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One-step synthesis of *n*-type Mg₂Ge

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Magnesium-based thermoelectric materials (Mg₂X, X = Si, Sn, Ge) have received considerable attention due to their availability, low toxicity and reasonably good thermoelectric performance. However, the synthesis of these materials with high purity is challenging due to the volatility and high vapor pressure of magnesium. In the current study, single phase *n*-type Mg₂Ge has been fabricated through the one-step reaction of elemental Ge and MgH₂ using spark plasma sintering (SPS). This technique was used previously on the synthesis of high purity nanocrystalline Mg₂Si as an alternative to melting procedures, believed to reduce the formation of oxides due to the liberation of hydrogen. X-ray diffraction (XRD) analysis of fabricated bulk samples shows single phase Mg₂Ge. Scanning electron microscopy (SEM) analysis equipped with energy-dispersive X-ray spectroscopy (EDS) indicates that the final composition has Mg deficiency, even when excess Mg of the stoichiometry is added to the starting materials. Previous reports highlighted the effect of non-stoichiometric amounts of Mg on the thermoelectric properties of Mg-based alloys, especially in *n*-type compounds where Mg vacancies act as electron acceptors and severely reduce the efficiency of dopants. Thermoelectric properties measurements show that intrinsic Mg₂Ge exhibits *n*-type behavior. This work investigates the efficiency of Bi as dopant for one-step fabrication of *n*-type Mg₂Ge to improve its thermoelectric performance. Bismuth doping results in a significant reduction of electrical resistivity while the compound remains *n*-type, proving Bi as an electron donor in Mg₂Ge, as suggested by theoretical studies. However, the impact of Bi-doping on the thermoelectric properties of Mg₂Ge is much smaller than predicted values. Detailed microscopy analysis revealed the formation of Bi-rich precipitates at the grain boundaries of the Mg-deficient Mg₂Ge matrix, indicating very limited solubility of Bi in this compound. It suggests low efficiency of Bi as an *n*-type dopant for Mg₂Ge.

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