Journal of Alloys and Compounds 754 (2018) 131–138

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Effect of synthesis processes on the thermoelectric properties of BiCuSeO oxyselenides

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ARTICLE INFO

Article history:
Received 13 March 2018
Received in revised form
26 April 2018
Accepted 27 April 2018
Available online 30 April 2018

Keywords:
Thermoelectric materials
BiCuSeO
Ball milling
Sintering
Thermoelectric properties

ABSTRACT

The BiCuSeO based ceramics have been prepared by mechanical alloying (MA) and resistance pressing sintering (RPS) process. The effects of the parameters of annealing, ball milling and sintering on the microstructure, thermoelectric properties, and mechanical properties are investigated systematically. The results indicates that the samples prepared by MA exhibit higher carrier concentration due to higher Cu vacancies concentration, smaller grain size resulting in stronger phonon scattering, and correspondingly higher thermoelectric properties than those prepared by annealing. By prolonging milling time and increasing ball milling strength, it can further refine grains, increase the carrier concentration, enhance phonon scattering and further improve thermoelectric properties. Coupled with Ca/Pb doping, the electrical conductivity at room temperature increased to 445 Scm^{-1}. The total thermal conductivity is below 0.90 $Wm^{-1}K^{-1}$ in the whole measured temperature range, which is attributable to the increased defects and gain boundaries. The maximum power factor of 0.75 $mWm^{-1}K^{-2}$ and *ZT* value of 1.15 were obtained for the $Bi_{0.84}Ca_{0.08}Pb_{0.08}CuSeO$ with BM time (t) = 16 h at 873 K.

1. Introduction

Thermoelectric materials, which are capable of converting waste heat into electrical power, are currently receiving significant scientific attention. However, the widespread use of thermoelectric technology is constrained by the relatively low conversion efficiency of present available thermoelectric materials. Thermoelectric oxides are vigorous candidates in terms of large-scale application because of their low cost, less toxicity and good stability in relatively high temperature range. Thermoelectric oxides include several types of oxide ceramics such as $Ca_3Co_4O_9$ [1], $NaCo_2O_4$ [2], and $SrTiO_3$ [3], which have been studied extensively over the past decades. However, the *ZT* values still remain low for the low electrical conductivity and high thermal conductivity because of the ionic nature of oxides, which limits the application.

Recently, the layered oxychalcogenides BiCuSeO with a ZrSiCuAs structure (space group *P*4/*nmm*) was reported to be a promising thermoelectric materials due to its extremely low thermal conductivity and large Seebeck coefficient. Especially, the highest *ZT* value of substituted BiCuSeO can be as high as 1.5, which is superior to all the other thermoelectric oxides [4]. However, the thermoelectric properties of pristine BiCuSeO are not desirable due to the intrinsic low carrier concentration (~1.0×10^{18} cm^{-3}) and carrier mobility (~20 $cm^2V^{-1}s^{-1}$) [5]. In the past few years, tremendous efforts have been made to modify the electrical/thermal transport properties by monovalent elements (K [6], Na [7] and Ag [8]), divalent elements (Mg [9], Ca [10], Sr [11], Ba [12], Pb [13], Cd [14] and Zn [15]), trivalent elements (Sb [16] and La [17]) and tetravalent element (Sn [18]) doping at Bi site, monovalent element (Ag [19]) doping at Cu site, dual doping with Ca and Pb at Bi site [4], dual doping with Pb at Bi site and Te at Se site [20], Cu-deficient [21] and texturation [22], 3D Modulation Doping [23] and composite structure [24]. Up to now, the highest *ZT* value of 1.5 was obtained for the Ca/Pb-dual-doped BiCuSeO oxychalcogenides coupled with all-scale structural optimization [4].

Persistent efforts have been devoted to improve *ZT* values through boosting power factor while most of them neglecting lowering thermal conductivity. In particular, nanostructuring has

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https://doi.org/10.1016/j.jallcom.2018.04.307
0925-8388/

been proven to be an effective approach to reduce the thermal conductivity by embedding nanoscale precipitates in the matrix [25]. Besides, it is well known that the preparation process has a great influence on the properties of materials, especially for the thermoelectric materials which are extremely sensitive to the composition and structure. However, few studies have paid attention to the preparation process (ball milling [26,27], ultra-fast self-propagating high-temperature synthesis [28,29], and flux synthesis [30]) of BiCuSeO. And no reports have ever studied the mechanical properties of BiCuSeO before. However, mechanical properties have a decisive influence on the machinability during the use of thermoelectric materials. Herein, we synthesize BiCuSeO by ball milling and annealing, respectively, followed by sintering, and report the effect of the parameters of annealing, ball milling and sintering on the thermoelectric and mechanical properties of BiCuSeO ceramics.

2. Experimental sections

2.1. The synthesis of powder

A series of samples with the chemical composition of BiCuSeO (called as BCSO below) and $Bi_{1-2x}Ca_xPb_xCuSeO$ ($x = 0$, 0.01, 0.02, 0.04, 0.06, 0.08) (called as BCPCSO below) were prepared from commercial powders (Bi_2O_3 (99.99%), Bi (99.999%), Cu (99.999%), Se (99.99%), CaO (99.99%), Pb (99.99%)). We synthesize the powder by ball milling and annealing, respectively.

1) The stoichiometric mixture of powders were ground: high-energy ball milling was performed at 300 or 400 rpm in argon atmosphere for 2 h/4 h/6 h/8 h/12 h and 4 h/8 h/12 h/16 h/20 h, respectively, followed by MA with analytical reagent (AR) ethanol absolute (≥99.7%) for 1 h.
2) The stoichiometric mixture of powders were placed in a quartz glass tube, vacuum sealed, then annealed at 300 or 800 °C for 3 h/8 h in a muffle furnace. Take out the powder, and grind with agate mortar.

2.2. The sintering for bulk

Then, the powder with high phase purity were sintered by resistance pressing sintering (RPS) at 823/873/923 K for 10 min under the axial compressive pressure of 40/50/60 MPa under argon atmosphere to form disk-shaped sample of Φ20 × 13 mm.

2.3. Characterization

The phase identification were characterized by X-ray diffraction

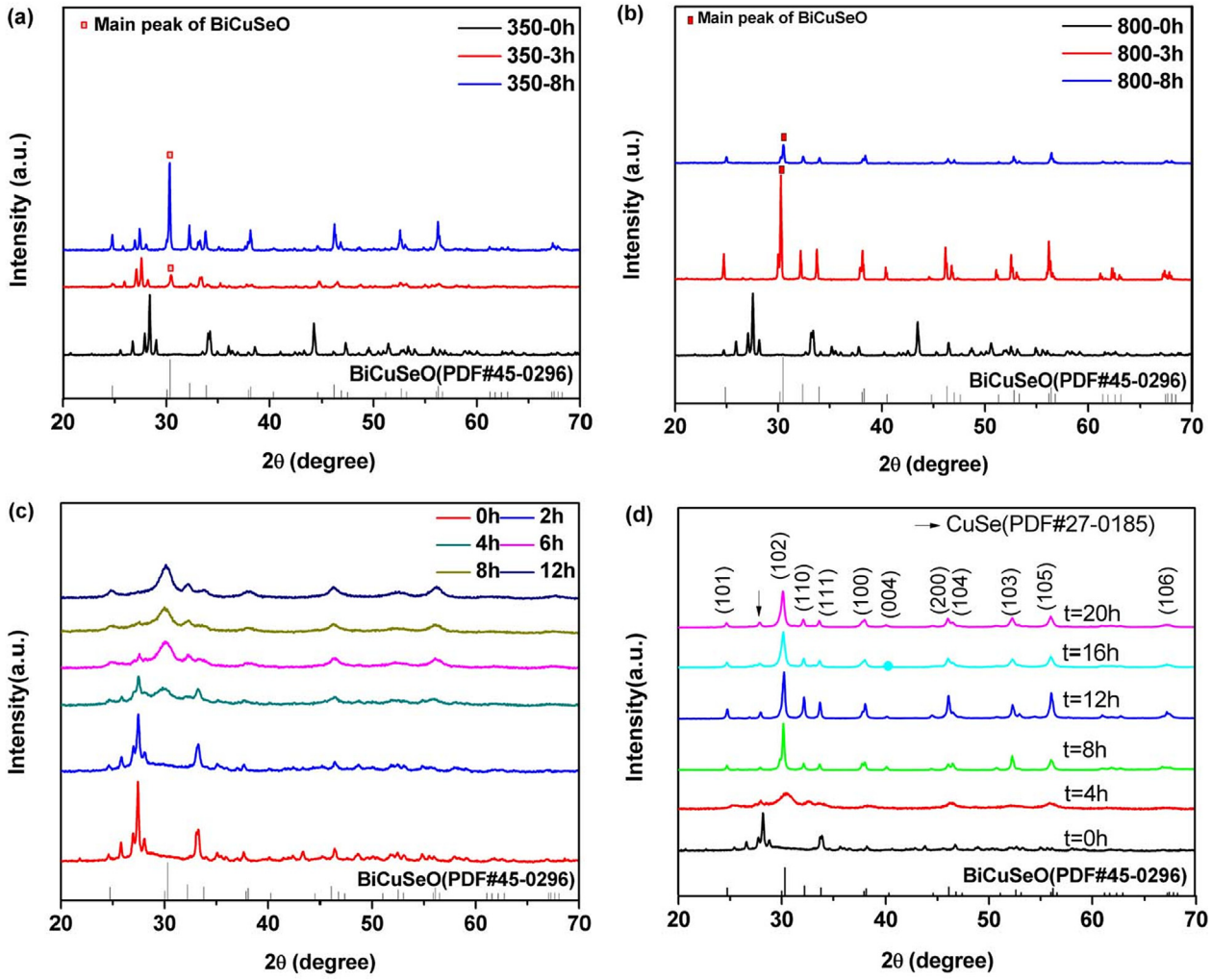

Fig. 1. XRD patterns from (a) annealing at 350 °C, (b) annealing at 800 °C, (c) balling milling at 300 rpm, (d) balling milling at 400 rpm.