table as thallium and has a similar Pauling ionic radius: $r(Tl^{1+}) = 1.15$ and $r(In^{1+}) = 1.04$ Å. Therefore, indium is an isoelectronic impurity with a geometric size similar to thallium, and will not lead to a significant distortion of the crystal lattice or of the electronic system of the host crystal. However, sharp differences in crystal structure of InBr (layered chains) and TlBr (cubic) make formation of the continuous solid solution $(InBr)_x$–$(TlBr)_{1-x}$ problematic.

Pb^{2+} was selected as a dopant in order to check the influence of ions with crystallochemical parameters, which are significantly different from the host ion, Tl^{1+}. Although Pb^{2+} in $PbBr_2$ has the same coordination number (8) as Tl^{1+} in TlBr, there is a significant difference in their Pauling ionic radii: $r(Tl^{1+}) = 1.15$ and $r(Pb^{2+}) = 1.43$ Å. Likewise, differences in valence lead to a distortion of the crystal structure and electronic system of TlBr. Substituting Tl^{+} with Pb^{2+} in the TlBr crystal lattice leads to the creation of additional cation vacancies (V_{Tl}^{1-}), preserving charge balance and compensating the lattice distortion. Therefore, the chemical formula of the new compound will look like ${Tl_{1-x}}^{1+}{Pb_x}^{2+}{V_x}^{1-}Br^{1-}$. The difference in the crystal structure of $PbBr_2$ (which could be interpreted as a hexagonal closed packed structure of

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Pb^{2+} ions with tetrahedral sites that are completely filled by Br^- ions) and TlBr (body centered cubic) demonstrates a problematic formation of a continuous solid solution $(PbBr_2)_x$–$(TlBr)_{1-x}$, as in the example with In doping.

2. Synthesis of solid system, crystal growth, and wafers preparation

The synthesis, crystal growth, and device preparation of both solid systems were performed in a similar manner. TlBr beads (99.999%, Aldridge) and InBr beads (99.999%, Aldridge) were loaded into a quartz ampoule in appropriate amounts for the synthesis of $(TlBr)_{0.973}$–$(InBr)_{0.027}$. The ampoule was then evacuated under heating, sealed, and placed into a vertical furnace with a temperature of about 500 °C for 100 h. A two-zone furnace with the same parameters as the TlBr crystal growth was used. The resulting crystal was 80 mm in length and varied gradually in color: from dark red at one end to greenish yellow at the tipped end.

The same method was used for preparation of the $(TlBr)_{0.972}$–$(PbBr_2)_{0.028}$ solid system. TlBr beads (99.999%, Aldridge) and $PbBr_2$ Puretronic powder (99.999%, Alfa) were loaded into a quartz ampoule. The grown crystal was non-uniform (probably a two phase polycrystalline structure), was 80 mm in length, and was non-translucent and gray in color, with the second phase precipitated on grain boundaries (white color).

Wafers were sliced from crystal with a wire saw and slurry, lapped on a glass plate with 5 μm alumina grit, polished with 1 μm alumina grit, and cleaned. Each wafer was about 2 mm in thickness and numbered in such a way that adjacent wafer numbers increase from the tail to tipped part of boules.

3. The crystal testing

3.1. X-ray diffraction

X-ray diffraction analysis of the Bridgman grown $(TlBr)_{0.973}$–$(InBr)_{0.027}$ and $(TlBr)_{0.972}$–$(PbBr_2)_{0.028}$ wafers was performed at MIT (Cambridge, MA) to characterize the crystalline phase and structure. As an example, Figs. 1(a) and (b) show XRD patterns obtained with $(TlBr)_{0.973}$–$(InBr)_{0.027}$ and $(TlBr)_{0.972}$–$(PbBr_2)_{0.028}$, respectively.

All In-doped TlBr wafers demonstrate patterns typical for a host TlBr crystal with a growth axis preferentially oriented in the ⟨1 1 0⟩ direction. Wafer #7 shows a relatively intensive peak corresponding to plane (0 0 2) of $InBr_2$. All other non-TlBr peaks have intensities below 10% (wafer #1: planes (0 0 2) and (3 1 1) of $InBr_2$, plane (2 0 2) of InBr; wafer #3: plane (0 0 2) of $InBr_2$, plane (2 5 0) of In_2Br_3; wafer #9: planes (0 0 2), (0 4 2) of $InBr_2$ and plane (2 2 0) of InBr, Fig. 1(a)). One can suggest that these peaks appeared due to random distributions of In-containing compounds in the crystal that led to a high background level. We can preliminarily assume that all wafers along the ingot have a TlBr lattice, with a random distribution of inclusions of second phases in the form of different compounds of indium bromide. All $(TlBr)_{0.972}$–$(PbBr_2)_{0.028}$ wafers mainly demonstrate different combinations of Bragg's peaks corresponding to TlBr and $PbBr_2$ crystallographic planes. Wafer #1 (Fig. 1b) shows only plane (0 5 1) of $PbBr_2$. Wafer #2 contains planes (1 0 0) and (1 1 0) of TlBr, as well as (1 2 1), (0 3 1), and (2 1 2) of $PbBr_2$ planes. Wafer #4 has TlBr planes (1 0 0), (1 1 0) and $PbBr_2$ planes (1 1 1), (2 0 1), and (3 2 1). Wafer #6 is a mixture of TlBr planes (1 0 0), (1 1 0), (2 1 0), (2 1 1) and $PbBr_2$ planes (1 2 1) and (3 1 2). Traces of Tl, Pb, PbO are also observed in wafers #4 and #6. Therefore, the grown $(TlBr)_{0.972}$–$(PbBr_2)_{0.028}$ crystal could be described as a two-phase mechanical mixture of TlBr and $PbBr_2$.

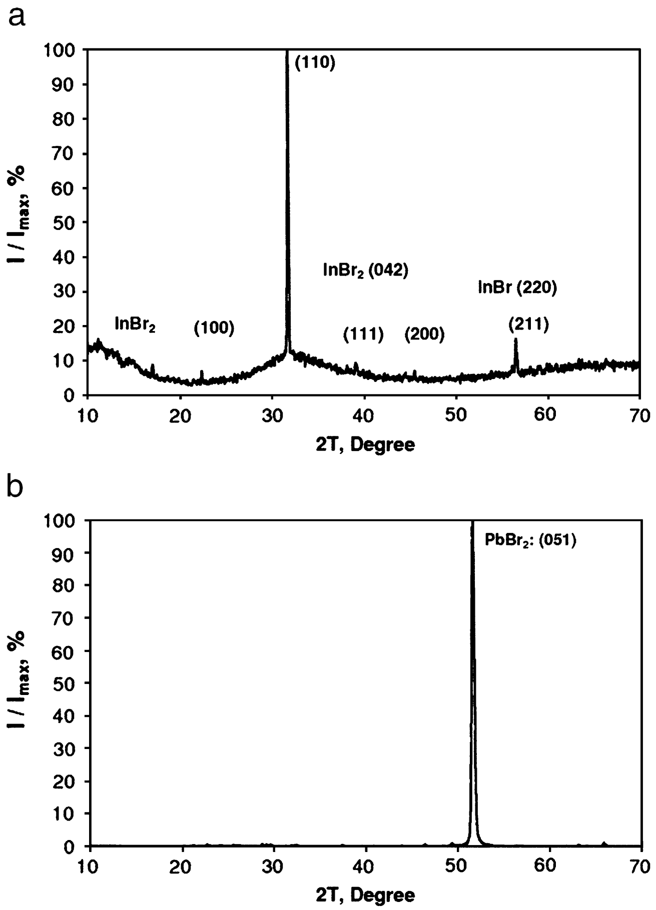

Fig. 1. X-ray diffraction patterns of $(TlBr)_{0.973}$–$(InBr)_{0.027}$ wafer #9 (a) and $(TlBr)_{0.972}$–$(PbBr_2)_{0.028}$ wafer #1 (b). The wafer number increases from tail to tip of the crystal boules.

3.2. Transmission spectra

The optical characterization involved the measurement of the optical transmission spectra of the crystals using a Bausch and Lomb monochromator. These transmission spectra of $(TlBr)_{0.973}$–$(InBr)_{0.027}$ are shown in Fig. 2. The transmittances of wafers #1, 2, and 3 are below the pure TlBr crystal transmittance, which coincides with what can