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Enhanced Thermoelectric Transport Properties of La$_{0.98}$Sr$_{0.02}$CoO$_3$-BiCuSeO Composite

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Abstract: We report a facile method to enhance the thermoelectric efficiency of La$_{0.98}$Sr$_{0.02}$CoO$_3$ by introducing BiCuSeO as a secondary phase with ultra-low thermal conductivity. Inclusion of secondary phase results in reducing the total thermal conductivity by suppressing the lattice and electronic thermal conductivities and also contributes to enhancement in the Seebeck coefficient. The wide grain size distribution of La$_{0.98}$Sr$_{0.02}$CoO$_3$-BiCuSeO composite facilitates in breaking the interlinked transport properties through increased scattering of different wavelength phonons. The combined effect of enhanced Seebeck coefficient and ultra-low thermal conductivity, results in an improved ZT value of 0.07 at 923 K. The proposed strategy can be opted for improvement in the thermoelectric efficiency of other thermoelectric materials as well.

Key words: La$_{0.98}$Sr$_{0.02}$CoO$_3$-BiCuSeO, composite, thermal conductivity, ZT.

1. Introduction

TE (Thermoelectric) materials are gaining considerable attention because of their ability for waste heat recovery and solid state refrigeration. The efficiency of TE materials can be addressed by the dimensionless Figure of Merit (*ZT*), expressed as $ZT = (S^2\sigma/k)T$, where σ, S and k are the electrical conductivity, Seebeck coefficient and total thermal conductivity, respectively. The product σS^2 is explicitly known as the power factor (*PF*). The total thermal conductivity k is the sum of electronic (κ_e) and lattice (κ_l) thermal conductivities. Here, for the thermoelectric materials, the interplaying nature of σ, S and κ is main issue to enhance the efficiency of TE

materials. Several strategies have been reported to improve the performance of TE materials, which includes: reduction in the thermal conductivity by decreasing the particle size below the mean free path of phonons [1], nano structuring by incorporating nanoparticles in the matrix [2], elemental doping [3, 4] and synthesis of novel nano structures [5]. Recently, the oxide ceramic materials are getting much attention from the TE community due to their high thermal and chemical stability, non-toxic behavior, low cost and high oxidation resistance, however, high intrinsic thermal conductivity restricts compromises their *ZT* values. Among the oxide materials, LaCoO$_3$ has been investigated extensively for its good σ and moderate *S* values. Several reports have discussed the effect of elemental doping at La site and Co site [6] with rare earth metals and alkaline earth metals and alkaline

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earth metals. Ni^{+3}, Fe^{+3} and Sr^{+2} have been observed as the most beneficial dopant in order to enhance the magnetic, and TE transport properties [7, 8] in LaCoO$_3$. The presence of vacancies generated at La/O sites has also been demonstrated for reducing the thermal conductivity [9]. However, to achieve high ZT with a single material is quite difficult. Then, composite formation may appear as a promising route to further enhance the TE performance of pure and doped LaCoO$_3$. P-type oxyselenide BiCuSeO compound consists of layered ZrSiCuAs type structure and is a promising candidate for TE materials because of its moderate power factor and ultra-low intrinsic thermal conductivity due to weak bonding among its layers.

In this work, a series of La$_{0.98}$Sr$_{0.02}$CoO$_3$ (LSCO) and BiCuSeO based composite materials are investigated for the TE transport properties at high temperature, by introducing BiCuSeO as a secondary phase. In order to increase carrier concentration in LaCoO$_3$, Sr^{2+} was doped at La^{3+} site [10, 11]. By considering the higher σ and moderate S values of LSCO, we mixed it with BiCuSeO which exhibits lower σ, higher S and ultra-low k. We anticipate improvement in the TE properties of their composites arising from their mutual behavior. Furthermore, the presence of two different phases along with their wide grain size distribution are realized to facilitate the phonon scattering of different wavelengths [12-14].

2. Synthesis Technique

La$_{0.98}$Sr$_{0.02}$CoO$_3$ (LSCO) was synthesized by sol-gel process, as already reported in Ref. [14]. BiCuSeO (BCSO) was fabricated by two steps solid state reaction. Stoichiometric amount of Bi (4N), Bi$_2$O$_3$ (4N), Cu (5N) and Se (5N) were mixed in high energy planetary ball milling at 450 RPM for 4 hours under vacuum. The powder was compacted to cylindrical pallet by using cold press and then the obtained pellet was sealed in an evacuated glass tube followed by subsequent annealing at 573 K for 4 hours and then at 923 K for 24 hours. The annealed pallets were ground in ball milling at 450

RPM for 12 hours. In the next step, the obtained LSCO and BSCO powders were mixed by ball milling at 450 RPM for 5 hours in ethanol under an inert environment to avoid any reaction, in different weight percent to form composites. Finally the obtained powders were densified by using SPS (spark plasma sintering) at 873 K under uniaxial pressure of 50 MPa for 5 minutes in vacuum. The obtained bulk cylindrical pellets were cut into rectangular bars having dimensions of 15 × 3 × 3 mm^3 for the simultaneously measurement of electrical conductivity and S, and in the pallets of diameter 10 mm for thermal conductivity measurements.

3. Characterization

The phase purity and crystal structure of pure and composite phases after SPS was studied using XRD (X-ray diffraction) by an analutical X'pert diffractometer (Tokyo Japan) with Cu-Kα radiations (λ = 0.15406 nm). The microstructures and elemental distribution were investigated by scanning electron microscope equipped with EDX (energy dispersive X-rays) detector (SEM, Zeiss Evo 18 Germany). The simultaneous measurement of S and σ was performed by LINSEIS LSR-3 (Seebeck & Electric Resistivity Unit) from 323 K to 923 K. The smaller pellets having diameters of 10 mm were used to measure Heat capacity (C_p) and thermal diffusivity (D) by NetzschLFA 457 using Laser Flash Method. The Hall coefficient (R_H), carrier concentration (n) and carrier mobility (μ) were measured by Ecopia Hall Measurement System (HMS-3000) at room temperature.

4. Results and Discussion

The XRD patterns for pure and composite phases obtained after SPS are shown in Fig. 1a. Both pure LSCO and BCSO specimens attributing single phase with high purity, are indexed with JCPDS card # 48-0123 and PDF#82-0464, respectively. All the composite samples represent the presence of LSCO and BCSO phases without any detectable impurities

phase, which is an evidence for retaining their identity after mixing. To observe the mutual distribution of BCSO and LSCO grains, SEM images were obtained from the freshly broken cross-sections of 50%-BCSO composite sample, as shown in Fig. 1b. It can be observed that the pure BCSO lath like grains having size of few micrometers are evenly distributed along with the nano-sized particles of LSCO. The elemental mapping was performed to confirm the distribution of the two phases as shown in Figs. 1c and 1d.

The distribution of such mesoscopic particles are expected to create centers for scattering for the phonons of different wavelengths which lead to reducing the lattice thermal conductivity.

To investigate the effect of secondary phase on the TE properties of LSCO, TE transport properties were measured as a function of temperature from room temperature to 923 K. Fig. 2a presents the electrical conductivity σ of the pure and composite phases, in which σ was found to increase with temperature indicating a semiconducting behavior. On the other

side, σ decreased with increased BCSO concentration in the composite samples and the highest σ of 158 S/cm was observed in pure LSCO. The Hall coefficient (R_H) was measured from four probe Hall Effect measurement system using Van der Pau method at room temperature. The carrier concentration n and carrier mobility μ were calculated (shown in Fig. 2b) from R_H as given by the expressions: $n = \left[{}^{1}/_{e \times R_H} \right]$ and $\mu = \sigma R_H$, where e is the elementary charge on an electron. With the increased BCSO contents, n decreases while μ increases. The decreased σ with the increased BCSO wt.% can be associated with decreased carrier concentration n, as shown in Fig. 2b. The low intrinsic σ of BCSO is another reason of decreased σ with increased BCSO contents. The S as a function of temperature is shown in Fig. 2c, which is found to decrease with increased temperature. However, S values for the entire specimen were positive indicating p-type nature of all the pure and composite phases. On the other side, S increased with
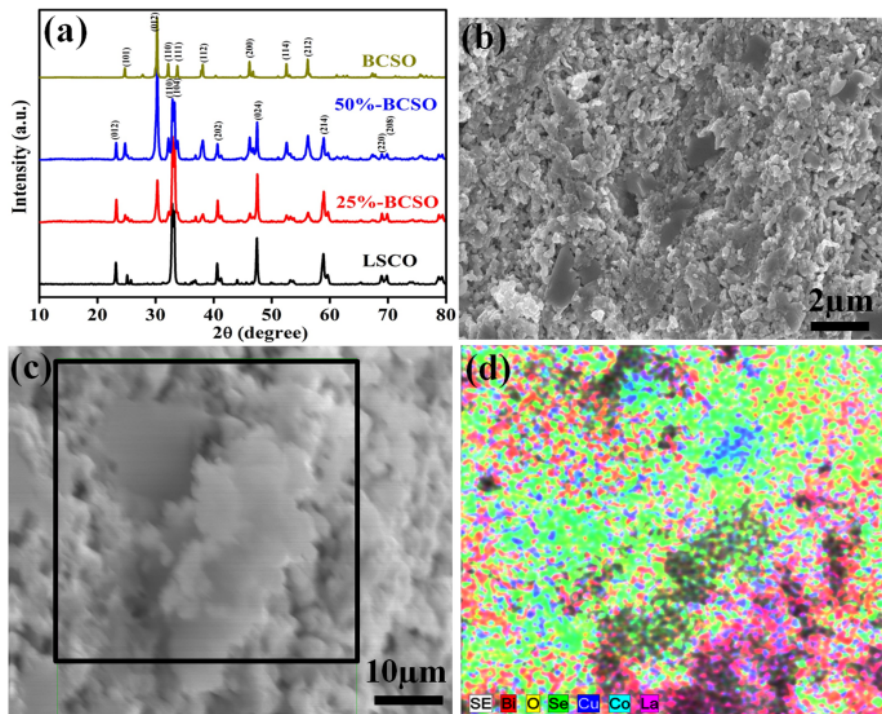

Fig. 1 **(a) XRD patterns for pure LSCO, BCSO and LSCO-BCSO composites, (b) the FESEM images of freshly broken surface for 50 wt.% BCSO containing LSCO-BCSO composite (c&d) the elemental distribution of 50 wt% BCSO composite of the selected area.**
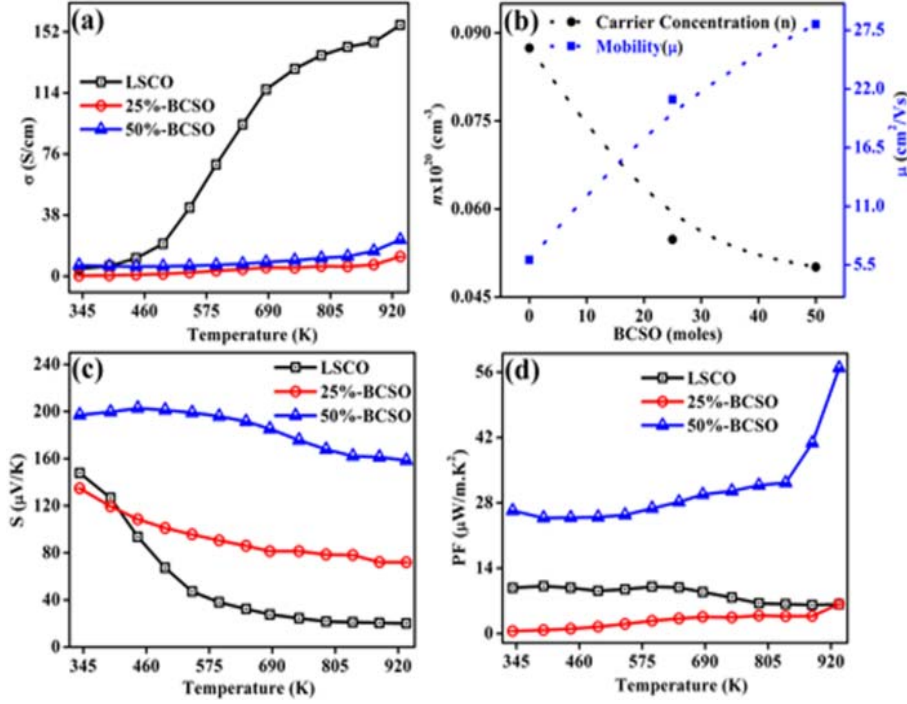
Fig. 2 (a) Temperature dependent electrical conductivity, (b) room temperature carrier mobility and carrier concentration, temperature dependent (c) Seebeck coefficient (*S*) and (d) power factor *(σS²)*.

increased wt.% of BCSO. The highest *S* of 145 μV/K has been obtained for 50%-BCSO which is much higher than that of the pure LSCO at 923 K. However, the difference at room temperature is very less as LSCO intrinsically attributes high S at low temperature. Increased S with increasing wt.% of BCSO can be associated with decreased carrier concentration which is directly associated with *S* as described by the following expression:

$$S = \frac{8m^*\pi^2 K_B^2}{3eh^2}(\frac{\pi}{3n})^{\frac{2}{3}}T \tag{1}$$

Where *m** is the carrier's effective mass, *e* is electronic charge, *h* is the planks constant, K_B is the Boltzmann constant, *T* is the working temperature and *n* is the carrier concentration. The above expression shows an inverse relation of *S* with carrier concentration *n* and a direct relation with temperature.

Fig. 2b clearly shows that the carrier concentration of the composite phases decreases with increasing BCSO concentration which results in increased *S*. The intrinsic BCSO has high S which is another potential reason for increased S in the LSCO-BCSO composites. Combining high *S* and moderate electrical conductivity,

increased PF has been observed. The highest PF value of 15 μW/m·K² was obtained for 50%-BCSO composite, which is much higher than that of the pure LSC, as shown in Fig. 2d.

The thermal transport properties of pure and composite phases were investigated as a function of temperature from room temperature to 923 K. For all the samples, the total thermal conductivity increased with increasing temperature and an ultra-low κ value of 0.80 W/m.K is obtained by 50%-BCSO composite, as shown in Fig. 3a. The decrease in total thermal conductivity is affected by both electronic and lattice thermal contributions. Low intrinsic thermal conductivity of BCSO is responsible for reduced electronic thermal conductivity which is directly associated with electrical conductivity as described by the expression: $\kappa_e = L\sigma T$, where *L* is Lorentz constant. Electronic thermal conductivity increased with increasing temperature as shown in Fig. 3b. On the other side, lattice thermal conductivity is found to be decreased by increasing BCSO wt.%.

The reduced lattice thermal conductivity of the composite can be related with the introduction of nano
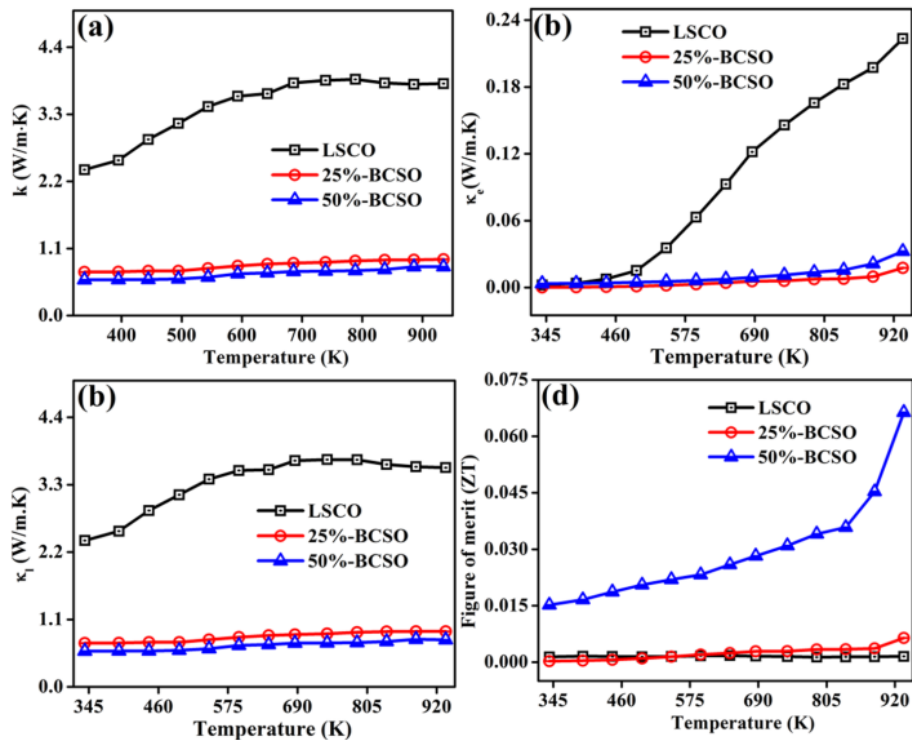
Fig. 3 **The temperature dependent (a) total thermal conductivity (k), (b) electronic thermal conductivity k_e, (c) lattice thermal conductivity (k_l) and (d) Figure of merit (ZT) of all the specimens from room temperature to 923 K.**

-particles as a secondary phase and this wide grain size distribution results in an increased number of grain boundaries which further scatters phonons of different wavelengths. The κ_l for all the samples increased with increasing temperature as shown in Fig. 3c and the minimum value 0.76 W/m.K is obtained for 50%-BCSO composite.

Combining the improved PF and the ultra-low thermal conductivity, an improved ZT value of 0.07 is obtained for 50%-BCSO composite, as shown in Fig. 3d. This enhancement in the ZT value suggests that further improvement is possible by tuning the compositions of each phase and by modifying the grain structures obtained by different synthesis routes.

5. Conclusions

La$_{0.98}$Sr$_{0.02}$CoO$_3$ (LSCO) and its composite with BiCuSeO (La$_{0.98}$Sr$_{0.02}$CoO$_3$-BiCuSeO) with different weight percent of BiCuSeO were synthesized by ball milling followed by SPS method.

Structural analysis confirms the presence of

composite phases without any detectable impurity which suggests that each phase retains its intrinsic identity.

A significant decrease in the total thermal conductivity is observed due to decrease in both lattice and electronic thermal conductivities.

Introduction of the secondary phase and wide grain size distribution facilitates in an enhanced phonon scattering which further reduces the lattice thermal conductivity.

The maximum ZT~0.07 has been obtained for the composite with 50 wt.% of BiCuSeO at 923 K.

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