Improved Thermoelectric–Photovoltaic Performance of Ag_2Se Originating from a Halogenation-Induced Wider Band Gap and Low Crystal Symmetry

ABSTRACT

Ag2Se has drawn widespread attention in wearable self-powered technologies because of its ductile nature, chemical stability, and low toxicity. However, its stable orthorhombic bulk phase is a narrow band gap material with compromised See beck coefficient. In this work, motivated by the discovery of stretchable Ag2Se and various studies demonstrating the positive role of halogenation toward semiconductor performance, synergistical enhancement of its See beck coefficient and quality factor integrating the weighted mobility and lattice thermal conductivity have been achieved by halogenation. Prediction of energy landscape within Ag2Se–X2 (X = F, Cl, and Br) was calculated through global evolutionary algorithm in combination with first-principles approach. Three low-lying energy moieties, Ag2SeBr4, Ag2SeCl6, and Ag2SeF6, and their 2D counterparts with P1 symmetry are deformable inorganic semiconductors exhibiting sufficient electronic, thermal, mechanical and lattice stabilities. Ultimately, their combined low-lying dispersive phonon modes resulting from low crystal symmetry and flattened conduction band due to increased band gap drastically improve the See beck coefficient, reduce the band energy offset, and maintain the high phonon scattering rate, in turn leading to an ultralow thermal conductivity (<0.50 W m–1 K–1 at 300 K), enhanced bipolar conduction suppression, and large increase in electronic quality factor, without relinquishing the ductility. As a result, at ∼9 × 1019 cm–3 optimal carrier concentration, a broad plateaued figure of merit ∼1.1 starting from 400 K is obtained for p-doped Ag2SeBr4 and Ag2SeCl6 bulk materials, which corresponds to a 5-fold increase compared to Ag2Se and extends better thermoelectric behavior for Ag2Se over a wider temperature plateau. These structures display broader and steeper absorption coefficient α(ω) ∼ 105 cm–1 in contrast to Ag2Se, encompassing the visible to ultraviolet regions. in particular, all samples have spectroscopic limited maximum efficiency (SLME) above 20% at a scalable thickness of ≥1.0 μm. This work also shows that other interactions, namely Ag2Se–AgX and Ag2Se–X mixtures, are incorrect synthesis approaches.