Improved Thermoelectric properties in (1-x)La_{0.95}Sr_{0.05}Co_{0.95}Mn_{0.05}O_3/(x)WC composite: Influence of Kapitza radius and interface thermal resistance

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Abstract: In this study, the synergistic effect of the particle size of the dispersed phase and the interface thermal resistance ($R_{\text{int}}$) between the phases on the phonon thermal conductivity ($\kappa_{\text{ph}}$) of the (1-x)La_{0.95}Sr_{0.05}Co_{0.95}Mn_{0.05}O_3/(x)WC thermoelectric composite, is demonstrated. Further, the correlation between the $R_{\text{int}}$ and the Kapitza radius is discussed using the Bruggeman’s asymmetrical model. In particular, the polycrystalline La_{0.95}Sr_{0.05}Co_{0.95}Mn_{0.05}O_3 sample is synthesized using a standard-solid state route. The presence of WC nanoparticle is confirmed from the electron microscopy images. Electrical conductivity ($\sigma$) increases, and the Seebeck coefficient ($\alpha$) decreases with the increase in conducting WC volume fraction in the composite. The simultaneous increase in $\sigma$ and a decrease in $\kappa_{\text{ph}}$ with the WC volume fraction results in an increased figure of merit ($zT$) for (1-x)La_{0.95}Sr_{0.05}Co_{0.95}Mn_{0.05}O_3/(x)WC composite. A maximum $zT \sim 0.20$ is obtained for (1-x)La_{0.95}Sr_{0.05}Co_{0.95}Mn_{0.05}O_3/(x)WC composite for x=0.010 at 463 K. The results obtained in the present study shows promise to design thermoelectric composites with desired phonon thermal conductivity considering the elastic properties between the phases.

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INTRODUCTION

Wastage of energy in the form of heat from several energy sources while in practical use has been a concern for decades [1]. Thermoelectric (TE) devices can be used in waste heat recovery technology for efficient use of available energy resources [2,3]. The efficiency of a TE device depends on a dimensionless quantity known as a figure of merit (zT) of TE materials. The zT is defined as $zT = \frac{\sigma \alpha^2}{\kappa_{ph} + \kappa_e} T$, where $\alpha$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $T$ is the absolute temperature, and $\kappa$ ($=\kappa_{ph}+\kappa_e$) is the total thermal conductivity, which consists of phonon thermal conductivity ($\kappa_{ph}$) and electronic thermal conductivity ($\kappa_e$). The interdependence between $\sigma$, $\alpha$, and $\kappa_e$ is challenging to achieve a high $zT$ in a single material [4]. The increase in $\sigma$ reduces $\alpha$; also, an increase in $\sigma$ increases $\kappa_e$, according to Wiedemann Franz law. Ioffe suggested that one of the primary requirements to achieve a high $zT$ is to reduce the $\kappa_{ph}$ of a material. The reduction in $\kappa_{ph}$ has been demonstrated in literature through several strategies, including lattice defects [5], mass disorder [6], nanostructuring [7], artificial superlattices [8], and or preparation of composite materials [9] that enhances the scattering of phonons. However, phonon scattering via impurities, lattice defects, lattice anharmonicity, in a single TE material may also scatter electrons and hence leads to a lower $\sigma$ [4]. Moreover, making composite materials can be promising for lowering $\kappa_{ph}$, considering the mismatched elastic properties (sound velocity) and the Kapitza radius between the phases [10].

Oxide materials are promising for the direct conversion of heat to electrical energy for power generation at high temperatures due to their chemical and thermal stability in an open environment [11]. Among the oxide materials, cobalt-based systems (LaCoO$_3$ [12,13], Ca$_3$Co$_4$O$_9$ [14,15], Na$_x$CoO$_2$ [16,17]) are promising for TE applications due to the presence of different charge states along with different spin-states of cobalt [18]. However, these oxide materials possess poor $zT$ due to low $\sigma$ and high $\kappa_{ph}$ [19]. An improvement in $zT$ is obtained in several oxide composites viz. Ca$_3$Co$_4$O$_9$/Ag [20], LaCoO$_3$/graphene[21], LaCoO$_3$/La$_0.7$Sr$_{0.3}$MnO$_3$ [22,23], due to reduced $\kappa_{ph}$. A notable reduction in $\kappa_{ph}$ was also shown in several composites with the addition of a nanostructured secondary phase [24–26]. However, the lowering of $\kappa_{ph}$ in nanostructured composite materials is mainly ascribed to the quantum size effects [19,27]. Also, these studies are often focused on general transport properties and do not consider the role of interface thermal resistance ($R_{int}$) and acoustic impedance mismatch (AIM) between the phases on $\kappa_{ph}$. On the other hand, these parameters are used in the analysis of heat transport mechanisms
in several ceramic (ZnS/diamond [10], SiC/Al [28], ZnO/In$_2$O$_3$ [29]) and polymer composites (glass/epoxy [9,30]). Moreover, this method did not receive significant research attention in optimizing the thermal conductivity for TE composite materials. A decrease in the phonon thermal conductivity of the composite when the particle size of the dispersed phase is smaller than the Kapitza radius, is realized [31]. However, the electrical conductivity of the dispersed phase is not promising and hence requires additional research to improve the TE properties in composite systems.

Because of the gap in the literature as mentioned above, a systematic study on the TE properties of a composite oxide that consists of La$_{0.95}$Sr$_{0.05}$Co$_{0.95}$Mn$_{0.05}$O$_3$ (a promising cobalt-based oxide system, $zT$=0.14 at 480 K [12]) and highly conducting WC (with different elastic properties than LSCMO) is performed. The addition of conducting WC improves the electrical conductivity as well as different elastic properties between the phase reduces $\kappa_{ph}$, and hence suitable for improved TE properties. In particular, the role of $R_{int}$ between the phases and particle size of the dispersed phase on $\kappa_{ph}$ is analyzed. Further, the experimental results for thermal conductivity are analyzed using the Bruggeman’s asymmetrical model.

**EXPERIMENTAL SECTION**

The polycrystalline La$_{0.95}$Sr$_{0.05}$Co$_{0.95}$Mn$_{0.05}$O$_3$ (LSCMO) sample was synthesized using a standard solid-state route. In a typical synthesis process, the stoichiometric amount of La$_2$O$_3$, SrCO$_3$, Mn$_2$O$_3$, and Co$_3$O$_4$ were taken and mixed homogeneously in an agate mortar pestle using acetone as a liquid medium. The mixed powder was calcined at 1473 K for 12 hours in a muffle furnace with a 3 K/min heating and cooling rate. Further, the calcined powder was ground again to obtain a homogeneous mixture. The (1-x)La$_{0.95}$Sr$_{0.05}$Co$_{0.95}$Mn$_{0.05}$O$_3$/(x)WC composite with $x$=0.000, 0.002, 0.005, 0.010, 0.020, and 0.050 is prepared by mixing the different volume fraction (x) of WC nanoparticle (Sigma Aldrich). The composite mixture was further ground to mix homogeneously in a liquid medium (acetone). The mixture was then sintered using a spark plasma sintering (SPS) technique at 973 K in a uniaxial pressure of 60 MPa. The obtained cylindrical pellets of 10 mm diameter and 12-13 mm height were cut to proper dimensions using a precise wire saw for further measurements. The surface of the sample for microstructure investigation was polished using an automatic grinding/polishing machine. The surface morphology of the polished sample was done using a scanning electron microscope equipped
with energy dispersive x-ray spectroscopy. X-ray diffraction of samples after synthesis and after sintering was obtained by the Rigaku diffractometer (\(\lambda=1.5406\) Å). The surface mapping of the Seebeck coefficient for the \((1-x)\text{LSCMO}/(x)\text{WC}\) composite was done using a scanning thermoelectric microprobe (STM) at 298 K with a spatial resolution of 50 µm.

Thermal diffusivity for all the samples was measured using the laser flash analysis (LFA-457, NETSCH) apparatus in the Ar (5N) atmosphere (30 ml/min). Specific heat was determined from the Dulong-Petit law. The sample density was measured using sample mass and its geometric volume. Electrical conductivity and Seebeck coefficient were measured under Ar (5N) atmosphere (50 ml/min) by the SBA 458 (NETSCH) apparatus. The uncertainty of the Seebeck coefficient and electrical conductivity measurements is 7% and 5%, respectively. The estimated uncertainty in thermal conductivity is 7%.

RESULTS AND DISCUSSION

X-ray diffraction pattern of the \((1-x)\text{La}_{0.95}\text{Sr}_{0.05}\text{Co}_{0.95}\text{Mn}_{0.05}\text{O}_3/(x)\text{WC}\) composite is shown in Fig. 1(a). The LSCMO shows a characteristic peak at \(\theta = 32.74^\circ\) (104) and 32.88° (110) having the following lattice parameters \((a=b=5.443\) Å, \(c=13.154\) Å). In composite samples, only intensity due to LSCMO is observed without any trace of impurity within the sensitivity of XRD. Also, the reflections due to WC is not prominently observed owing to its lower volume fraction in the composite. The diffraction pattern for WC is also shown in Fig.1.
Fig. 1: (a) X-ray diffraction pattern for (1-x)L$_{0.95}$Sr$_{0.05}$Co$_{0.95}$Mn$_{0.05}$O$_3$/WC composite. Bragg’s position and Miller indices for L$_{0.95}$Sr$_{0.05}$Co$_{0.95}$Mn$_{0.05}$O$_3$ and WC are marked. Scanning electron microscopy (SEM) images for (1-x)L$_{0.95}$Sr$_{0.05}$Co$_{0.95}$Mn$_{0.05}$O$_3$/WC composite for x=0.010.

Fig. 1(b-c) show the scanning electron microscopy (SEM) images for (1-x)LSCMO/WC composite for x=0.010. The presence of WC nanoparticle (shown by red arrows) is seen in the composite samples. The WC nanoparticles are at the grain boundaries. The particle size of the WC is in the range of 100-150 nm, where LSCMO particle size lies in the range of 1-3 μm. The experimental densities of the samples were measured using the sample mass and its geometrical volume. The theoretical densities of the composite were calculated using the volume-weighted arithmetic mean. The relative density for all the samples is greater than 96%.
The local variation in the Seebeck coefficient for all the samples is measured using a scanning thermoelectric microprobe at 300 K. Figure 2(a-d) depicts the Seebeck coefficient mapping for (1-x)La\(_{0.95}\)Sr\(_{0.05}\)Co\(_{0.95}\)Mn\(_{0.05}\)O\(_3\)/(x)WC composite. The scale bar is kept constant for all the samples. It is found that with the increase in the WC nanoparticle in the composite, the average value of \(\alpha\) decreases. A minimal \(\alpha\) at any point on the STM map due to WC is not observed, as the tip resolution of the STM is 50 \(\mu\)m (higher than the particle size of WC (100-150 nm)). However, a decrease in average \(\alpha\) in composites is observed and attributed to the collective contributions from both LSCMO and WC phases.

The Seebeck coefficient (\(\alpha\)), electrical conductivity (\(\sigma\)), and power-factor (\(\alpha^2\sigma\)) for LSCMO/WC composite are shown in Fig. 3(a-c). The positive value of the Seebeck coefficient indicates a p-type of conduction in the system, as shown in our previous studies for LSCMO [12]. At 300 K, \(\alpha\) for LSCMO is 260 \(\mu\)V/K. For \(x=0.002\), \(\alpha\) increases to 263 \(\mu\)V/K and decreases with the further increase in WC volume fraction in the composite. The Seebeck coefficient decreases from 260 \(\mu\)V/K for \(x=0.000\) to 255 \(\mu\)V/K for \(x=0.005\) to 251 \(\mu\)V/K for \(x=0.010\) to 231 \(\mu\)V/K for \(x=0.020\) to 186 \(\mu\)V/K for \(x=0.050\). The Seebeck coefficient for all the samples decreases with the rise in temperature. Also, the slope change in the \(\alpha\) vs. temperature curve is identical for all the samples, depicting that the spin-state transition is identical in all the samples [16][32][33].
Figure 3(b) shows the electrical conductivity ($\sigma$) as a function of temperature for all the composite samples. The electrical conductivity is found to increase with the increase in WC volume fraction in the composite. The increase in $\sigma$ in the composite is due to the significantly high electrical conductivity of WC (50000 S/cm) [34]. The increase in $\sigma$ with WC volume fraction in the composite is consistent with the decrease in $\alpha$. Also, $\sigma$ increases with the increase in temperature for all the samples depicting the semiconducting behavior. The $\sigma$ for LSCMO at 300 K is ~40 S/cm, and it increases to ~60 S/cm for $x=0.010$ and to ~90 S/cm for $x=0.050$. A small rise in $\sigma$ in the composite with WC, having too high electrical conductivity (50000 S/cm), may be attributed to the presence of contact resistance between the LSCMO and WC phases.

Further, the power factor ($\alpha^2 \sigma$) as a function of temperature for all the samples is shown in Fig. 3(c). The power factor is found to increase with the increase in WC volume fraction in the composite, and it is attributed to the increase in electrical conductivity with a minimal reduction in the Seebeck coefficient. The power factor first increases and then decreases with the increase in temperature and is consistent with the previous studies in cobaltates [23][12]. The decrease in power factor at higher temperatures is attributed to a decrease in the Seebeck coefficient.

Figure 4(a) shows the temperature-dependent thermal conductivity ($\kappa$) of the LSCMO/WC composite. An increase in $\kappa$ with the rise in temperature is observed for all the samples. It is attributed to the rise in $\sigma$ of the composite with an increase in temperature. Also, the thermal conductivity of the composite is found to increase with the increase in WC volume fraction. This increase in $\kappa$ may be attributed to the high thermal conductivity of the WC [35]. However, it is noted that the rise in $\kappa$ for the composite samples does not follow the rule of mixture. Therefore, to understand the exact nature of thermal conductivity in the composite samples, electronic and
phonon thermal conductivity was separated from total thermal conductivity. The electronic thermal conductivity ($\kappa_e$) is calculated using the Wiedemann-Franz law, i.e., $\kappa_e = L \sigma T$, where $L$ is Lorenz number and is calculated using the following equation $L = 1.5 + \exp(-|\alpha|/116)$ [36]. The $\kappa_{ph}$ is estimated by subtracting the $\kappa_e$ from $\kappa$. The $\kappa_{ph}$ as a function of temperature for the composite is shown in Fig. 4(b). The $\kappa_{ph}$ increases with an increase in temperature up to ~500 K and then decreases with a further rise in temperature. The decrease in $\kappa_{ph}$ at higher temperatures is attributed to the decrease in the phonon mean free path that enhances the phonon scattering. However, $\kappa_{ph}$ is found to decrease with the increase in WC volume fraction in the composite. To elucidate the decrease in $\kappa_{ph}$ with the increase in WC volume fraction in the composite, first the acoustic impedance mismatch (AIM) model and the Debye model are used to calculate the interface thermal resistance ($R_{int}$) between the phases. Further, Bruggeman asymmetrical model that considers the $R_{int}$ was used to estimate the theoretical $\kappa_{ph}$ and compare it with the experimental value.

![Image](image.png)

FIG. 4 (a) Total thermal conductivity ($\kappa$), (b) phonon thermal conductivity ($\kappa_{ph}$) as a function of temperature for (1-2)Ge$_{0.87}$Mn$_{0.05}$Sb$_{0.08}$Te/(z)WC composite.

The acoustic impedance mismatch (AIM) model predicts the probability of phonon reflection and transmission at the interface between the two phases in a composite system. First, the fraction of phonons ($q$) having the incident angle below a critical value at the interface can be estimated using the following relation: $q = \frac{1}{2} \left( \frac{v_m}{v_d} \right)^2$ [10], where $v_m$ and $v_d$ are the sound velocities of the matrix (LSCMO) and the dispersed phase (WC). The sound velocities measurement for both the phases are shown in Table I, and it gives a $q = 0.128$. It shows that 12.8% of these phonons have the incident angle within the critical angle. Further, the
transmission coefficient \( (p) \) of the phonons at the interface of two materials can be calculated using the following equation:

\[
p = \frac{4Z_A Z_B}{(Z_A + Z_B)^2} \quad [37],
\]

where \( Z_i = v_i \rho_i \) is called acoustic impedance, \( \rho_i \) is the density, and \( v_i \) is the velocity of the \( i^{th} \) material. The measured values of \( v \) and \( \rho \) are used to calculate the acoustic impedance for both the materials. The acoustic impedance for both phases gives a \( p \) value of 0.581. It indicates that, phonons which incident on the interface below the critical angle, 58.1 % of these can transmit through the interface. Hence, the transmission probability \( (\eta = pq) \) for these LSCMO/WC interface is 0.0746. Further, the \( R_{int} \) for the LSCMO-WC phase is calculated using the Debye model given by the equation:

\[
R_{int} = \frac{4}{\rho c_p v_D \eta},
\]

where \( c_p \) is the specific heat capacity, \( v_D \) is the Debye velocity, \( v_i \) and \( v_t \) are the sound velocities in longitudinal and transverse directions. The interface thermal resistance \( (R_{int}) \) between the LSCMO and WC phases, calculated from the Debye model, is \( 7.05 \times 10^{-7} \) m\(^2\)K/W. Further, the theoretical Kapitza radius \( a_K (=R_{int} \cdot \kappa_m) \) for the LSCMO/WC composite is \(~720 \) nm at 300 K, where \( \kappa_m \) is the thermal conductivity of the matrix (LSCMO).

### TABLE I: Measured values of sample density (\( \rho \)), sound velocity (\( v \)) used in acoustic impedance model (AIM) to calculate the acoustic impedance (\( Z \)) and Transmission coefficient (\( p \)) of phonons for LSCMO and WC samples.

| Sample Name | \( \rho \) (g/cm\(^3\)) | \( v \) (m/sec) | \( Z \) (kg/(m\(^2\)s)) | \( p_{uv} \) (%) |
|-------------|----------------|----------------|----------------|----------------|
|             | \( v_I \) (Trans.) | \( v_L \) (Long.) | Trans. | Long. | Trans. | Long. | |
| LSCMO       | 5.94           | 1600           | 2610          | 13246         | 25066   | 58.1  |
| WC          | 15.43          | 2110           | 3170          | 67892         | 110787  |       |

Further, the effect of \( R_{int} \) and \( a_K \) on the phonon thermal conductivity \( \kappa_{ph} \) of the composite is discussed using the Bruggeman’s asymmetrical model, given by the formula [38]

\[
(1 - x)^3 = \left( \frac{k_m}{k} \right)^{\frac{1+2\alpha}{1-\alpha}} \left( \frac{k - k_d(1 - \alpha)}{k_m - k_d(1 - \alpha)} \right)^{\frac{3}{1-\alpha}}
\]

where \( k_d \) and \( k \) are the phonon thermal conductivity of the dispersed phase (WC) and the composite, respectively. The \( x \) is the volume fraction of the dispersed phase, and \( \alpha = a/a_K \), where \( a \) is the particle size of the dispersed phase.
FIG. 5: (a) Schematic of acoustic impedance mismatch (AIM) model depicting the probability for phonon transmission (p) and reflection (1-p) for the difference in AIM (Z_A/Z_B). The Z_A/Z_B is marked for the LSCMO/WC composite. (b) Calculated phonon thermal conductivity (κ_{ph}) of (1-x)La_{0.95}Sr_{0.05}Co_{0.95}Mn_{0.05}O_3/(x)WC composite for x=0.010 as a function of the WC particle size at 298 K, obtained from the Bruggeman’s asymmetrical model. (c) Calculated phonon thermal conductivity as a function of WC volume fraction for the different particle size of WC at 298K. The symbols represent the κ_{ph} obtained from the total κ.

The schematic of the acoustic impedance mismatch (AIM) model is shown in Fig. 5(a). The probability of phonon transmission (p) and reflection (1-p) for the difference in acoustic impedance (Z_A/Z_B) is shown. For large Z_A/Z_B, the probability of phonon reflection increases at the interface between two materials. The dotted line marks the probability of phonon transmission at the interface between LSCMO/WC in Fig. 5(a). Figure 5(b) shows the phonon thermal conductivity (κ_{ph}) calculated for different particle sizes of WC for the (1-x)LSCMO/(x)WC composite for x=0.010 using Bruggeman’s asymmetrical model (dashed lines). The κ_{ph} decreases with the decrease in the particle size of the dispersed phase. It is also noted that when the particle size of the dispersed phase is smaller than a threshold value, called Kapitza radius (a_K), the κ_{ph} of the composite is smaller than the κ_{ph} of the matrix. The change in κ_{ph} as a function of WC volume fraction (x) for the different particle size of WC is shown in Fig. 5(c). It is observed that when the particle size of WC is larger than the Kapitza radius (~720 nm), the κ_{ph} of the composites increases with the increase in WC volume fraction. It suggests that even there is an acoustic impedance mismatch between the LSCMO and WC, the κ_{ph} does not decrease when the particle size is larger than the Kapitza radius. It also indicates a correlation between the interface thermal resistance and the Kapitza radius [31][10].

Further, an almost constant value of κ_{ph} is observed when the particle size of the dispersed phase is close to the Kapitza radius (~720 nm). However, the κ_{ph} of the composite can be lower than the κ_{ph} of the matrix when the particle size of the dispersed phase is smaller than the Kapitza
radius. The experimental value of the $\kappa_{\text{ph}}$ (star symbol) agrees well to the theoretical prediction (solid lines). The decrease in $\kappa_{\text{ph}}$ for particle size smaller than $a_K$ is attributed to the increase in the contact area between phases due to an increased surface to volume ratio [31]. At this condition, $R_{\text{int}}$ between the phases becomes more prominent and hence reduces the $\kappa_{\text{ph}}$.

![Graph showing zT vs. temperature for different compositions](image)

**FIG. 6:** (a) Figure of merit ($zT$) (b) average $zT$, and (c) efficiency ($n$) calculated from the average $zT$ value for the (1-$z$)Ge$_{0.87}$Mn$_{0.05}$Sb$_{0.08}$Te/$z$WC composite.

The measured value of $\alpha$, $\sigma$, and $\kappa$ are used to calculate the figure of merit ($zT$) in the LSCMO/WC composite. Figure 6 depicts the temperature-dependent $zT$ for the LSCMO/WC composite. The $zT$ is found to increase with the increase in WC volume fraction in the composite. It is attributed to the simultaneous increase in $\sigma$ and a decrease in $\kappa_{\text{ph}}$ in the composite. The maximum $zT$ for LSCMO/WC composite is 0.20 at 463 K, which is one of the highest $zT$ obtained in the LaCoO$_3$ based system at this temperature [22,39–42].

**CONCLUSION**

The role of interface thermal resistance and particle size of the dispersed phase on the phonon thermal conductivity ($\kappa_{\text{ph}}$) is discussed in the LSCMO/WC composite, using the Bruggeman’s asymmetrical model. In particular, polycrystalline LSCMO is synthesized using a standard solid-state route. The pure phase formation of LSCMO and the presence of WC in the composite was confirmed from the structural analysis. The addition of conducting WC (having mismatched elastic properties than LSCMO) improves the electrical conductivity ($\sigma$) with a minimal reduction in the Seebeck coefficient. The phonon thermal conductivity ($\kappa_{\text{ph}}$) was extracted by
subtracting electronic thermal conductivity, using the Wiedemann Franz law, from the total thermal conductivity. The decrease in $\kappa_{\text{ph}}$ with the increase in the WC volume fraction is analyzed using the acoustic impedance mismatch model and the Bruggeman asymmetrical model. The $\kappa_{\text{ph}}$ of the composite decreases when the particle size of the WC (dispersed phase) is smaller than the Kapitza radius. The simultaneous increase in $\sigma$ and a decrease in $\kappa_{\text{ph}}$ with the addition of WC nanoparticle improve the figure of merit in the system. A maximum $zT$ of 0.20 is obtained for LSCMO/WC composite with $x=0.010$ at 463 K. The results obtained in this study can generate excitement in the field of composite materials to optimize the electrical and thermal conductivity based on the elastic properties of materials for improved TE applications.

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References

[1] T.M. Tritt, M.A. Subramanian, Thermoelectric Materials, Phenomena, and Applications: A Bird’s Eye View, 31 (2020).
[2] H. Ohta, K. Sugiura, K. Koumoto, Recent progress in oxide thermoelectric materials: P-type Ca3Co4O9 and n-Type SrTiO3-, Inorg. Chem. (2008). https://doi.org/10.1021/ic800644x.
[3] J.W. Fergus, Oxide materials for high temperature thermoelectric energy conversion, J. Eur. Ceram. Soc. 32 (2012) 525–540. https://doi.org/10.1016/j.jeurceramsoc.2011.10.007.
[4] M. Dutta, T. Ghosh, K. Biswas, Electronic structure modulation strategies in high-performance thermoelectrics, APL Mater. 8 (2020) 040910. https://doi.org/10.1063/5.0002129.
[5] R. Stern, T. Wang, J. Carrete, N. Mingo, G.K.H. Madsen, Influence of point defects on the thermal conductivity in FeSi, Phys. Rev. B. 97 (2018) 195201. https://doi.org/10.1103/PhysRevB.97.195201.
[6] D.A. Dalton, W.P. Hsieh, G.T. Hohensee, D.G. Cahill, A.F. Goncharov, Effect of mass disorder...
on the lattice thermal conductivity of MgO periclase under pressure, Sci. Rep. 3 (2013) 1–5. https://doi.org/10.1038/srep02400.

[7] D. Sivaprahasam, S.B. Chandrasekhar, S. Kashyap, A. Kumar, R. Gopalan, Thermal conductivity of nanostructured Fe0.04Co0.96Sb3 skutterudite, Mater. Lett. 252 (2019) 231–234. https://doi.org/10.1016/j.matlet.2019.05.140.

[8] P.C. Sreeparvathy, V. Kanchana, Novel natural super-lattice materials with low thermal conductivity for thermoelectric applications: A first principles study, J. Phys. Chem. Solids. 111 (2017) 54–62. https://doi.org/10.1016/j.jpcs.2017.07.009.

[9] A. Kumar, R. Kumar, D.K. Satapathy, Bi2Se3-PVDF composite: A flexible thermoelectric system, Phys. B Condens. Matter. 593 (2020) 412275. https://doi.org/10.1016/j.physb.2020.412275.

[10] A.G. Every, Y. Tzou, D.P.H. Hasselman, R. Raj, The effect of particle size on the thermal conductivity of ZnS/diamond composites, Acta Metall. Mater. 40 (1992) 123–129. https://doi.org/10.1016/0956-7151(92)90205-S.

[11] J.W. Fergus, Oxide materials for high temperature thermoelectric energy conversion, J. Eur. Ceram. Soc. (2012). https://doi.org/10.1016/j.jeurceramsoc.2011.10.007.

[12] A. Kumar, D. Sivaprahasam, A.D. Thakur, Improvement of thermoelectric properties of lanthanum cobaltate by Sr and Mn co-substitution, J. Alloys Compd. 735 (2018) 1787–1791. https://doi.org/10.1016/j.jallcom.2017.11.334.

[13] J. Androulakis, P. Migiakis, J. Giapintzakis, La 0.95 Sr 0.05 CoO 3 : An efficient room-temperature thermoelectric oxide Thermoelectric properties of LaNi 1–x Co x O 3 solid solution La 0.95 Sr 0.05 CoO 3 : An efficient room-temperature thermoelectric oxide, Appl. Phys. Lett. J. Appl. Phys. J. Appl. Phys. 84 (2004) 23713–2568. https://doi.org/10.1063/1.1647686.

[14] J. Pei, G. Chen, D.Q. Lu, P.S. Liu, N. Zhou, Synthesis and high temperature thermoelectric properties of Ca3.0–x–yNdxCayCo4O9+δ, Solid State Commun. 146 (2008) 283–286. https://doi.org/10.1016/j.ssc.2008.03.012.

[15] D. Kenfaui, D. Chatteigner, M. Gomina, J.G. Noudem, Texture, mechanical and thermoelectric properties of Ca3Co4O9 ceramics, J. Alloys Compd. 490 (2010) 472–479. https://doi.org/10.1016/j.jallcom.2009.10.048.

[16] W. Koshibae, K. Tsutsui, S. Maekawa, Thermopower in cobalt oxides, Phys. Rev. B - Condens. Matter Mater. Phys. (2000). https://doi.org/10.1103/PhysRevB.62.6869.

[17] I. Terasaki, Y. Sasago, K. Uchinokura, Large thermoelectric power in NaCo2O4 single crystals, Phys. Rev. B - Condens. Matter Mater. Phys. 56 (1997) R12685. https://doi.org/10.1103/PhysRevB.56.R12685.

[18] K. Mydeen, P. Mandal, D. Prabhakaran, C.Q. Jin, Pressure- and temperature-induced spin-state transition in single-crystalline La1-x Srx CoO3 (x=0.10 and 0.33), Phys. Rev. B - Condens. Matter Mater. Phys. 80 (2009) 1–6. https://doi.org/10.1103/PhysRevB.80.014421.

[19] K. Koumoto, Y. Wang, R. Zhang, A. Kosuga, R. Funahashi, Oxide thermoelectric materials: A nanostructuring approach, Annu. Rev. Mater. Res. 40 (2010) 363–394. https://doi.org/10.1146/annurev-matsci-070909-104521.

[20] Z. Shi, F. Gao, J. Xu, J. Zhu, Y. Zhang, T. Gao, M. Qin, M. Reece, H. Yan, Two-step processing of thermoelectric (Ca 0.9 Ag 0.1 ) 3 Co 4 O 9 /nano-sized Ag composites with high ZT, J. Eur.
[21] A. Kumar, K. Kumari, S.J. Ray, A.D. Thakur, Graphene mediated resistive switching and thermoelectric behavior in lanthanum cobaltate, J. Appl. Phys. 127 (2020) 235103. https://doi.org/10.1063/5.0009666.

[22] A. Kumar, K. Kumari, B. Jayachandran, D. Sivaprasasam, A.D. Thakur, Thermoelectric properties of (1-x)LaCoO3.xLa0.7Sr0.3MnO3 composite, J. Alloys Compd. 749 (2018) 1092–1097. https://doi.org/10.1016/j.jallcom.2018.03.347.

[23] A. Kumar, K. Kumari, B. Jayachandran, D. Sivaprasasam, A.D. Thakur, Thermoelectric Properties of (1−x )LaCoO3.(x)La0.95Sr0.05CoO3 composite, Mater. Res. Express. 6 (2019) 055502. https://doi.org/10.1088/2053-1591/aade73.

[24] K. Xu, H. Liu, Introducing Ta2O5 nanoparticles into Ca3Co4O9 matrix for increased thermoelectric property through phonon scattering, Ceram. Int. (2020). https://doi.org/10.1016/j.ceramint.2020.07.057.

[25] P. Jood, R.J. Mehta, Y. Zhang, G. Peleckis, X. Wang, R.W. Siegel, T. Borca-Tasciuc, S.X. Dou, G. Ramanath, Al-doped zinc oxide nanocomposites with enhanced thermoelectric properties, Nano Lett. 11 (2011) 4337–4342. https://doi.org/10.1021/nl202439h.

[26] N. Wang, H. He, X. Li, L. Han, C. Zhang, Enhanced thermoelectric properties of Nb-doped SrTiO3 polycrystalline ceramic by titanate nanotube addition, J. Alloys Compd. 506 (2010) 293–296. https://doi.org/10.1016/j.jallcom.2010.06.195.

[27] M. Wolf, K. Menekse, A. Mundstock, R. Hinterding, F. Nietschke, O. Oecokler, A. Feldhoff, Low Thermal Conductivity in Thermoelectric Oxide-Based Multiphase Composites, J. Electron. Mater. 48 (2019) 7551–7561. https://doi.org/10.1007/s11664-019-07555-2.

[28] D.P.H. Hasselman, K.Y. Donaldson, A.L. Geiger, Effect of Reinforcement Particle Size on the Thermal Conductivity of a Particulate- Silicon Carbide- Reinforced Aluminum Matrix Composite, J. Am. Ceram. Soc. 75 (1992) 3137–3140. https://doi.org/10.1111/j.1151-2916.1992.tb04400.x.

[29] X. Liang, M. Baram, D.R. Clarke, Thermal (Kapitza) resistance of interfaces in compositional dependent ZnO-In2O3 superlattices, Appl. Phys. Lett. 102 (2013) 223903. https://doi.org/10.1063/1.4809784.

[30] K. Pietrak, T.S. Wiśniewski, M. Kubiś, Application of flash method in the measurements of interfacial thermal resistance in layered and particulate composite materials, Thermochim. Acta. 654 (2017) 54–64. https://doi.org/10.1016/j.tca.2017.05.007.

[31] Ashutosh Kumar et al., Effective Thermal Conductivity of SrBi4Ti4O15-La0.7Sr0.3MnO3 Oxide composite: Role of Particle Size and Interface Thermal Resistance, J. Eur. Ceram. Soc. (2020). https://doi.org/10.1016/j.jeurceramsoc.2020.08.069.

[32] K. Asai, A. Yoneda, O. Yokokura, J.M. Tranquada, G. Shirane, K. Kohn, Two Spin-State Transitions in LaCoO3, J. Phys. Soc. Japan. 67 (1998) 290–296. https://doi.org/10.1143/JPSJ.67.290.

[33] K. Asai, O. Yokokura, N. Nishimori, H. Chou, J.M. Tranquada, G. Shirane, S. Higuchi, Y. Okajima, K. Kohn, Neutron-scattering study of the spin-state transition and magnetic correlations in La1-xSrxCoO3 (x=0 and 0.08), Phys. Rev. B. 50 (1994) 3025–3032. https://doi.org/10.1103/PhysRevB.50.3025.
[34] C. KITTEL, Introduction to Solid State Physics (7th ed.). Wiley-India. ISBN 81-265-1045-5., 1995.

[35] K. Chen, W. Xiao, Z. Li, J. Wu, K. Hong, X. Ruan, Effect of graphene and carbon nanotubes on the thermal conductivity of WC-Co cemented carbide, Metals (Basel). 9 (2019) 377. https://doi.org/10.3390/met9030377.

[36] H.S. Kim, Z.M. Gibbs, Y. Tang, H. Wang, G.J. Snyder, Characterization of Lorenz number with Seebeck coefficient measurement, APL Mater. 3 (2015) 041506. https://doi.org/10.1063/1.4908244.

[37] E.T. Swartz, R.O. Pohl, Thermal boundary resistance, Rev. Mod. Phys. 61 (1989) 605–668. https://doi.org/10.1103/RevModPhys.61.605.

[38] D.A.G. Bruggeman, Berecmlung Verschiedener Physikalischer Konnstanten Won Heterogenen Substanzen I. Dielehrtrizitatskonstanten und Leitfähigkeiten der Miscilkiirper aus Isotropen Substanzen, Ann. Phys. 416 (1935) 636–664.

[39] K. Iwasaki, T. Ito, T. Nagasaki, Y. Arita, M. Yoshino, T. Matsui, Thermoelectric properties of polycrystalline La1-xSrxCeO3, J. Solid State Chem. 181 (2008) 3145–3150. https://doi.org/10.1016/j.jssc.2008.08.017.

[40] A. Kumar, K. Kumari, B. Jayachandran, D. Sivaprahasam, A.D. Thakur, Thermoelectric Properties of (1 – x)LaCoO3.(x)La0.95Sr0.05CoO3 composite, Mater. Res. Express. 6 (2019) 055502.

[41] T. He, J. Chen, T.G. Calvarese, M.A. Subramanian, Thermoelectric properties of La 1–x A x CoO 3 (A = Pb, Na), Solid State Sci. 8 (2006) 467–469. https://doi.org/10.1016/j.solidstatesciences.2006.01.002.

[42] F. Li, J.F. Li, Effect of Ni substitution on electrical and thermoelectric properties of LaCoO3 ceramics, Ceram. Int. 37 (2011) 105–110. https://doi.org/10.1016/j.ceramint.2010.08.024.