

# Interpretation of Thermal Conductivity of Ceramic Oxides

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**Abstract:** A thermal conductivity of  $\text{LaCoCuO}_3$  ceramic oxides is analyzed using phonon scattering effects by incorporating the scattering of phonons with point defects, grain boundaries and phonons in the model Hamiltonian. Phonons are the sole carriers for the heat in the test material and the behavior of thermal conductivity is an artifact of strong phonon-defects, phonon-grain boundaries and phonon-phonon scattering mechanism. The thermal conductivity has been modeled in terms of the relaxation-time approximation, characterized by Debye temperature  $\theta_D$ . It is seen that the phonon-phonon scattering is dominating and mainly responsible for decrease in thermal conductivity at higher temperatures.

## INTRODUCTION

Several materials including oxide thermoelectrics have been investigated as candidates for thermoelectric applications [1, 2] for their applications in waste heat recovery and Refrigeration. Cobalt oxide materials are very important for their good thermal stability, high oxidation resistance and low toxicity. Lanthanum- and cobalt-site substitutions have been applied in the  $\text{LaCoO}_3$  system to enhance the thermoelectric performance [3, 4]. Li *et al.* has reported the significant improvement in the thermoelectric figure of merit ( $ZT$ ) of  $\text{LaCoO}_3$  by substituting Cu at Co site [5]. The maximum peak value of  $ZT$  is observed for  $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$  at  $x=0.15$ . The increase in  $ZT$  is due to increase in thermoelectric power and decrease in thermal conductivity.

The effect of Cu content on the microstructure and thermoelectric property of  $\text{Bi}_{2-x}\text{Cu}_x\text{S}_3$  bulk samples was also investigated by Ge *et al* [6]. It was found that the subtle tailoring of Cu content could reduce both the electrical resistivity and the thermal conductivity at the same time, and consequently enhancing the thermoelectric properties. The low thermal conductivity is supposed to be due to the nanoscopic Cu-rich regions embedded in the host matrix. A peak  $ZT$  value of 0.34 at 573 K is achieved for the  $\text{Bi}_{1.995}\text{Cu}_{0.005}\text{S}_3$  composition, which is the highest value reported in  $\text{Bi}_2\text{S}_3$  systems [6].

Further, the charge carriers in  $\text{LaCoO}_3$  are introduced by heterovalent substitution on the cobalt sites. The results on the electron doped  $\text{LaCo}_{1-y}\text{Ti}_y\text{O}_3$  and hole doped  $\text{LaCo}_{1-y}\text{Mg}_y\text{O}_3$  systems show that the large spin polarons are formed for both types of carriers [7]. A remarkable result on temperature dependence of electrical resistivity of the lightly doped  $\text{LaCo}_{1-y}\text{Ti}_y\text{O}_3$  is observed, where the resistivity is decreased by about four orders with optimum doping. The positive and maximum thermopower is observed at around 150–200 K for  $\text{LaCo}_{0.67}\text{Cu}_{0.33}\text{O}_{3-\delta}$  (for  $\delta=0.04$ ) which points to the dominant hole character of mobile carriers in a very narrow band [8]. Androulakis *et al.* has presented electrical resistivity, thermal conductivity, and thermopower of polycrystalline Sr-doped  $\text{LaCoO}_3$  with composition  $\text{La}_{0.95}\text{Sr}_{0.05}\text{CoO}_3$  and found a very respectable room-temperature thermoelectric figure of merit value of 0.18 [9].

## THE MODEL

A simple model where the phonons are described in the Debye model is used for evaluation of thermal conductivity. The use of the Debye model is reasonable since the temperature region of interest lies around the Debye temperature.

We begin with a model Hamiltonian that follows

$$\begin{aligned}
H = & \sum_k \varepsilon_k a_k^+ a_k + \sum_q \omega_q b_q^+ b_q + D_p \sum_{k,q} \left[ \frac{\hbar}{2\rho\omega_q} \right]^{1/2} a_{k+q}^+ a_k (b_q + b_{-q}^+) \\
& + \frac{M_i}{2N} \sum_{q_1, q_2} e^{i(q_1+q_2)r_i} \left[ \frac{\hbar\omega_{q_1} \hbar\omega_{q_2}}{4} \right]^{1/2} (b_{q_1} - b_{-q_1}^+) (b_{q_2} - b_{-q_2}^+) + H_{ph-ph}.
\end{aligned} \tag{1}$$

Here, initial two terms are electrons as carriers and phonon excitation. The third and fourth terms represent the phonon-carrier and phonon-impurity interactions respectively and the last term stands for the phonon-phonon interaction. The notations  $a$  ( $a^+$ ) and  $b$  ( $b^+$ ) are the creation (annihilation) operators for electrons and phonons. Further,  $\varepsilon_k$  is electron free energy, phonon frequency of a wave vector  $q$  is  $\omega_q$ ,  $D_p$  is the deformation-potential constant.  $M_i$  is the relative ionic-mass difference  $[(M''-M)/M'']$ , respectively.  $N$  is number of cells.  $\rho$  being the mass density of ions and  $r_i$  stands for the position of defects.

The thermal conductivity following model Hamiltonian (equation 1) can be calculated from the Kubo formula. The lattice thermal conductivity in continuum approximation follows

$$\kappa_{ph} = \frac{k_B \hbar^2}{2\pi^2 v_s} \int_0^{\omega_D} d\omega \omega^2 \tau(\omega) (\beta\omega)^2 \frac{e^{\beta\omega}}{(e^{\beta\omega} - 1)^2}. \tag{2}$$

with  $k_B$  is the Boltzman constant,  $v_s$  is the sound velocity,  $\omega_D$  is the Debye frequency and  $\beta = \hbar/k_B T$ . The relaxation time is proportional to the imaginary part of the phonon self-energy. In the weak interaction case, it has been calculated to the lowest order of the various interactions. The relaxation times are expressed as

$$1/\tau(\omega) = 2|\text{Im} P(\omega/v_s, \omega)| \tag{3}$$

$$= 1/\tau_{ph-d} + 1/\tau_{ph-e} + 1/\tau_{ph-gb} + 1/\tau_{ph-ph}, \tag{4}$$

with the various relaxation rates are defined as

$$\tau_{ph-d}^{-1}(\omega) = (P_d / k_B^3) \omega^4 \hbar^3, \tag{5}$$

$$\tau_{ph-e}^{-1}(\omega) = P_e \omega n_F(\Delta), \tag{6}$$

$$\tau_{ph-gb}^{-1}(\omega) = P_{gb} v_s / L, \tag{7}$$

$$\tau_{ph-ph}^{-1}(\omega) = P_p (T\omega\hbar / k_B)^3. \tag{8}$$

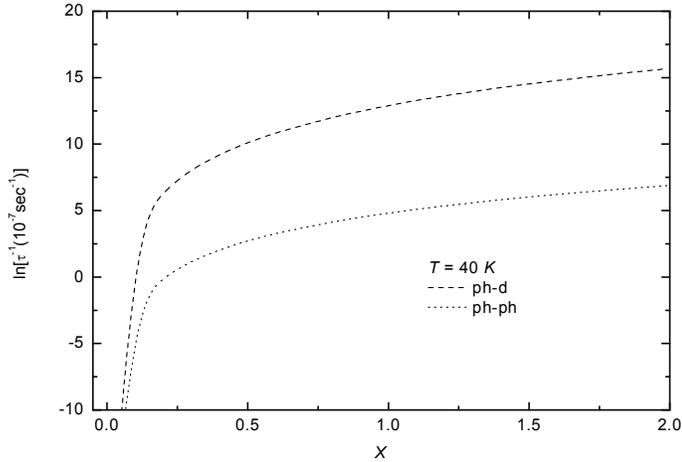
where  $L$  is the sample size,  $n_F$  is the Fermi-Dirac distribution function and  $\Delta$  is the gap function. The notation  $\tau_{ph-d}$ ,  $\tau_{ph-e}$ ,  $\tau_{ph-gb}$ , and  $\tau_{ph-ph}$  are the phonon scattering relaxation time due to defects, carriers, grain boundaries, and phonon-phonon interactions respectively.

## RESULTS AND DISCUSSION

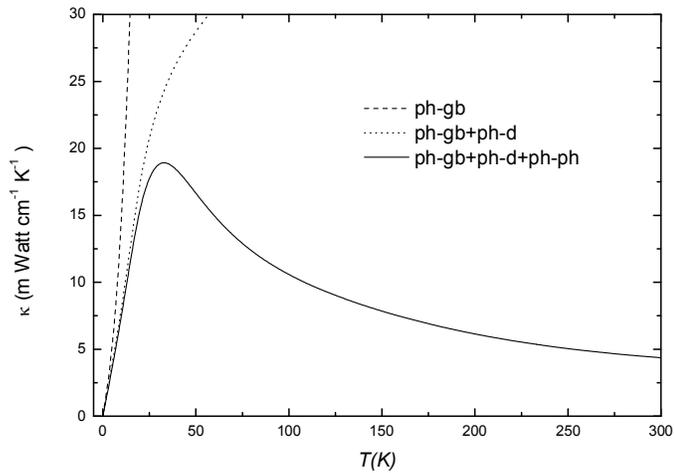
Figure 1 shows various scattering phonon relaxation rates as a function of  $x$  ( $= \hbar\omega/k_B T$ ) at  $T = 40$  from Eq. (4-6). It can be seen that the phonon-defect and phonon-phonon scattering rates are low at lower temperatures and increases with increase in temperature. The scattering rates increases rapidly at low frequencies ( $x$ ), becomes almost saturate at high frequencies and become almost independent of frequency. Above features of relaxation rates can very well explain the negative temperature dependence of thermal conductivity and relative contribution due to various scattering processes towards thermal conductivity.

Figure 2 shows our results for phonon thermal conductivity of LaCoCuO At very low temperature ( $T < 40$  K), the quasi particle excitation condensed into the ground state and they cannot scatter phonons. The phononic thermal conductivity, thus, increases exponentially with temperature. In figure 3 (dashed line) shows that thermal conductivity increase abruptly with temperate, when only phonon-grain boundary scattering is considered, in the

absence of the other scattering mechanism. Since phonon-defect and phonon-phonon scatterings show temperature dependence behaviour, thus they decrease the thermal conductivity as temperature is increased. Although the phonon thermal conductivity experiences an exponential increase at low temperature, the presence of the defect scattering set a limit on its growth. Further the phonon-phonon scattering dominates at higher temperature as phonon-phonon scattering shows power temperature dependence; as a consequence the phononic thermal conductivity diminishes as the temperature increases further.



**Figure 1:** Variation of phonon relaxation rates as a function of  $x (= \hbar\omega/k_B T)$  for  $T = 40$  K.



**Figure 3.** Variation of thermal conductivity as function of temperature in the presence of various phonon scattering mechanism.

## CONCLUSION

Above results show that appropriate doping in host material is seems to be the best solution for tuning thermal transport in ceramic/oxide materials. The atomic substitution in alloys can efficiently scatter phonons, that is the main reason behind the improvement in thermoelectric properties. Thus, systematic theoretical investigation is required which is expected to serve as a guide for producing the next generation thermoelectric materials.

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