New nonlinear crystal for three-wave interactions with transmission extending from 1.7 to 25 µm

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Abstract: We have grown single crystals of $PbIn_6Te_{10}$, with clear transparency from 3 to 20 µm, and showed that it possesses sufficient birefringence for phase-matching of three-wave parametric interactions and a nonlinear coefficient of 51 pm/V.

OCIS Codes: (190.4400) Nonlinear optics, materials; (190.4410) Nonlinear optics, parametric processes

The objective of the present work was to search for new inorganic nonlinear crystals for three-wave parametric processes in the near- to far-IR (above 15 µm and up to 25-30 µm) spectral range. The long-wave transparency edge of typical selenide compounds is limited by multi-phonon absorption which starts at 14-18 µm and the transmission drops to zero near 19 µm for $AgGaSe_2$, 20 µm for GaSe, and 25 µm for CdSe [1]. The commercially available crystal with longest wavelength limit, CdSe, exhibits unfortunately only modest (~18 pm/V) nonlinearity. Indeed elemental Te, known for more than 35 years, is transparent from 3.5 to 36 µm and possesses the highest known nonlinear coefficient for an inorganic material, of the order of 600 pm/V [1], however, its high linear losses, similar to the elemental Se, do not permit real applications apart from some diagnostics (e.g. of low average power ultrashort pulses) in the far-IR. Some binary non-centrosymmetric telluride crystals with optical quality also exist, e.g. CdTe and ZnTe, but they are cubic and their application as nonlinear crystals is also limited to diagnostics utilizing the relatively long coherence length in the far-IR in the absence of birefringent phase-matching. More recently, single crystals of the chalcogenide type $AgGaTe_2$ (analogue of $AgGaS_2$ and $AgGaSe_2$ with expected transparency limit around 25 µm) were grown with sufficiently large sizes and optical quality, however, the birefringence of this material also turned out to be slightly too small for phase-matching [2]. Another chalcopyrite type telluride, $LiGaTe_2$ [3], showed sufficient birefringence, but unfortunately, besides the bad chemical surface stability, the peculiar features of such Li-type ternary compounds leading to extended short-wave transmission also lead to shorter long-wave transparency limit (<15 µm in the case of $LiGaTe_2$). On the other hand, it should be emphasized that extended short-wave limit is also an attractive property for any IR nonlinear crystal because it enables pumping at near-IR wavelengths for down conversion and is normally associated with better thermo-mechanical properties and damage resistivity.

Recently, we initiated an investigation of another family of ternary tellurides for which in fact only structural properties were known [4,5]. Deiseroth et al. [4] gave an overview of the X-ray data for crystals with the non-metallic β-Mn phase type, including binary tellurides (Ga_7Te_{10}, In_7Te_{10}) and three new ternary compounds synthesized by them ($SnGa_6Te_{10}$ and $PbIn_6Te_{10}$, for which tiny single crystals could be extracted, and $PbGa_6Te_{10}$, obtained only in polycrystalline form). These compounds crystallize in the non-centrosymmetric point group D_3 (32), space group R32 (D_3^7). The structural similarity of the binary (B_7Te_{10}) and ternary (AB_6Te_{10}) compounds might be an important factor for the crystal growth of the latter, especially in cases when the unit cell volumes and melting temperatures are similar. From the data in [4], we obtained $V(Ga_7Te_{10})/V(PbGa_6Te_{10})$~0.983 and $V(In_7Te_{10})/V(PbIn_6Te_{10})$~1.004. Such close values are in fact not unexpected since the binary compounds can be regarded as a degenerate form of the ternary ones, in which the sub-lattice of the trivalent and divalent metals is occupied by the same ion. Thus, when crystallizing e.g. $PbIn_6Te_{10}$ from the melt, it is not obvious which of the two ions, In^{2+} or Pb^{2+}, will occupy the position of the divalent metal. The nominal concentration of In in the melt will be six times higher than that of Pb but the growth scenario will be governed by the relative segregation coefficients of the two ions for the chosen actual concentrations and thermodynamic conditions.

In order to estimate the potential of such crystals for nonlinear optics we attempted to grow, for the first time to our knowledge, large size crystals of $PbIn_6Te_{10}$ and In_7Te_{10}. For the synthesis, high purity, (5Ns for Pb and Te and 6Ns for In) raw materials were used. The melting temperatures were estimated from differential thermal analysis

(DTA) and they were (630 ± 5)°C for $PbIn_6Te_{10}$ and (670 ± 5)°C for In_7Te_{10}. The single crystals were grown by the Bridgman-Stockbarger technique with a crystallization front velocity of 6 mm/day and a temperature gradient in the crystallization zone of 10-15°C/cm. Cooling was performed in the regime of switched off furnace. Unfortunately it was impossible to grow high quality binary In_7Te_{10}. Therefore, the further efforts were focused on the ternary $PbIn_6Te_{10}$ (PIT). Single PIT crystals of sizes up to few centimetres were obtained from which optical elements and prisms could be cut (Fig. 1a). In view of the above mentioned crystallo-chemical similarity between the binary and ternary compounds, the lower parts of the grown boules were used for a charge composition corresponding to stoichiometric $PbIn_6Te_{10}$.

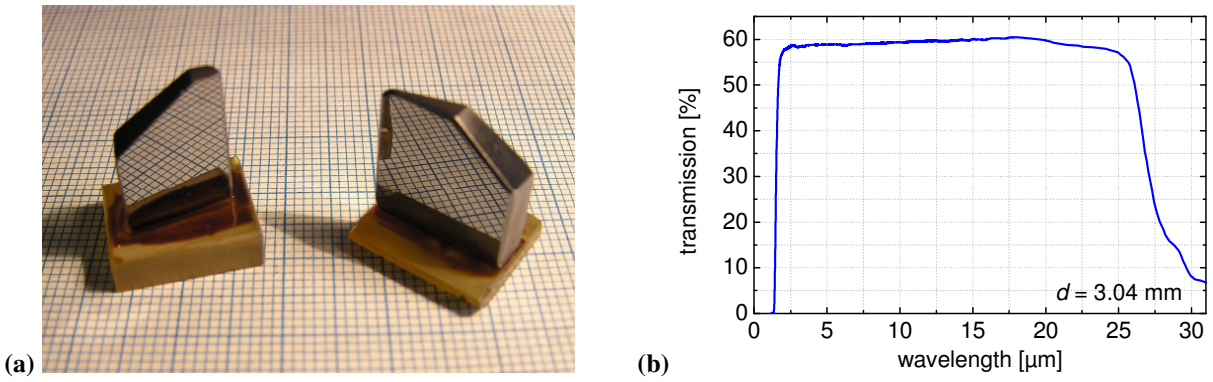

Fig. 1. Prisms of $PbIn_6Te_{10}$ (PIT) prepared for refractive index measurements (a) and unpolarized transmission spectrum of PIT recorded with a ~3 mm thick plate (b).

The clear transparency of PIT extends from 3 to 20 μm where the absorption coefficient does not exceed (0.07 ± 0.03) cm^{-1}. At an absorption level of 0.3 cm^{-1}, PIT is transparent from 1.7 to 25 μm (Fig. 1b), while the zero-level transmission limit (to compare with the given in the introduction values for $AgGaSe_2$, GaSe and CdSe) should be above 31 μm. From the measured absorption coefficient $\alpha(\lambda)$ and fitting the dependences of $(\alpha\lambda)^2$ vs $(1/\lambda)$ and $(\alpha\lambda)^{1/2}$ vs $(1/\lambda)$ we obtained direct and indirect band-gaps of E_g(direct) = 1.08 eV (1.15 μm) and E_g(indirect) = 0.96 eV (1.29 μm), respectively (Fig. 2).

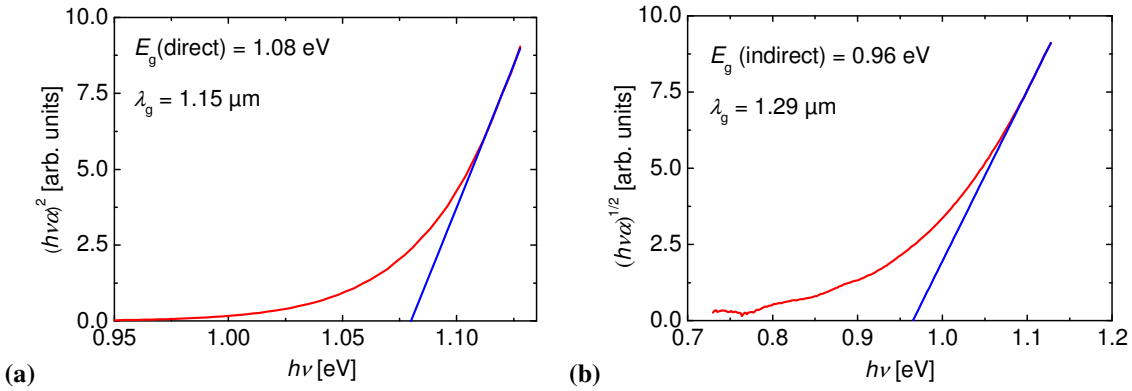

Fig. 2. Direct (a) and indirect (b) band-gap determination of PIT using a 0.25 mm thick plate and unpolarized light.

The refractive indices of PIT were measured in the 1.5-10.4 μm spectral range by the auto-collimation method using prisms with an apex angle of about 12° and aperture of 12×15 mm^2 (Fig. 1a). The accuracy was better than 0.005. We found that PIT is optically positive with a characteristic birefringence of n_e - n_o~0.05 which means that it is phase-matchable. From the Sellmeier equations constructed on the basis of the dispersion data measured (Table 1), we estimated a short wave second-harmonic generation (SHG) limit of ~3.6 μm (fundamental wavelength). The short- and long-wave SHG limits for ee-o type-I interaction are determined from the solutions of the equation

$\Delta n(\lambda_F) = \delta n(\lambda_F, \lambda_F/2)$, where $\Delta n = n_e(\lambda_F) - n_o(\lambda_F)$ is the birefringence at the fundamental and $\delta n = n_o(\lambda_F/2) - n_o(\lambda_F)$ is a measure for the dispersion of the ordinary wave between the fundamental and the second harmonic. Thus, the long-wave limit can be estimated only from extrapolation of the available refractive index data and it should be around 21 μm. In these two limits the phase-matching angle approaches 90° and in between it reaches a minimum value of 32° for SHG at 8.3 μm (fundamental).

Table 1. Sellmeier coefficients of $PbIn_6Te_{10}$ at room temperature: $n^2=A_1+A_3/(\lambda^2-A_2)+A_5/(\lambda^2-A_4)$ where λ is in μm.

crystal	n	A_1	A_2	A_3	A_4	A_5
PIT	n_o	11.162067	0.720740	0.900821	3153.47	6347.934
1.5-10.4 μm	n_e	11.938574	0.442087	1.227212	3819.91	9616.588

In optically positive crystals of the $D_3(32)$ point group the effective nonlinearity for three-wave interactions is given by $d_{eff}(oe\text{-}o) = d_{11}\cos\theta\cos 3\varphi$ and $d_{eff}(ee\text{-}o) = d_{11}\cos^2\theta\sin 3\varphi$. The polar and azimuthal angles θ and φ are defined in a crystallo-physical frame XYZ (coinciding with the dielectric frame xyz) whose Z axis coincides with the *c*-crystallographic axis (optical axis) and whose X axis coincides with one of the crystallographic *a*-axes. The nonlinear coefficient d_{11} of PIT was measured by comparing the SHG efficiency to that obtained with $ZnGeP_2$ (ZGP). A $KNbO_3$-based femtosecond OPA was used as a laser source, operating at 4.7 μm at a repetition rate of 1 kHz; more details on this set-up can be found elsewhere [6]. Care was taken to have sufficient spectral and angular acceptance so that these effects and the spatial walk-off due to birefringence could be neglected. The 0.48 mm thick PIT test plate and the 0.53-thick ZGP reference sample were cut at $\theta = 48°$, $\varphi = 30°$, and $\theta = 50.5°$, $\varphi = 0°$, respectively. The angular acceptance (FWHM) amounts to 5.8° for PIT and 5° for ZGP and the birefringence angle is ρ=0.9° in PIT and ρ=0.7° in ZGP. The group velocity mismatch amounts to 170 fs/mm for PIT and 70 fs/mm for ZGP, this difference could only lead to underestimation of the PIT nonlinearity but with 350 fs long fundamental pulses at 4.7 μm (typical spectral FWHM of 100 nm) it is not expected to cause significant error. For a fundamental energy of 3-4 μJ, the spot size was selected large enough so that spatial walk-off effect was negligible and the internal energy conversion efficiency remained below 10% (small signal approximation). The observed phase-matching angles for both samples were very close to the cut angles and for calculation of the relative nonlinearities we only took into account the effect of the different index of refraction on the Fresnel losses and the coupling coefficient. For both crystals we made 5 test series, each of them consisting of 8-10 measurements with fine crystal tuning on a SHG signal maximum. The results can be summarized as: $d_{eff}(PIT) = (0.290 \pm 0.015)\cdot d_{36}$ (ZGP) or $d_{11}(PIT) = (0.647 \pm 0.034)\cdot d_{36}(ZGP)$. Having in mind that $d_{36}(ZGP) = 79$ pm/V for this process [6], we arrived at $d_{11}(PIT) = (51 \pm 3)$ pm/V**.**

In conclusion, we grew for the first time to our knowledge nonlinear crystals of $PbIn_6Te_{10}$, with good transparency extending from the near-IR to above 25 μm and showed that this crystal possesses sufficient birefringence for phase-matching. Its quite high nonlinear coefficient of 51 pm/V, combined with such a wide transparency, could make it a unique material for nonlinear frequency conversion in the mid- and far-IR spectral ranges. It could be pumped by Er^{3+}-laser sources operating in the 2.9 spectral range, Cr^2-lasers in the 2.5 μm spectral range (still without substantial two-photon absorption) or even, after improvement of the residual loss, near 2-μm, by well established powerful Ho^{3+}- or Tm^{3+}-laser based systems.

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