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Thermoelectric Properties of Hot-Pressed β-$K_2Bi_8Se_{13-x}S_x$ Materials

THEODORA KYRATSI[1,2] and MARIA IOANNOU[1]

1.—Department of Mechanical and Manufacturing Engineering, University of Cyprus, 1678 Nicosia, Cyprus. 2.—e-mail: kyratsi@ucy.ac.cy

In this work, hot-pressed pellets of the $K_2Bi_8Se_{13}$ family of compounds were prepared for the first time. The pellet fabrication of selected members of the $K_2Bi_8Se_{13-x}S_x$ series was studied. Sintering parameters, such as temperature, pressure, and duration, were investigated based on a statistical design-of-experiments approach to identify the optimum conditions for fabrication of high-quality pellets. These optimum conditions were then applied for the $K_2Bi_8Se_{13-x}S_x$ series, and the thermoelectric properties of the stoichiometric members for x = 0, 4, 6, and 8 were studied. Doping experiments were also investigated using sulfur excess in the x = 6 member in an attempt to modify its properties.

Key words: Design of experiments, Taguchi tables, analysis of variance, hot-pressed pellets, solid solutions

INTRODUCTION

β-$K_2Bi_8Se_{13}$[1] is a promising thermoelectric material. Its complex crystal and electronic structure can lead to high Seebeck coefficient,[2] as well as low thermal conductivity that arises from a large, low-symmetry unit cell and weakly bound K^+ ions in the cages that tend to rattle,[3,4] as revealed by their high thermal displacement parameters.[1] This low-symmetry monoclinic structure[1] includes two different interconnected types of Bi/Se building blocks and K^+ atoms in tunnels. The two different Bi/Se blocks are connected to each other at special mixed-occupancy K/Bi sites that seem to be crucial in defining the electronic structure near the Fermi level and consequently govern the electronic properties. This is supported by the results of *ab initio* density functional band structure calculations on this material.[5]

$K_2Bi_8Se_{13}$-based materials have needle-like morphology, and their physical properties were found to be anisotropic[6] when prepared as oriented ingots by the Bridgman technique.[6,7] Powder techniques have been previously applied to eliminate their anisotropic properties as well as to improve their mechanical behavior.[8–10] Work involving substitution at the heavy-metal sites (i.e., $K_2Bi_{8-x}Sb_xSe_{13}$),[6] the chalcogenide sites (i.e., $K_2Bi_8Se_{13-x}S_x$),[11] as well as at the alkali-metal sites ($K_{2-x}Rb_xBi_8Se_{13}$)[12] has also been carried out, based on the common strategy of affecting the thermal conductivity via the formation of solid solutions.

In this work, $K_2Bi_8Se_{13-x}S_x$ materials were prepared, for the first time, as highly dense hot-pressed pellets, and their thermoelectric properties were evaluated. Optimization of the hot-pressing conditions was investigated based on a statistical design-of-experiments approach and analysis of variance (ANOVA).[13–16] The thermoelectric properties were studied in terms of stoichiometry (x values) as well as doping using sulfur excess in the $K_2Bi_8Se_7S_6$ member, aiming for its modification.

EXPERIMENTAL PROCEDURES

Reagents

Chemicals in this work were used as obtained, including bismuth metal (99.999% purity; Alfa Aesar), selenium metal (99.999% purity; Alfa Aesar), sulfur (−100 mesh particle size, powder; Sigma-Aldrich), and potassium metal (rod, 99.5% purity; Sigma-Aldrich).

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