$Pb_{1-x}Sn_xTe$ thermoelectric with Cr resonant donors

A. Królicka[1], K. Dybko[1,2], R. Minikayev[1], A. Reszka[1] , J. Więckowski[1], A. Szewczyk[1], A. Grochot[1], H. Przybylińska[1], W Knoff[1], K. Gas[1], M. Sawicki[1], A. Mirowska[3], A. Materna[3], M. Piersa[3], T. Story[1]

[1]Institute of Physics, Polish Academy of Sciences, Warsaw, Poland
[2]International Research Centre MagTop, Institute of Physics, Polish Academy of Sciences Warsaw, Poland
[3]Institute of Electronic Materials Technology, Warsaw, Poland

The IV-VI semiconductors, like PbTe, SnTe as well as their substitutional alloys $Pb_{1-x}Sn_xTe$ are well known for their applications in thermoelectric generators. Recently, it was demonstrated that by combining very strong doping, nanostructuring, and band conversion effects, the thermoelectric figure of merit parameter *ZT* could be substantially improved, comparing with currently used materials with *ZT*=0.5-1 [1,2]. The thermoelectric properties of $Pb_{1-x}Sn_xTe$ can be also controlled by incorporation of 3d transition metals, such as Mn, Cr or Fe. A particular example of such materials are $Pb_{1-x}Sn_xTe$:Cr alloys in which mixed valence $Cr^{2+/3+}$ ions form donor centers, resonant with the conduction band in PbTe but located in the valence band in SnTe [3-6]. The main physical factor influencing thermoelectric properties is the position of Cr level in the band structure of $Pb_{1-x}Sn_xTe$, which is controlled by the Sn content. We exploit the effect of the resonant enhancement of the density of states which, in this alloy, can uniquely be achieved for both *n*- and *p*-type cases [4-6]. As the solubility of Cr in IV-VI semiconductors is limited (typically 0.5 at. % of cations), we expect both single- and multi-phase crystalline materials.

In this work, we investigate the effect of Cr resonant center on thermoelectric properties of bulk crystals of $Pb_{1-x-y}Sn_xCr_yTe$ grown by the Bridgman method in the composition range $0<x<0.6$ and $y=0.01$. The rock-salt crystal structure, chemical composition and the presence of various Cr-Te phases was examined by scanning electron microscopy with energy-dispersive spectroscopy (SEM/EDS) and X-ray diffraction techniques. As Cr^{3+} ions are paramagnetic centers with spin S=3/2 their presence and concentration were monitored by electron paramagnetic resonance (EPR) and SQUID magnetometry techniques. In sharp contrast, Cr^{2+} ions are in the IV-VI materials the van Vleck paramagnetic centers, not active in EPR regime. To verify the thermoelectric parameters of $Pb_{1-x}Sn_xTe$:Cr we carried out the measurements of the Hall effect, the electrical conductivity, the thermoelectric power, and the thermal conductivity. We observed that the Fermi level position is controlled by the competition of two electrically active defects: Cr^{3+} donor centers and metal vacancies – dominant *p*-type native defects in $Pb_{1-x}Sn_xTe$. These measurements allowed for determination of the parameter *ZT*=0.2 at room temperature.

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