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Enhancement of the thermoelectric properties of $BaCu_2Se_2$ by potassium doping

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ABSTRACT

Layered compounds play an important role in thermoelectric materials exploration, as their thermal and electrical conductivities could be affected by different layers. Herein, we have synthesized a new layered $Ba_{0.7}K_{0.3}Cu_2Se_2$ phase with the $ThCr_2Si_2$ structure through 30% K doping on the Ba sites in the pristine orthorhombic $BaCu_2Se_2$. The layered $Ba_{0.7}K_{0.3}Cu_2Se_2$ exhibits intrinsically low lattice thermal conductivity due to its extremely short phonon mean free path. $Ba_{0.7}K_{0.3}Cu_2Se_2$ also features high hole mobility and reasonable Seebeck coefficient at high doping levels. The enhancement of electrical conductivity is mainly ascribed to the increase of the hole concentration and the unchanged high hole mobility. As a result, the peak *ZT* of $Ba_{0.7}K_{0.3}Cu_2Se_2$ reaches 0.32 at 800 K, which is of significance by comparing to its undoped $BaCu_2Se_2$ counterpart.

1. Introduction

The performance of thermoelectric materials is evaluated by a dimensionless figure of merit *ZT*, defined by $ZT=(S^2\sigma/k)T$, where *S*, σ, *k*, *T* are Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively. Layered compounds can be expected to play an important role in exploring new thermoelectric (TE) materials, as their thermal and electrical transport properties could be determined by different layers [1]. Recently, p-type layered oxyselenides such as BiCuSeO caught intensive interest owing to their excellent thermoelectric performance [2–5]. In BiCuSeO, the $(Cu_2Se_2)^{2-}$ layer constitutes a conductive pathway which accounts for carrier transportation [6], and the fairly large power factor value (0.633 mW m^{-1} K^{-2}) of this material suggests good electrical transport properties in general. Furthermore, Cu-based chalcogenides have intrinsically low lattice thermal conductivity. Thus, the successful development of BiCuSeO has led to a great deal of efforts in exploring novel CuSe-based layered compounds with promising TE applications.

The *ZT* of $BaCu_2Se_2$ with orthorhombic structure (α-$BaCu_2Se_2$) was reported to be about 0.02 at 300 K, with the notable Seebeck coefficient of 390 μV K^{-1} [7]. Through Na substitution on Ba sites, the *ZT* peak of this material can reach the unit value at 773 K, which signals that $BaCu_2Se_2$ based materials could be promising thermoelectric materials [8]. Electronic structure calculation suggested that layered tetragonal phase in $BaCu_2S_2$ have higher hole mobility and larger Seebeck coefficient than its orthorhombic phase [9], which suggest that tetragonal β-$BaCu_2Se_2$ phase could have the similar properties. However, β-$BaCu_2Se_2$ is metastable and the synthesis was proved to be difficult previously [10]. Considering the tetragonal phase can be stabilized by substitution of K on the Ba sites for $BaCu_2S_2$ [11], and improved thermoelectric properties have been achieved [12,13], we therefore expect that even better TE properties could be realized in K doped tetragonal $BaCu_2Se_2$ phase.

Herein, we report the enhanced thermoelectric properties from the doped tetragonal $Ba_{1-x}K_xCu_2Se_2$ phase. The peak *ZT* value of $Ba_{0.3}K_{0.7}Cu_2Se_2$ reaches 0.32 at 800 K. In addition, the phase diagram of $Ba_{1-x}K_xCu_2Se_2$ with various K doping level is also presented.

2. Material and methods

Samples with the nominal compositions of $Ba_{1-x}K_xCu_2Se_2$ ($0 \le x \le 0.4$) were synthesized with the same approach as reported in Ref. [7]. Samples with the nominal composition of $Ba_{1-x}K_xCu_2Se_2$ ($x=0$, 0.05, 0.08, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4) were synthesized using two-step solid state reaction route. The starting raw materials were Ba metal (99%, Alfa), K (99.5%, Sigma), Cu powder (99.9%, Alfa) and Se powder (99.5%, Alfa). K_2Se was prepared beforehand by liquid ammonia method. Firstly, Cu, Se and K_2Se powders were mixed up and cold pressed with Ba granules. The pellet was loaded into a small alumina crucible

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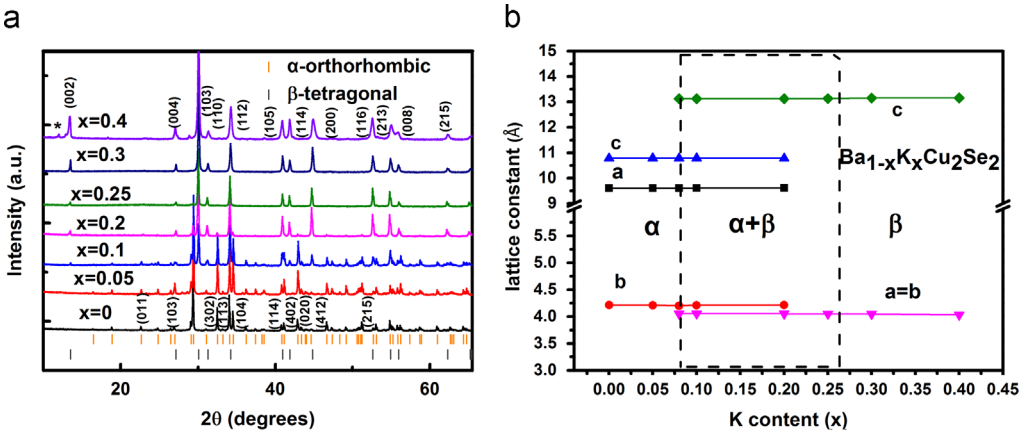

Fig. 1. (a) PXRD patterns for a series of $Ba_{1-x}K_xCu_2Se_2$ ($0 \le x \le 0.4$) samples. The asterisk symbol stands for impurity phase of $K_3Cu_8Se_6$. The orange bars and grey bars stand for α phase and β phase, respectively. (b) The lattice parameters and multiple phases versus K content.

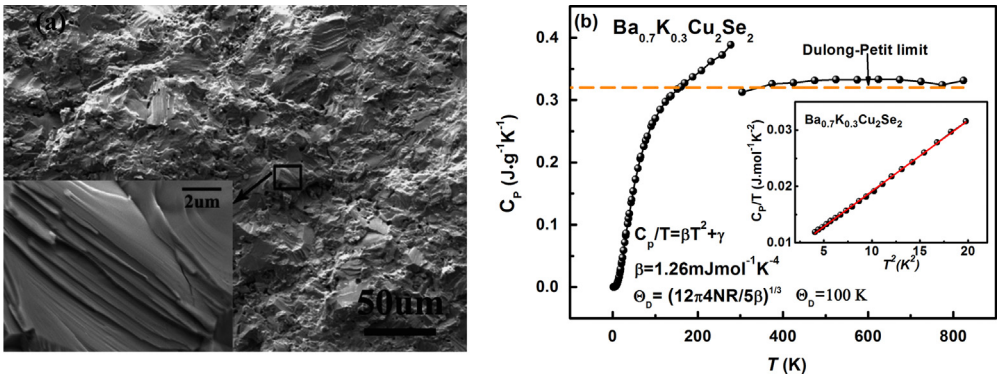

Fig. 2. (a) The SEM image of $Ba_{0.7}K_{0.3}Cu_2Se_2$ sample. The inset is the magnified picture of the region marked by a square in (a) and (b). Temperature dependence of specific heat from 2 to 824 K measured by the combination of PPMS and Laser flash. The orange dash line presents Dulong–Petit limit. The inset is the fitting curve of formula $C_p/T = \beta T^2 + \gamma$ under the Debye model.

and sealed in evacuated quartz tubes. The tubes were subsequently heated up to 700 °C and held for 24 h, and then cooled down to room temperature naturally with furnace. The obtained bulk materials were ground, pressed, sealed and heated again at 600 °C for 24 h. In the last, the obtained powders were sintered under vacuum at 773 K for 7 min within the spark plasma sintering (SPS) system by using the graphite die. The details of characterization can be found in the supplementary section.

3. Results and discussion

Fig. 1(a) shows the Powder X-ray Diffraction (PXRD) patterns for a series of $Ba_{1-x}K_xCu_2Se_2$ ($0 \le x \le 0.4$) samples. With $0 \le x \le 0.05$, all main peaks except those for BaSe can be indexed based on an orthorhombic cell with space group *Pnma* (62), which corresponds to α-$BaCu_2Se_2$ (ICDD No. 79-1647) having a three-dimensional framework of distorted $CuSe_4$ tetrahedral [10]. When the K content exceeds 0.05, another set of reflection peaks corresponding to tetragonal β-$BaCu_2Se_2$ (ICSD No. 89576) appears. The complete phase change happens at $x=0.3$, suggesting the existence of a phase transition regime with K content in the range of 0.05 to 0.3. When x exceeds 0.35, another impure phase $K_3Cu_8Se_6$ arises. The structural parameters of existing phases in $Ba_{1-x}K_xCu_2Se_2$ ($0 \le x \le 0.4$) calculated from the XRD data using Rietveld refinement are shown in Fig. 1(b).

Fig. 2(a) shows the SEM image of $Ba_{0.7}K_{0.3}Cu_2Se_2$ sample, which is found to be compact and composed of randomly oriented grains about tens of micrometers in size. The inset shows a terrace structure, which is reminisce of the layered structure in tetrahedral $Ba_{0.7}K_{0.3}Cu_2Se_2$. Fig. 2(b) presents the temperature dependence of specific heat $C_p(T)$ for $Ba_{0.7}K_{0.3}Cu_2Se_2$ from 2 K to 800 K. The average value of C_p from 300 K to 823 K is determined to be 0.33 J g^{-1} K^{-1}, which is close to the value of 0.32 J g^{-1} K^{-1} calculated by Dulong–Petit law. The Debye temperature Θ_D is estimated to be 100 K on the basis of Debye formula in the lower inset of Fig. 2(b). Based on the Debye model described in Ref. [14], we obtained the average sound velocity $\nu_m = 2011$ m s^{-1}. Using the calculated ν_m, the measured C_p and lattice thermal conductivity k_{latt}, the phonon mean free path l_m is calculated by the simplified formula $k_{latt} = 1/3 C_v \nu_m l_m$ [15] and shown in the inset of Fig. 3(d). The l_m values are in the range of 5.1 Å to 7.4 Å, which are comparative to the lattice parameters of $Ba_{0.7}K_{0.3}Cu_2Se_2$. This suggests that the amplitude of lattice vibration in $Ba_{0.7}K_{0.3}Cu_2Se_2$ could be suppressed to very short length comparable to the lattice parameters, thus leading to strong phonon scatterings and very low lattice thermal conductivity.

Fig. 3 shows the temperature-dependent thermoelectric properties of $Ba_{1-x}K_xCu_2Se_2$ ($x=0.3$, 0.35). As shown in Fig. 3(a), both of the samples present metal-like behavior. For $Ba_{0.7}K_{0.3}Cu_2Se_2$, the σ is greatly enhanced to 2000 S cm^{-1} at 323 K compared to that of $BaCu_2Se_2$ [7]. This can be ascribed to the increased carrier concentration n_H (6×10^{20} cm^{-3} at 300 K), and the unchanged hole mobility μ_H, which slightly decreased to 18 cm^2 V^{-1} s^{-1} from 19.5 cm^2 V^{-1} s^{-1} for the undoped sample. The constant-like hole mobility also shows that the effect of doping scattering on the electrical transport properties is nearly negligible. Temperature dependent S is shown in Fig. 3(b), where the positive S indicates