Journal of ELECTRONIC MATERIALS, Vol. 42, No. 7, 2013
DOI: 10.1007/s11664-013-2490-6

Thermal Instability of β-Zn_4Sb_3: Insights from Transport and Structural Measurements

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β-Zn_4Sb_3 exhibits poor thermal stability, with zinc-rich specimens recently shown to be more stable. In this work, temperature-dependent transport measurements [Seebeck coefficient (S) and electrical conductivity (σ)] between room temperature (RT) and 525 K were carried out on a zinc-poor specimen. The sequentially measured S and σ data in the same measurement cycle show sharp changes in their absolute values between 450 K and 500 K during the heating cycle, which is not retraced back during cooling. A repeat measurement carried out on the specimen after ~1 month again shows the sharp changes in the absolute values between 450 K and 500 K, indicating reversibility of the process. Temperature-dependent synchrotron measurements were further carried out between RT and 525 K. Formation of elemental Sb was observed beyond 400 K. Between 450 K and 500 K, movement of zinc from lattice to interstitial position is observed, which is also accompanied by the onset of ZnSb formation. The overall zinc content within the β-Zn_4Sb_3 phase is observed to increase with increasing temperature. These observations indicate that both the overall zinc content and the Zn_I/Zn_L ratio are crucial in stabilizing the β-Zn_4Sb_3 phase.

Key words: Thermoelectrics, transport properties, Seebeck coefficient, electrical conductivity, synchrotron radiation diffraction

INTRODUCTION

β-Zn_4Sb_3 is a promising p-type thermoelectric (TE) material for application at intermediate temperatures (room temperature to 350°C).[1,2] However, this material has poor thermal stability and can degrade into undesirable TE phases when thermally cycled.[3,4] A recent report on the thermal stability of this material indicated zinc-rich specimens to be more stable and also variations in the observed trends in the electrical conductivity depending on the zinc content.[5] Additionally, the onset of degradation was observed to take place below the reported stability temperature.

Presented at ICT.
(Received July 22, 2012; accepted January 10, 2013; published online February 22, 2013)

Thus, in the present work, the cause of the thermal instability is probed based on temperature-dependent transport measurements and synchrotron radiation powder diffraction analysis of a zinc-poor β-Zn_4Sb_3 specimen. Sequential measurements of electrical conductivity (σ) and Seebeck coefficient (S) in the same measurement cycle were performed between room temperature and 525 K. Additionally, multitemperature synchrotron measurements were carried out in the same temperature range. The occupancy of zinc atoms was calculated from structural refinement of the synchrotron data, while additional phases were detected from peak identification in the patterns. Based on the observations, the importance of the zinc content and the zinc interstitial-to-lattice ratio on the thermal stability is discussed.