Morphological and Anisotropic Features of the Needle-like $K_2Bi_8Se_{13}$-type Pressed Pellets

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Abstract

The series of materials $K_2Bi_8Se_{13-x}S_x$ is promising for thermoelectric investigations. These materials have needle-like morphology and highly anisotropic properties. In order to explore if we could minimize the anisotropy in properties and whether this could result in enhancements of their mechanical properties, we applied powder processing techniques. In this work, pressed pellets of β-$K_2Bi_8Se_{13}$-type materials were fabricated using uni-axial pressing. The morphology and the structure of these samples were investigated in planes parallel and perpendicular to the pressing axis by means of powder X-ray diffraction, scanning electron microscopy, infrared (IR) reflectivity and Seebeck coefficient.

Introduction

Candidate thermoelectric materials should posses high electrical conductivity, high Seebeck coefficient and low thermal conductivity. β-$K_2Bi_8Se_{13}$ is a promising material for thermoelectric investigations[1]. 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 cages ("phonon glass-electron crystal" conjecture)[3]. Moreover, it possesses a three-dimensional structure, with needle-like morphology that makes the material highly anisotropic[4].

Solid solution formation based on the β-$K_2Bi_8Se_{13}$ structure was achieved via substitution on the heavy metal sites (i.e. $K_2Bi_{8-x}Sb_xSe_{13}$)[4], the chalcogenide sites (i.e. $K_2Bi_8Se_{13-x}S_x$)[5] as well as at the alkali metal sites ($K_{2-x}Rb_xBi_8Se_{13}$)[6]. These series gave a wide range of n- as well as p-type material behavior[7]. Additionally, a modified Bridgman technique has been developed[8] in order to grow highly oriented samples. The investigation of thermoelectric properties of these materials indicates that their maximum thermoelectric performance is along the needle axis. Controlling the grain orientation is important for improving the thermoelectric properties of $K_2Bi_8Se_{13-x}S_x$, because they are strong anisotropic materials. Powder techniques have been recently applied, as a different approach, in order to minimize the anisotropy in the properties as well as to improve the mechanical behavior of these anisotropic materials. The morphology and thermoelectric properties of cold pressed pellets on $K_2Bi_8Se_7S_6$ have been also studied in terms of pressure-less sintering temperature and grain size[9].

In the present work, pellets were fabricated in order to explore the potential of applying powder technology in these materials and make isotropic samples for thermoelectric applications. The objective of this study was to investigate the morphology and the structure of these samples in planes parallel and perpendicular to the pressing axis in terms of powder X-ray diffraction, scanning electron microscopy, optical spectroscopy and Seebeck coefficient.

Experimental

The starting material $K_2Bi_8Se_{13-x}S_x$ (x=6) was synthesized with stoichiometric elemental combination as described elsewhere[5]. Subsequently, powdered samples were prepared via planetary ball mill with grinding speed of 200rpm. Bulk material was placed in a tungsten carbide jar partially filled with balls and the powder to ball weight ratio was held constant at 1:25 throughout the experiments. The powder was ball milled using 15mm grinding balls for 5 and 10min. The jar was sealed under high purity nitrogen atmosphere to prevent contaminants from the air from entering. The powder was then sieved in order to make pressed pellets using powder with a variety of grain sizes. The pellets were cold pressed by mean of uni-axial pressing and then sintered under vacuum (pressure-less sintering) at 400^oC for 12 hrs.

The morphology and the structure of fabricated pellets were investigated in planes parallel and perpendicular to the pressing axis with powder X-ray diffraction and scanning electron microscopy. Seebeck coefficient was measured using constantan reference in system developed by MMR Technologies. Infrared reflectivity spectra were recorded at nearly normal incidence in the 70-900cm^{-1} spectral region, at room temperature, with a Bruker 113V FTIR spectrometer.

Results and Discussion

Crystal Structure

The highly anisotropic structure of $K_2Bi_8Se_7S_6$ consists of two different interconnected rods of Bi/Se and K^+ atoms in tunnels (Figure 1). The cubic (NaCl$^{(100)}$-type) and the hexagonal (NaCl$^{(111)}$-type) Bi/Se rods are connected to each other at particular high (8 or 9) coordination mixed-occupancy K/Bi sites (Bi(8)/K(3)and Bi(9)/K(1)).

Material morphology

$K_2Bi_8Se_7S_6$ is anisotropic three-dimensional monoclinic structures, which extended along the b-axis with very short repeating length (~4Å). This is a feature of almost all ternary and quaternary bismuth chalcogenide compounds and it is responsible for the needle-like crystal growth habits of these materials. This needle-like morphology is shown in Figure

2a for the $K_2Bi_8Se_7S_6$ material as it is obtained from synthesis.

These materials exhibited higher thermoelectric performance along the crystal growth direction[4]. Thus it is important to be able to control the crystal orientation and prepare highly oriented ingots or try to eliminate the anisotropy using powder techniques. Regarding highly oriented ingots, the Bridgman technique had been applied for the growth of anisotropic samples[8]. To grind the samples a convectional ball milling process was applied.
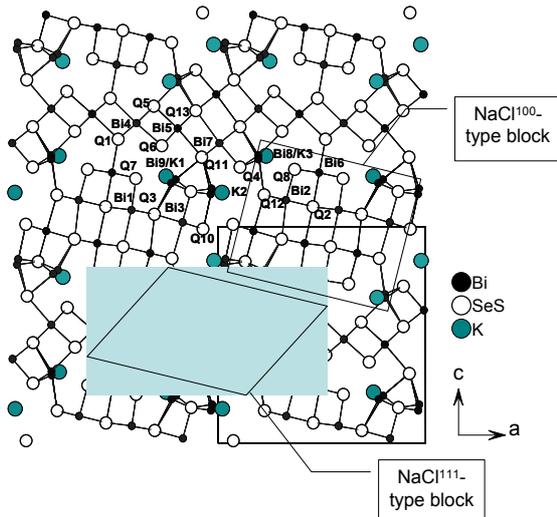

Figure 1: Crystal Structure of $K_2Bi_8Se_7S_6$

After ball milling, the morphology of the materials change significantly as shown in the SEM image and discussed in previous work[9]. Figure 2 (b-c) shows the SEM morphologies of the starting powders. At higher grain size the particles are longer in one direction due to the needle morphology of the material. This feature seemed to be eliminated when additional ball milling was applied (figure 2(d)). The comparison of figures 2 (c) and (d) shows that further increase of the milling time (from 5min to 10 min) changes the particles size and shape where finer and more spherical particles were produced.

Pressed Pellet

Figure 3 shows SEM images of the sintered compacts with starting powder size of 63-180μm, 25-63μm, <25μm and powder size <25μm with additional ball milling of 5 min (thus even lower grain size) at sections parallel and perpendicular to pressing direction. The samples showed dense microstructures with few pores. The different grain size and their boundaries are clearly shown. The images demonstrate regions with needle like morphology which illustrates the morphology of the pristine material. This is in agreement with previous findings[9]. Moreover, the microstructures of the samples with large grain sizes are well aligned along the planes on the direction perpendicular to the pressing axis. On the contrary, the fracture surfaces of pressed pellets with small grain size showed no indication of preferential orientation. These results indicate that the large grain pellets are more oriented.

To study the orientation, XRD patterns were taken from both sections perpendicular and parallel to the pressing direction. The black and the grey lines in the Figure 4 represent the X-ray pattern of the samples measured parallel and perpendicular to the pressing direction respectively. The patterns parallel and perpendicular are similar on contrary, as expected, to the highly oriented samples that had been prepared with Bridgman technique and showed lack of simultaneous occurrence of peaks in the two orientations [4].
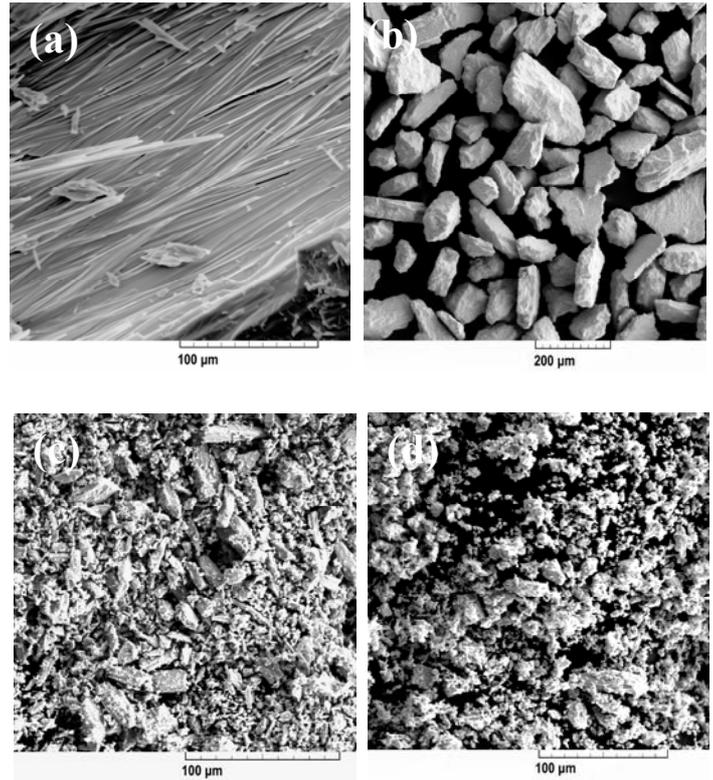

Figure 2: SEM images of $K_2Bi_8Se_{13-x}S_x$ (x=6) (a) needles (cleaved ingot), powder after ball milling and sieving process (b)63-180μm, (c)<25μm and (d)<25μm with additional ball milling.

IR Reflectivity Measurements

The IR reflectivity measurements are presented in Figure 6 for various grain sizes. As can be seen, there appear two bands at about 155 and 250cm^{-1} (shown by arrows in Figure 6). These bands are more profound with the low sized grains and parallel geometry, and almost disappear in the high grain size samples.
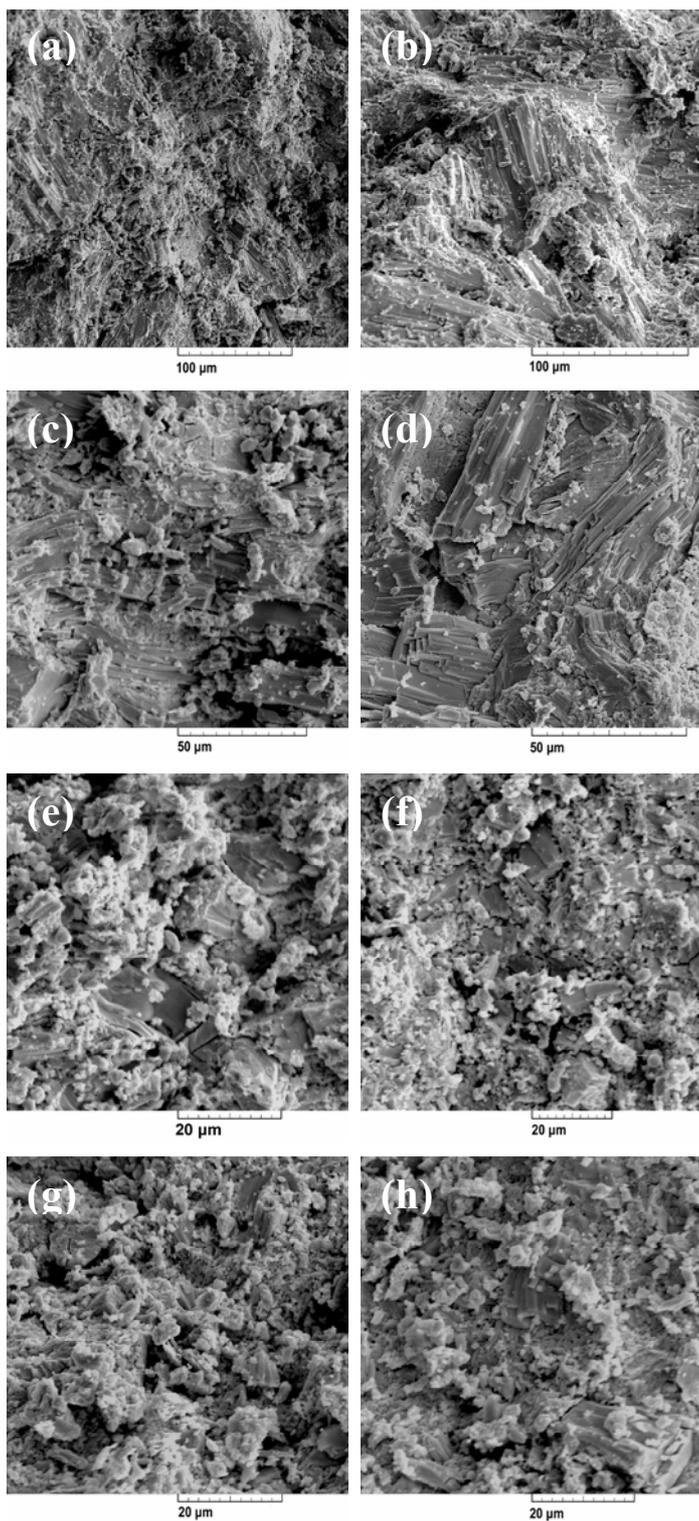
Figure 3: The SEM microstructure of sintered pellets parallel (a,c,e, g) and perpendicular(b,d,f,h) to the pressing direction. Pellets are fabricated with various grains size, (a,b) 63-180µm, (c,d) 25-63µm, (e,f) <25µm and (g,h)<25µm with5min additional ball milling.
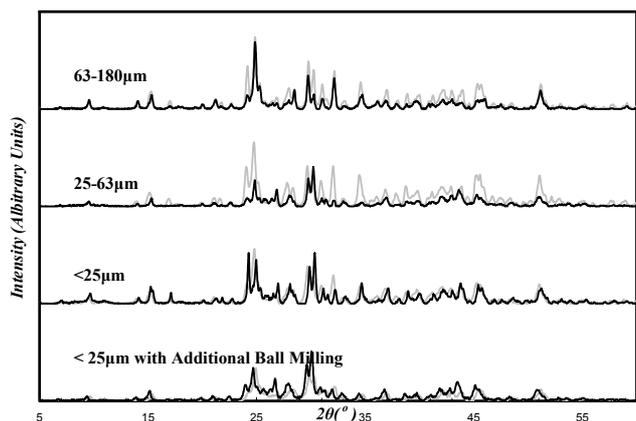

Figure 4: Powder X-ray diffraction pattern of $K_2Bi_8Se_{13-x}S_x$ (x=6) pressed pellets parallel and perpendicular to the pressing direction.

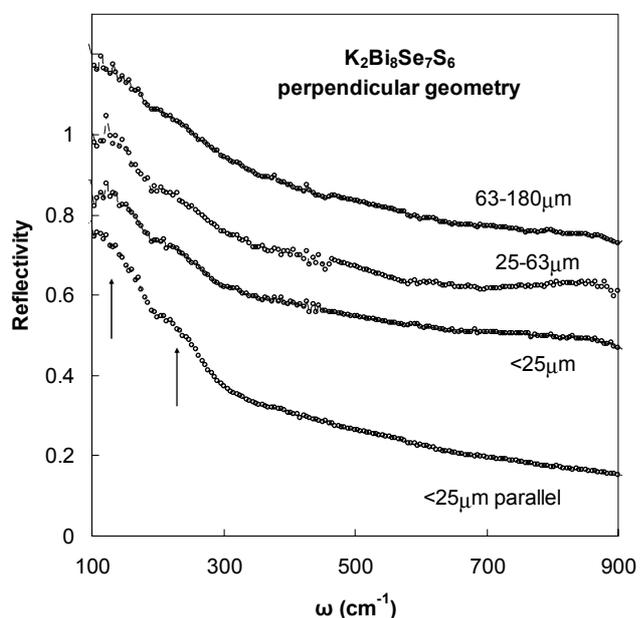*Figure 5: IR reflectivity spectra of $K_2Bi_8Se_7S_6$ for different samples at various grain sizes. Spectra are shifted vertically for clarity*

Seebeck coefficient

The Seebeck coefficient for the $K_2Bi_8Se_7S_6$ pellets measured parallel and perpendicular to the pressing direction for the various grain sizes as a function of temperature is presented in Figure 6. All samples show similar trend with temperature; increase of Seebeck coefficient (absolute values) in the measured temperature range. This behaviour is typical for most bismuth alkali chalcogenide compounds[10].

Figure 7 shows the grain size dependence of the Seebeck coefficient measured at 205K parallel and perpendicular to the pressing direction. The absolute Seebeck coefficient shows a decrease with increasing the grain size. This can be attributed to lower carrier concentration which appears to ensue upon decreasing the grain size. These changes may be considered as an effect of the grain boundary and it is in agreement with previous work on Bi_2Te_3 alloys[11].

Furthermore, the Seebeck coefficient was the same regardless of the direction, for small grain sizes. At coarse grain the Seebeck coefficient measured parallel to the pressing axis was deviated and this is in agreement with the anisotropy that was observed with XRD patterns and SEM images.
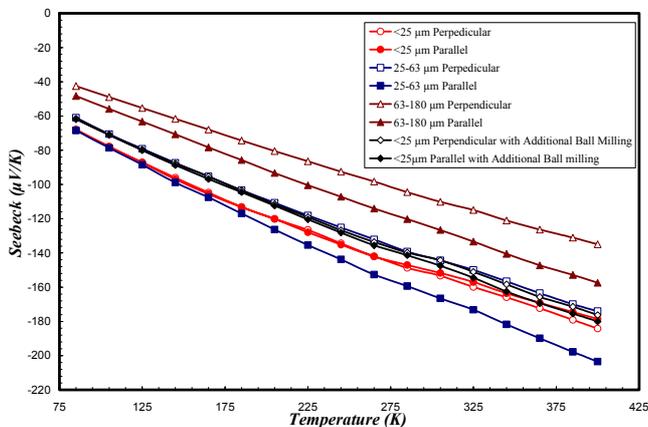

Figure 6: Temperature dependence of Seebeck coefficient of $K_2Bi_8Se_7S_6$ pellets constructed with various particle sizes and measured parallel and perpendicular to pressing direction
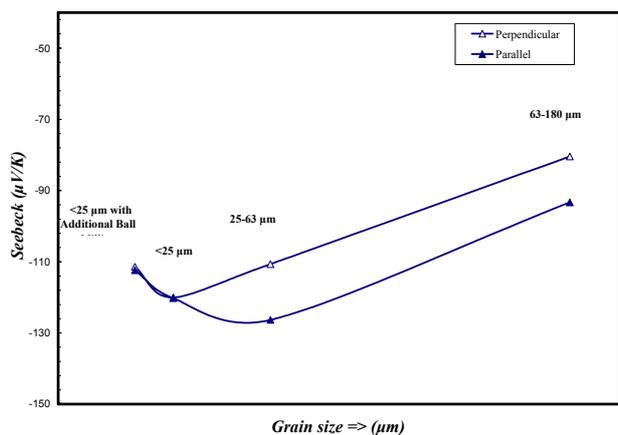

Figure 7: The Seebeck coefficient of $K_2Bi_8Se_7S_6$ pellets at 205K vs. particle size; measured parallel and perpendicular to pressing direction

Conclusions

To prepare reliable thermoelectric modules, isotropic, mechanically strong materials with good thermoelectric properties are needed. The objective of this study was to examine the possibility of fabricating pellets of $K_2Bi_8Se_7S_6$ with isotropic properties by applying powder technologies to our highly anisotropic materials.

The pellets were fabricated using various grain sizes after applying a dry ball milling process. SEM images of the pressed pellets showed needle-like regions without strong preferential orientation at fine powders. X-ray powder diffraction also suggested that the pellets with small grain sizes are more isotropic and this is encouraging for the fabrication of isotropic samples for further thermoelectric characterization. The Seebeck coefficients increased with decreasing the particle size and the values were almost the same regardless of sample direction for the small grain sizes suggesting the isotropy on these materials.

Further work is planned in order to investigate the electrical conductivity and the scattering mechanisms that affect the mobility in two directions.

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