Thermoelectric properties of $Pb_{1-x}Sn_xTe$ crystals doped with vanadium deep donors

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PbTe and SnTe as well as their substitutional alloys $Pb_{1-x}Sn_xTe$ are IV-VI semiconductor materials well known for topological crystalline insulator (TCI) properties as well as for their applications in mid-infrared devices and thermoelectric generators. Optimal application of these materials requires controlling of both type and concentration of conducting carriers: from almost semi-insulating bulk materials desired in TCIs to heavily doped (n,p=10^{19} - 10^{20} cm^{-3}) thermoelectric elements. In $Pb_{1-x}Sn_xTe$ the electrically active native defects (metal vacancies) determine very high background hole concentration (p=10^{18} - 10^{19} cm^{-3}). Controlling electrical properties requires doping with extrinsic donors (Bi, J) or acceptors (Na, Ag) and/or thermal annealing. Thermoelectric properties of $Pb_{1-x}Sn_xTe$ can also be controlled by incorporation of 3d transition metals, like Cr, Fe or V. The solubility of these transition metals in IV-VI semiconductors is limited to heavily doping regime (typically below 0.5 at.%) but they form a special class of resonant donor centers with the mixed valence 3+/2+ charge state depending on Sn content and Fermi level position.

In this work, we examine $Pb_{1-x}Sn_xTe$:V bulk crystals with nominal Sn content of x=0.2 and V content of 1 at.% grown by the Bridgman method under varying thermal regime and doping procedure. The crystals studied cover the composition range corresponding to the expected in-gap position of $V^{2+/3+}$ donor level [1]. Electron microscopy SEM-EDX analysis of chemical composition confirmed the Sn concentration smoothly varying along an ingot from x=0.13 to x=0.3 and an indication for very small V content (below 0.5 at. %) increasing towards the end of an ingot. To examine electrical properties, we measured the electrical conductivity and the Hall effect in the temperature range T=5-300 K revealing only p-type metallic conductivity with carrier concentration $p\approx 7*10^{18}$ cm^{-3} and resistivity ratio $\rho(300K)/\rho(5K)\approx 10$ due to the temperature dependence of mobility. We also measured, at room temperature, the thermoelectric power α and determined the key applicational parameter - thermoelectric power factor $P_\sigma=\alpha^2/\rho\approx 8\mu W/K^2cm$ (comparable to observed in good PbTe-based thermoelectric materials). No in-gap pinning of Fermi level by $V^{2+/3+}$ donors and semi-insulating state was experimentally found, presumably because only small part of V centers introduced into $Pb_{1-x}Sn_xTe$ (estimated 0.1 at.%) becomes electrically active. As a result, the electrical conductivity of our $Pb_{1-x}Sn_xTe$:V bulk crystals still remains dominated by native defects. This balance can be changed by further doping with V or reduction of vacancies concentration by annealing.

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[1] E.P. Skipetrov et al., Semiconductors **46**, 741 (2012); Low Temp. Phys. **37**, 210 (2011).