Impact of Chromium Addition on the Transport Properties of $Mg_3(Sb,Bi)_2$

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Abstract:

$Mg_3(Sb,Bi)_2$ compounds are a promising new material in the search for high efficiency thermoelectric (TE) module components. However, the effect of transition metal doping on the properties of these compounds is not well explored. This research examined the impact of chromium addition coupled with varied sintering temperatures on the electrical and thermal conductivity of $Mg_3(Sb,Bi)_2$ compounds. While the initial goal of the project was to measure the effect of chromium atoms acting as interstitials, it was found that favorable TE properties resulted from higher chromium concentrations at the grain boundaries. Using this new model to target the microstructure, samples prepared with high chromium concentrations and increased sintering temperatures yielded improvements in electrical conductivity and charge carrier mobility, leading to an increase in the low temperature figure of merit (ZT).

Summary of Research:

Introduction and Background. Waste heat recovery is an important step in improving the energy efficiency of the modern power grid. One of the most promising solutions to this problem is the implementation of thermoelectric (TE) modules. TE modules are composed of materials that when subjected to a temperature gradient produce a corresponding potential difference, which can be used for power generation.

While TE modules are reliable, sustainable, and scalable for a variety of applications, the development of these devices is in its infancy due to their low efficiency and high cost. One of the biggest barriers to advancement is in the materials themselves; an effective TE material has a high electrical conductivity but a low thermal conductivity, two material properties that are challenging to decouple. Bismuth telluride-based materials have been the long-standing champion at low to medium temperature ranges but are quite expensive to produce. Research focus has shifted towards developing low-cost alternatives, and the recent discovery of $Mg_3(Sb,Bi)_2$ is promising a new generation of materials. $Mg_3(Sb,Bi)_2$ is competitive with BiTe, but further alloying and modifications of the microstructure are necessary to improve its efficiency.

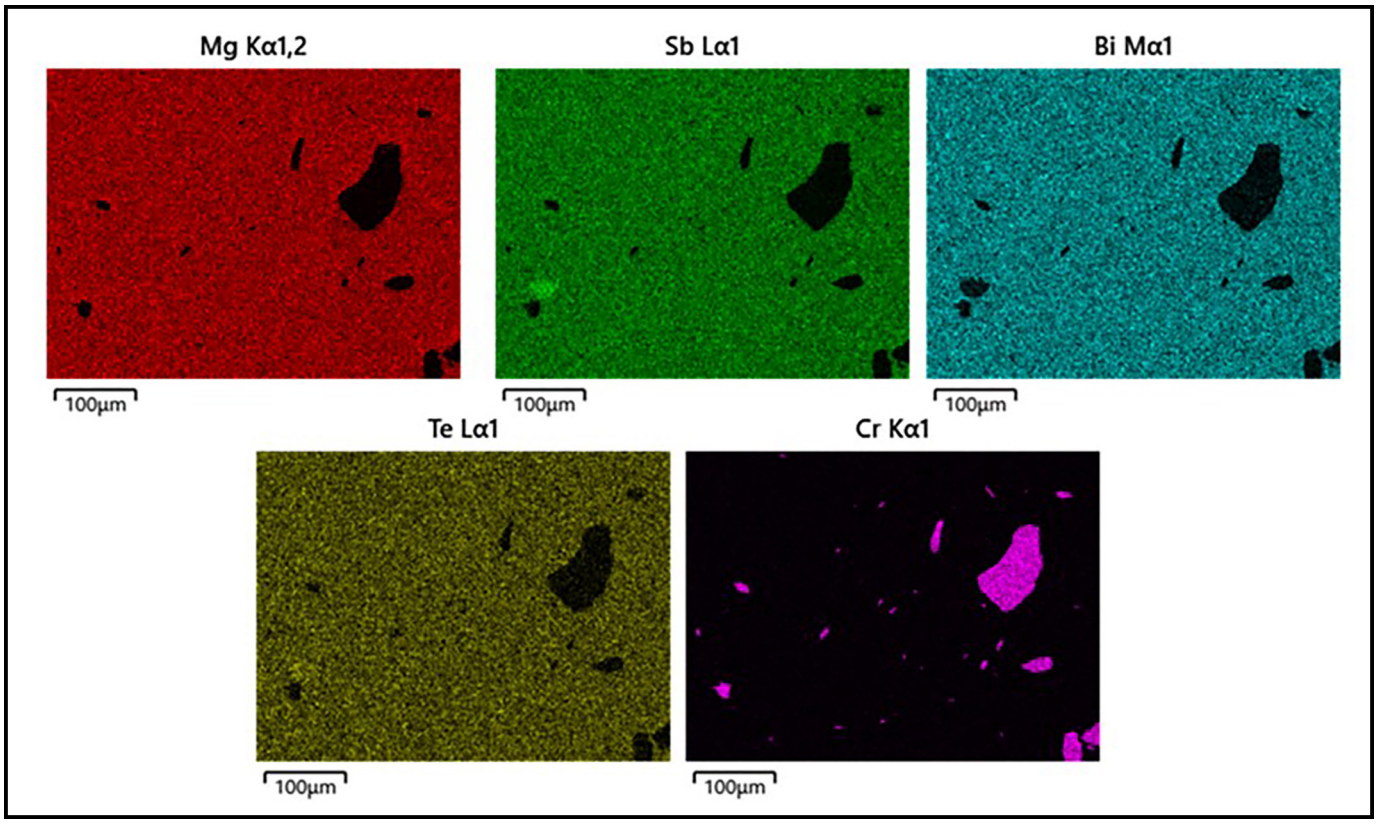
Previous research into transition metal doping of these compounds has yielded favorable TE properties. Specifically, copper atoms acting as interstitials were found to reduce thermal conductivity, leading to an improved figure of merit [1]. However, there is little research on the impact of chromium doping. The goal of this work was to explore the impact of this element on the transport properties of $Mg_3(Sb,Bi)_2$ compounds

Methodology. Samples with varying chromium concentrations were prepared by combining raw magnesium, bismuth, antimony, tellurium, and chromium into ball milling jars inside of an argon filled glove box. The samples were then milled for five hours, and the resulting powder was spark plasma sintered at 973 K and 1023 K. The densified material was then cut into one 2 mm thick 10 mm diameter disk and one 2 mm square bar. The thermal transport properties of each sample were characterized by Laser Flash Analysis (LFA), and the electrical conductivity and Seebeck coefficient by the ZEM-3 Thermoelectric Characteristics Evaluation System. For both systems, the sample was tested at 50 K intervals from room temperature to 673 K. The microstructure was analyzed using bulk x-ray diffraction (XRD) and scanning electron microscopy (SEM).

Results and Future Work:

The XRD spectra of the 973 K series samples showed little variation from reference $Mg_3(Sb,Bi)_2$ samples with the exception of one peak corresponding to a secondary chromium phase in the two highest concentration samples. The presence of these secondary phases was further confirmed by electron dispersion spectroscopy (Figure 1). The electrical properties of these samples were relatively poor, except for the sample with the greatest chromium concentration (Figure 2).

Because of the prevalence of secondary chromium phases and the poor electrical properties of the material, it was inferred that the chromium atoms were not occupying any lattice sites and instead remained in the secondary phases and at the grain boundaries. When compared with previous work studying



niobium doping of a similar compound, it was found that the same increase in conductivity and weighted mobility occurred at high transition mental concentrations [2]. This was due to a decrease in the grain boundary resistance, improving carrier mobility and overall material performance [3]. After observing this same trend in the chromium doped samples, the project focus shifted from interstitial doping to exploring the relationship between the microstructure and transport properties.

The series of five samples was prepared again at a sintering temperature of 1023 K with the goal of increasing grain size. While secondary phases were still present in this material, these samples saw a dramatic increase in conductivity and weighted mobility when compared with the previous series, especially in the low temperature range (Figure 2). This increase in conductivity led to an overall improvement in the ZT value for the second series (Figure 3).

To verify the presence of chromium at the grain boundaries, the thermal conductivity and Seebeck coefficient of each sample was measured, and the lattice parameter was calculated. Little change in these values was observed regardless of chromium concentration or sintering temperature, evidence that chromium was not acting as an interstitial and distorting the lattice.

Further work is needed to confirm the grain boundary resistance model, both to quantify changing grain size and to understand the fraction of chromium at the grain boundaries. It is unknown if higher chromium concentrations or sintering temperatures would continue to yield favorable properties, a potential route for future experimentation.

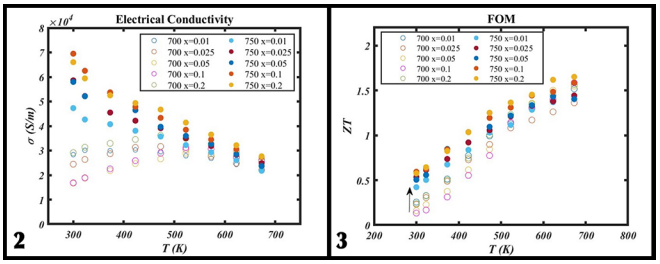


Figure 1, top: EDS images of high concentration Cr sample prepared at 973 K showing Cr secondary phases.

Figure 2, left: Comparison of electrical conductivity at varying Cr concentrations and sintering temperatures.

Figure 3, right: Comparison of ZT values for low and high temperature sample series.

References:

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[2] Luo, et al. (2021). Nb-Mediated Grain Growth and Grain-Boundary Engineering in Mg_3Sb_2-Based Thermoelectric Materials. Advanced Functional Materials 31. https://doi.org/10.1002/adfm.202100258

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