The influence of order/disorder phenomena and nanoscopic defects on the thermoelectric properties of In_5Ch_5X (Ch = S, Se; X = Cl, Br)

Kledi Xhaxhiu[1]
Klaus Bente[2]

[1] Department of Chemistry, Faculty of Natural Sciences, University of Tirana, Blv. Zog I, No. 25/1, 1001 Tirana, Albania
[2] Institute of Mineralogy, Crystallography and Materials Science, Faculty of Chemistry and Mineralogy, University of Leipzig, Scharnhorststrase 20, 04275 Leipzig, Germany

kledi.xhaxhiu@fshn.edu.al; kledi.xhaxhiu@unitir.edu.al

Abstract

The mixed-valence compounds In_5S_5Br, $In_5S_3Se_2Br$, In5SSe$_4$Br, and In_5Se_5Br crystallize in the orthorhombic SG *P*mn2$_1$ and reveal real structures with no anomalies while consisting of 3:3 arrangements. Interestingly they show thermoelectric properties. As the selenium content in the structure of In_5S_5Br increases, the Seebeck potential increases. In_5S_5Br exhibits low Seebeck potentials within the studied range (ΔT = 0–80 K) and a maximum value of 0.34 mV for ΔT = 80 K. It behaves as a *p*-type semiconductor. The substitution of two sulphur species by selenium, as in $In_5S_3Se_2Br$, shows *n*-type conductivity and approx.−16.00 mV for the same ΔT. Further substitutions of sulphur in the structure maintain the *n*-type conductivity and increase dramatically the Seebeck potential to -225.26 mV (ΔT = 80 K). Repeating cycles of Seebeck potential variation over time for In_5Se_5Br and In_5SSe_4Br, show differences in their potentials, shape of maxima as well as in their recovery time. Electrical conductivities from 0.3 pS for In_5S_5Br up to 13 pS for In_5Se_5Br, strongly influence their thermoelectricity. In contrast to In_5Ch_5Br (Ch = S, Se), the non isotypic sibling compounds In_5Ch_5Cl obtained by full substitution of bromine with clorine, presented a variety of anomalies in their real structure. Beside the existence of the 4:2 and 2:4 arrangements (observed from the average structure) the HRTEM images and the SAED patterns evidenced the existence of layers with 3:3 arrangements within the structure. In addition, their real structures reveal the presence of polymorphic intergrowth of layers with different arrangements, the polysynthetic twinning and the intergrowth of large separated domains containing In_6S_7. Similarly to In_5Ch_5Br (Ch = S, Se) they behave as *p*- and *n*-type semiconductors but show no thermoelectric properties. The extinction of the thermoelectric properties of In_5Ch_5Br (Ch = S, Se) is merely atributed to its structural anomalies.

References

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