Phonon thermal transport and phonon–magnon coupling in polycrystalline BiFeO₃ systems

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Abstract
Temperature-dependent thermal conductivity of polycrystalline BiFeO₃, Bi₀.⁹Ba₀.₀⁵Ca₀.₀⁵FeO₂.⁹₅ and Bi₀.⁹Ca₀.₁FeO₂.⁹₅ materials was measured using a direct heat pulse technique. Thermal conductivity of the BiFeO₃-based materials is analyzed using a phonon model to probe the thermal transport mechanisms in these ferrites. It is found that the calculated thermal conductivity of the BiFeO₃-based compounds is in good agreement with experimental data. The suppression of the low-temperature phonon peak in the thermal conductivity of the doped BiFeO₃ materials is mainly attributed to the phonon-point-defect scattering. In addition, the contribution of optical phonon–magnon resonance scattering to optical phonon thermal transport reveals the presence of phonon–magnon coupling in these BiFeO₃ materials. Finally, magneto-thermal conductivity measurements show the magnon thermal transport in pure and doped BiFeO₃ systems.

Keywords: multiferroics, phonon thermal transport, phonon–magnon coupling

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(Some figures may appear in colour only in the online journal)

1. Introduction

Bismuth ferrite (BiFeO₃) is widely investigated in the last decade because of a large variety of interesting phenomena it exhibits, such as spontaneous polarization, spontaneous magnetization, piezoelectricity, spin wave (magnons) branches, magnetoelectric coupling, photovoltaic and exchange bias [1–4]. Particularly, BiFeO₃ is well-known as a room-temperature multiferroic material [2–8], as it possesses a ferroelectric nature below the Curie temperature, $T_C = 1100$ K and also exhibits antiferromagnetic ordering below the Néel temperature, $T_N$ of 643 K [7]. In a recent theoretical study, multiple magnetodielectric resonances in incommensurate multiferroic BiFeO₃ were observed due to the coupling of the optical phonons at zero wave vector to magnons at integer multiples of the cycloid wave vector [9]. In addition to the possible existence of these spin excitations, electromagnons were also observed experimentally in the multiferroic BiFeO₃ using a low-energy Raman scattering study [10].

It is well-established that one of the primary mechanisms for magnetoelectric coupling in highly ordered BiFeO₃ lies within the interactions between spin waves (magnons) and polarization waves (optical phonons) [11, 12], which give rise to low frequency magneto-optical resonances in the dielectric susceptibility below the lowest optical phonon at 2THz [9]. The so-called electromagnon excitation could presumably be a source of origin for the observed dielectric anomaly below 100 K in the pure and Ca doped BiFeO₃ [13, 14]. It is found that the observed magneto-dielectric effects in the Bi₀.⁹Ca₀.₁FeO₂.⁹₅ material [14] can be explained by considering the enhancement of weak ferromagnetic moments to the energy gain of the Dzyaloshinskii–Moriya (DM) interaction under an external magnetic field [15]. From these studies, it was noticed that the coupling among lattice, spin and charge...
degrees of freedom persists at low temperatures in BiFeO$_3$, which also depends on the chemical pressure induced by Ca doping [13, 14]. Recently, Lu et al. have reported a detailed investigation of the heat capacity of a BiFeO$_3$ single crystal in the temperature range 2–300 K [16]. From the analyses of the low-temperature heat capacity data, Lu et al. proposed the existence of an anisotropy gap of magnon modes of the order of 6 meV. However, the first principle calculation by Wang et al. suggested that the deviation of the Debye $T^3$ law at low temperatures is due to the traces of gapless magnons of an isotropic antiferromagnet [17].

With the growing attention in the ferroelectric-magnetism coexisting multiferroic system, thermal transport in rare-earth manganites, RMnO$_3$ [18–23] and multiferroic LiCu$_2$O$_2$ [24] was investigated to reveal the phonon–magnon coupling in these systems. Low-temperature heat transport is an important physical property of solids and is useful for probing different kinds of elementary excitations, such as phonons, electrons and magnons etc. Thermal conductivity ($\kappa$) is strongly dependent on the statistical laws of these excitations and their transport properties, which are directly related to the nature of the ground state of materials [25]. For example, the temperature-dependent thermal conductivity at very low temperatures can directly show phononic transport, pairing symmetries of superconductors, Fermi-liquid state of the metals and nature of the spin liquid in quantum magnets [20]. The understanding of scattering mechanisms between different types of quasi-particles is of great importance, while the low-temperature heat transport can be an effective way to detect such couplings. In particular, the spin-phonon or magnon–phonon couplings in the insulating magnetic materials can be revealed by the measurements of magnetic field dependent thermal conductivity [19, 20, 24]. In the case of magnetic excitations, either transporting heat or strongly scattering phonons can be sensitively probed by the thermal conductivity measurements. On the other hand, the magnetic phase transitions, including the changes of either the ground state or the spin structure, can also be detected by measuring temperature dependent $\kappa$ [18–22, 24]. Recently, the effective thermal conductivity of BiFeO$_3$ thin films in the temperature range 100–400 K has been estimated using time domain thermo-reflectance measurements [26]. It is found that the thermal conductivity of BiFeO$_3$ thin films is affected by size effects due to thin film geometry and also by domain wall effects. Very recently, Uma and Philip have measured the magneto-thermal conductivity on the polycrystalline and nanocrystalline BiFeO$_3$ materials over the temperature range 120–250 K [27]. In the present article, our main aim is to investigate the phonon–magnon or magnetoelastic coupling in the pure and Ca doped BiFeO$_3$ materials using temperature-dependent thermal conductivity measurements. It is noticed that the magnon and its interaction with the phonon has a substantial contribution to thermal transport in these ferrite systems, which could possibly be responsible for the observed dielectric anomaly below 100 K in these materials [9, 13, 14].

2. Experiments

We have synthesized pure and Ca doped BiFeO$_3$ samples by the sol–gel route described elsewhere [7, 8] and their physical properties such as structural, electrical, magnetic and magnetoelastic properties have also been studied [7, 8, 13, 14]. We present here an investigation on temperature-dependent thermal conductivity of polycrystalline BiFeO$_3$, Bi$_{0.9}$Ba$_{0.05}$Ca$_{0.05}$FeO$_{2.95}$ and Bi$_{0.9}$Ba$_{0.05}$Ca$_{0.05}$FeO$_{2.95}$ ceramic samples over the temperature range of 4–300 K, measured using a direct heat-pulse technique. Samples were cut into a rectangular parallelepiped shape (size of $\sim 1.5 \times 1.5 \times 6.0$ mm$^3$) with one end glued (with thermal epoxy) to a copper block as a heat sink. A calibrated chip resistor (100Ω at room temperature) served as a heat source was glued to the other end. The temperature difference was measured by an $E$-type differential thermocouple with junctions thermally attached to two well-separated places along the sample. The temperature difference was controlled to be less than 1 K to minimize the heat radiation. During measurements, the samples were placed in a good vacuum (about $10^{-4}$torr) to avoid heat loss through convection. Further details about the measurement technique can be found elsewhere [28]. Magneto-thermal conductivity measurement on these BiFeO$_3$ samples was also carried out at room temperature to trace the role of magnons in thermal transport of these materials.

3. Results and discussion

The measured temperature-dependent thermal conductivity, $\kappa(T)$ of the pure and Ca doped BiFeO$_3$ samples is shown in figure 1. The room-temperature thermal conductivity of pure BiFeO$_3$ has a similar value ($\sim 3.5$ Wm$^{-1}$K$^{-1}$) to that of the BiFeO$_3$ thin films [26], however its temperature-dependence is somewhat different from that of the normal insulators [25],
which usually follows a 1/T-dependence at high temperatures due to the phonon–phonon Umklapp scattering. On the other hand, the room-temperature κ value is noticeably reduced to \(-2\) Wm\(^{-1}\)K\(^{-1}\) upon doping of Ca and Ba in BiFeO\(_3\). For pure BiFeO\(_3\), it is seen that the value of κ increases with lowering temperature and reaches a peak value of about \(-7.0\) Wm\(^{-1}\)K\(^{-1}\) at around 30 K. This feature is commonly seen in crystalline solids and the maximum (phonon peak) takes place at the temperature where the phonon mean free path is approximately equal to the crystal site distance, ascribed to the phonon–phonon scattering (Umklapp process). However, the magnitude of the phonon peak is strongly suppressed below 1.0 Wm\(^{-1}\)K\(^{-1}\) upon the doping, most likely due to the introduction of point-defects/impurities through the substitution of Ca and Ca–Ba into Bi sites of BiFeO\(_3\). Such a behavior will be further discussed in detail later using a phonon model.

Moreover, the κ(T) of the doped BiFeO\(_3\) samples shows weak temperature dependence in the range 20–50 K, followed by an exponential growth with temperature above 50 K as shown by the arrows in the figure 1 and then appears to be saturated above 200 K. The observed excess thermal conduction (the rapid increase in κ above 200 K) is mainly ascribed to the lattice phonons. This characteristic agrees well with the observation in substituted magnetic materials, as the optical phonons could be a possible channel for heat transport, which contributes about 40% to the total phonon thermal conduction in the doped La\(_2\)CuO\(_4\) [29]. Hence, the present observation in κ(T) of the BiFeO\(_3\)-based systems indicates that there is another heat transport channel in addition to acoustic phonon thermal transport. It should also be noted here that considerable heat transport by optical phonons could be possible in these studied compounds if their energy is not too high to be excited at higher temperatures of about \(\leq 300\) K, similar to the observation in the substituted La\(_2\)CuO\(_4\) [29].

Although optical modes of vibration are usually ignored for the analysis of heat conduction because of their small group velocity, they could still be a significant factor to κ under certain conditions, e.g. there are many of such modes [30]. There are 3N-3 optical modes in a solid with N atoms per primitive unit cell. The number (27) of these modes will be considered in the material such as BiFeO\(_3\), which has 10 atoms in the primitive unit cell. Due to the relatively high energy of optical vibrations, they could only be excited at elevated temperatures. This characteristic agrees well with the observation in the measured κ(T) data of these BiFeO\(_3\) samples, in which the excess thermal conduction is observed at high temperatures above 50 K. This feature is much more obviously seen in the doped BiFeO\(_3\) samples, most likely due to the enhancement in phonon-grain boundary scattering as they have a smaller grain size than that of pure BiFeO\(_3\) [8]. Subsequently, we have attempted to analyze the measured thermal conductivity data of these materials by using a phonon model described earlier by Jiang et al [21], where the contribution of the optical phonon as the excess thermal conduction at high temperatures is taken into account. Hence, both acoustic and optical phonons have contribute significantly to thermal conductivity in the heat transport process of these ferrite materials. It should be noted here that the electronic contribution to thermal conductivity can be neglected due to the insulating nature of the materials in the present study [8] and hence the heat conduction is mainly ascribed to the lattice phonons.

The thermal conductivity can be simply expressed as a sum of the two contributions κ = κ\(_{\text{ph}}\) + κ\(_{\text{oph}}\), where κ\(_{\text{ph}}\) and κ\(_{\text{oph}}\) are the acoustic and optical phonon thermal conductivities respectively. Using the Debye model, the acoustic phonon thermal conductivity [21], can be expressed as

\[
\kappa_{\text{ph}} = \frac{k_B}{2\pi^2 v_{\text{ph}}(k_B T)^3} \int_0^{\theta_B/T} \frac{x^4 e^x}{(e^x - 1)^2} \tau_{\text{ph}}(\omega, T) \, dx, \quad (1)
\]

where \(k_B\), \(h\), \(\tau_{\text{ph}}(\omega, T)\) and \(\theta_B\) are the Boltzmann constant, the reduced Planck’s constant, the mean lifetime of phonon and the Debye temperature in the acoustic phonon system, respectively and \(x \equiv h\omega/k_BT\). For further simplification, we assume that all mechanisms of phonon scattering act independently. In this case,

\[
\tau_{\text{ph}}^{-1}(\omega, T) = \frac{v_{\text{ph}}}{L} + A_1 \omega^4 + B_1 \omega^2 T \exp\left(\frac{-\theta_B}{b T}\right) + \tau_{\text{red}}^{-1}, \quad (2)
\]

where the four terms correspond to the acoustic phonon scattering at grain boundaries, at point defects, phonon–phonon process and the resonant scattering, respectively. \(A_1\), \(B_1\) and \(b\) are free parameters and the parameter \(L\) is comparable to the smallest sample dimension. The resonant term can be written as

\[
\tau_{\text{red}}^{-1} = \frac{D}{\omega^4} \left[ 1 - \tanh^2 \left( \frac{\hbar \omega}{2k_BT} \right) \right], \quad (3)
\]

where \(D\) is the parameter representing the strength of resonant scattering. Equation (3) describes the phonon scattering by magnetic objects such as magnons. In the process of acoustic phonon and magnon collisions, a resonant frequency denoted as \(\omega_0\) in equation (3), will be observed at the intersection of the two dispersion curves, which is also the frequency of the magnetoelastic coupling mode.

While the optical phonon is also taken into account in the heat transport process along with the acoustic phonon, we can formulate the optical phonon thermal conductivity in a similar way to that of the acoustic phonon. Based on the Einstein model, the thermal conductivity for all optical branches [21], can be described as

\[
\kappa_{\text{oph}} = n m_{\text{oph}}^2 R \left( \frac{\theta_E}{T} \right)^2 \exp\left( \frac{\theta_E}{T} \right) \left[ \exp\left( \frac{\theta_E}{T} \right) - 1 \right]^{-1} \tau_{\text{oph}}(\omega_0, T), \quad (4)
\]

where \(\theta_E\) is the Einstein temperature and \(n\) is the number of optical branches and

\[
\tau_{\text{oph}}^{-1}(\omega_0, T) = \frac{v_{\text{ph}}}{L} + A_2 \omega_0^4 + B_2 \omega_0^2 T \exp\left(\frac{-\theta_E}{b T}\right) + \tau_{\text{red}}^{-1}, \quad (5)
\]

where \(\theta_E \equiv h\omega_0 d/k_B\). For simplicity, an effective frequency \(\omega_{\text{eff}}\) (= \(\omega_0\)) for all optical vibration branches is used here. Here, all the terms and parameters in equations (4) and (5) have the
The calculated acoustic phonon (\(\kappa_{\text{aph}}\)) and optical phonon thermal conductivities of the pure BiFeO\(_3\) are also reported in Table 1. The measured and calculated thermal conductivity as a function of temperature of pure BiFeO\(_3\) along with its calculated acoustic and optical phonon thermal conductivities and (b) the measured thermal conductivity of pure BiFeO\(_3\) can be satisfactorily reproduced using the phonon model (described in equations (1)-(3)). It is seen that the phonon model (as shown by the solid lines in the figure 2(b)) describes measured \(\kappa(T)\) doped BiFeO\(_3\) materials quite well over a wide temperature range of 4–300 K. Some of the obtained parameters for the \(\kappa_{\text{aph}}\) and \(\kappa_{\text{oph}}\) of the pure and doped BiFeO\(_3\) samples are listed in tables 1 and 2. The value of other parameters such as \(a_0\), \(a_0\)eff, \(a_1\) and \(a_2\) (\(<2N^{1/3}\)) are about 3.8 \(\times\) 10\(^{13}\) Hz [16], 1 \(\times\) 10\(^{13}\) Hz, 2 \(\times\) 10\(^{13}\) Hz [9] and 4.31, respectively. The value of the Debye temperature (\(\theta_D\)) used for the BiFeO\(_3\)-based samples is about 292 K [16], and the values of Einstein temperature (\(\theta_E\)) used here are about 200, 340 and 310 K for BiFeO\(_3\), Bi\(_{0.9}\)Ba\(_{0.05}\)C

\[a_{0.05}\text{FeO}_{2.95}\] and Bi\(_{0.9}\)Ca\(_{0.1}\)FeO\(_{2.95}\), respectively. The group velocity of the optical phonon is very low compared to that of the acoustic phonon (\(v_{\text{aph}} \approx 3.3 \times 10^4\) m s\(^{-1}\)). As the parameter \(v/L\) for optical phonon thermal transport is found to be an order of magnitude smaller than that of acoustic phonon (tables 1 and 2). Therefore, the large number of optical modes compensates for their low velocity and hence the contribution from \(\kappa_{\text{oph}}\) cannot be ignored [31].

Furthermore, it is noticed that the values of \(v_{\text{oph}}/L\) and pre-factor \(A_1\) for the acoustic phonon thermal conductivity are found to increase significantly with substitution of Ca and Ba–Ca in BiFeO\(_3\) (table 1). This observation shows the importance of grain boundary and point-defect scatterings of phonons in the lattice thermal conductivity of the doped BiFeO\(_3\) systems. Generally, the grain boundary scattering is a dominant mechanism for the low-temperature lattice thermal conductivity, which is clearly functioning in the doped BiFeO\(_3\) samples as the phonon peak feature in these compounds is strongly suppressed. It is most likely due to the fact that the estimated grain size \(L\) of the doped BiFeO\(_3\) samples (~1 \(\mu\)m) is found to be much smaller than that of pure BiFeO\(_3\) (~15 \(\mu\)m), consistent with the observation by the scanning electron microscopy study reported earlier [8]. On the other hand, the point-defect scattering has a strong influence on the appearance of the shape and position of the phonon peak which occurs near 30 K in the presently studied ferrite systems. Therefore, the variations of lattice thermal conductivity at low temperatures in the doped BiFeO\(_3\) samples are essentially due to the modification of the phonon-point-defect scattering by the doping. From table 1, it is evident that the parameter \(A_1\) increases drastically upon doping of Ca and Ba in BiFeO\(_3\), suggesting the introduction of a great amount of point defects by the doping, according to the model proposed by Klemens [32]. In fact, the point-defect scattering is most likely originated from the mass fluctuations between Bi and the dopant (Ca and Ba), since their atomic mass and atomic radius differences are quite large (>30\%). However, the deviation from \(1/T\) dependence at high temperatures for the doped BiFeO\(_3\) samples could be a generic feature of the thermal conductivity with a considerable amount of contribution from the optical phonons, which usually have a weak temperature dependence [29]. Hence, the magnetic heat transport can be carefully introduced to explain the abnormal temperature dependence in these materials with many atoms per unit cell and/or dispersive optical phonons which have a high group velocity [29, 30].

The group velocity of optical phonons for the doped systems might have reduced as the energy of low-frequency optical

\[
\begin{array}{cccc}
\text{Sample} & \nu_{\text{oph}}/L \quad (\times10^7 \text{s}^{-1}) & A_1 \quad (\times10^{-42} \text{s}^3) & B_1 \quad (\times10^{-18} \text{sK}^{-1}) & D_1 \quad (\times10^8 \text{s}^{-1}) \\
\text{BiFeO}_3 & 22.0 & 13.1 & 2.8 & 1.0 \\
\text{Bi}_{0.9}\text{Ba}_{0.05}\text{Ca}_{0.05}\text{FeO}_{2.95} & 600.0 & 82.0 & 85.0 & 2.0 \\
\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95} & 240.0 & 82.0 & 63.0 & 2.0 \\
\end{array}
\]

### Table 2. The deduced free-fitting parameters for relaxation time of optical phonon thermal conductivity in pure and doped BiFeO\(_3\) materials using the equations (4) and (5).

\[
\begin{array}{cccc}
\text{Sample} & \nu_{\text{oph}}/L \quad (\times10^7 \text{s}^{-1}) & A_2 \quad (\times10^{-46} \text{s}^3) & B_2 \quad (\times10^{-21} \text{sK}^{-1}) & D_2 \quad (\times10^8 \text{s}^{-1}) \\
\text{BiFeO}_3 & 5.0 & 2.0 & 1.0 & 2.0 \\
\text{Bi}_{0.9}\text{Ba}_{0.05}\text{Ca}_{0.05}\text{FeO}_{2.95} & 7.5 & 4.0 & 0.3 & 0.4 \\
\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_{2.95} & 5.6 & 3.0 & 0.1 & 0.4 \\
\end{array}
\]
The calculated acoustic phonon thermal conductivity as a function of temperature of the pure (y-axis in left panel) and doped BiFeO₃ materials (y-axis in right panel) and the calculated optical phonon thermal conductivity versus temperature for the BiFeO₃-based systems.

Figure 3. (a) The calculated acoustic phonon thermal conductivity as a function of temperature of the pure (y-axis in left panel) and doped BiFeO₃ materials (y-axis in right panel) and (b) the optical phonon thermal conductivity versus temperature for the BiFeO₃-based systems.

The estimated acoustic and optical phonon thermal conductivities of the pure and doped BiFeO₃ samples are displayed in figures 3(a) and (b), respectively. It is noticed that the phonon peak in the acoustic phonon thermal conductivity near 30 K is found to be strongly suppressed from ~7 Wm⁻¹K⁻¹ to below 1.0 Wm⁻¹K⁻¹, as well as shifted slightly to a lower temperature upon doping of Ca [33]. On the other hand, the values of parameters of $v_{opt}/L$, $A_2$, and $B_z$ for optical phonon thermal transport vary slightly upon doping, whereas the resonant term ($D_2$) is found to reduce significantly (table 2) as compared to that of pure BiFeO₃. According to the kinetic theory of lattice thermal conductivity, the acoustic phonon heat transport has the strongest temperature dependence (follows the Debye $T^3$ law) at low temperatures than that of optical heat transport, which is clearly evident in the figures 2 and 3.

The estimated acoustic and optical phonon thermal conductivities of the pure and doped BiFeO₃ samples are displayed in figures 3(a) and (b), respectively. It is noticed that the phonon peak in the acoustic phonon thermal conductivity near 30 K is found to be strongly suppressed from ~7 Wm⁻¹K⁻¹ to below 1.0 Wm⁻¹K⁻¹, as well as shifted slightly to a lower temperature upon doping of Ca and Ba onto the Bi sites of BiFeO₃ (figure 3(a)). Besides, the room-temperature acoustic phonon thermal conductivity of the doped BiFeO₃ samples is reduced to ~0.2 Wm⁻¹K⁻¹ from 2.9 Wm⁻¹K⁻¹ of pure BiFeO₃. Conversely, the room-temperature optical phonon thermal conductivity of the doped BiFeO₃ samples is found to be increased above 1.5 Wm⁻¹K⁻¹ from 0.7 Wm⁻¹K⁻¹ of pure BiFeO₃ (figure 3(b)). It is also noticed that the optical phonon starts to contribute significantly to thermal conductivity near 40 K (25 K) for the doped (pure) BiFeO₃, which is marked by the arrows in figure 3(b) and then tends to saturate above 200 K. Such a feature is essentially due to the reduction in the optical phonon–magnon resonant scattering term, as the parameter $D_2$ decreases by a factor of 5 upon the doping of Ca and Ba (table 2). As a result, the optical phonon–magnon resonant scattering term contributes about 35 and 60% to optical phonon thermal transport in the pure and doped BiFeO₃ systems respectively, reflecting the fact that the lattice distortions induced by the doping play an important role in determining the magnetic ground state [8, 34] and the softening of low-energy optical phonon modes [33].

Now, we are in the position to discuss the contribution of the phonon–magnon scattering to the thermal conductivity in BiFeO₃-based materials. From the thermal transport study, it is noticed that the enhancement in the phonon–magnon scattering term, which may have resulted from the improved magnetic ordering in BiFeO₃ by the doping [8]. It should also be noted here that Bi₁₀₀₋₉Ba₀.₀₅Ca₀.₀₅FeO₂.₉₅ and Bi₁₀₀₋₉Ca₀.₁FeO₂.₉₅ materials are weak ferromagnetic while pure BiFeO₃ is antiferromagnetic. The resonance term between the optical phonon and magnon indicates the phonon–magnon interaction [9, 10], which may be a source of origin for the anomalous features below 100K in dielectric data of the BiFeO₃-based materials [13, 14]. It is also found that the dielectric anomaly in the doped BiFeO₃ samples is shifted to a higher temperature of above 50 from 23 K of pure BiFeO₃ [14]. This seems to have a direct correlation with the establishment of exponential increment in the $\kappa(T)$ for the pure and doped BiFeO₃ systems near 30 and 50 K respectively, at which the optical phonon thermal transport starts to contribute significantly to total thermal conductivity (see figures 1 and 3). It appears that the alterations in spin ordering (spin waves with different wave vector, [8]) and low-energy optical phonons (softened polarization waves, [33]) in the doped BiFeO₃ samples might have led to an improved phonon–magnon or magnetoelectric coupling due to the DM coupling between them, which in turn results in a substantial contribution to the optical phonon thermal conductivity.

In order to understand the interaction between different degrees of freedom such as charge, spin and lattice (phonon), herewith we are including the discussion on the magnetic ordering and the response of Raman modes in BiFeO₃ with the Ca content (from the [8] and [33]) to illustrate the coupling between these order parameters. We found that antiferromagnetic transition temperature ($T_N$) increases gradually with increasing Ca content from 643 K (BiFeO₃) to 647 K (Bi₁₀₀₋₉Ba₀.₀₅Ca₀.₀₅FeO₂.₉₅), due to the reduction in bond length of Fe–O–Fe as a result of chemical pressure induced by Ca doping [8]. Besides, the value of magnetic susceptibility for the Ca doped samples is found to increase sharply near $T_N$ with lowering temperature [8, 36], mainly due to a sharp rise in the paramagnetic susceptibility at $T_N$. Such a feature is associated with the antisymmetric spin coupling via an anisotropic superexchange interaction [35], which is a possible origin for the weak ferromagnetic ordering in the Ca doped BiFeO₃ [8]. It is also found that both remnant magnetization and coercive field increase quite linearly with the Ca content [8, 33]. Moreover, we have shown in our earlier studies that the coupling among the different order parameters such as charge,
and then starts to move towards positive value above 35 kOe. At lower magnetic field, the magnetic spins of the samples are still in canted states along the hard direction, which seems to be responsible for the observed weak field dependence in $\kappa$. However, these spin-flop and canted states transform into the saturated spin-flip states at the high magnetic fields [40], which could lead to a repopulation of magnons as a result of a small anisotropy gap of the magnon modes, and in turn a stronger field dependence in the measured $\kappa(H)$ [16, 41]. However, the observed decrease with $\kappa$ value in the magnetic fields is most likely due to the presence of magnon heat transport in these doped BiFeO$_3$ samples, as magnons tend to be less populated with an applied magnetic field [24]. Here, the magnons could be acting as heat carriers at elevated temperatures in these BiFeO$_3$ materials, especially in the doped BiFeO$_3$ samples [27]. It is worth mentioning here that we have reported an enhanced magneto-electric coupling in the doped BiFeO$_3$ samples from the magneto-dielectric measurements [14, 5] due to the strong DM interaction between lattice and spin order parameters upon an applied magnetic field [15]. Furthermore, the observed switchable magneto-dielectric effect in the doped BiFeO$_3$ samples can be attributed to the symmetry allowed second order coupling between the order parameters (polarization and magnetization) in the Ginzburg–Landau free energy [14, 6]. Our present magneto-thermal conductivity measurements, on the other hand, reveal that both phonons and magnons mediate heat transport in these BiFeO$_3$-based materials. 

4. Conclusion

An investigation on temperature-dependent thermal conductivity of polycrystalline BiFeO$_3$, Bi$_{0.9}$Ba$_{0.05}$Ca$_{0.05}$Fe$_{2.95}$ and Bi$_{0.9}$Ca$_{0.1}$FeO$_2$$_{2.95}$ multiferroic materials was carried out using a direct heat pulse technique. The room-temperature value of thermal conductivity was considerably reduced from ~3.5 to ~2 W m$^{-1}$ K$^{-1}$ upon the doping of Ca and Ba in BiFeO$_3$. In addition, the observed phonon peak in BiFeO$_3$ near 30 K is found to be strongly suppressed upon the doping. From the theoretical analysis by a phonon model, it is revealed that the suppression of the phonon peak in the thermal conductivity of the doped BiFeO$_3$ systems is essentially attributed to the phonon-point-defect scattering mechanism. It is also noticed that the phonon–magnon coupling in the BiFeO$_3$-based material is enhanced upon Ca doping, as the contribution of the optical phonon–magnon resonant scattering term to optical phonon thermal transport becomes more predominant with Ca content. Besides, the contribution from optical phonons to thermal transport in BiFeO$_3$ is found to increase considerably upon doping at high temperatures, presumably due to the enhancement of magnon-phonon coupling and softening of low-energy optical phonons driven by lattice distortions. Finally, it is observed that the magnons could act as heat carriers at elevated temperatures in pure and doped BiFeO$_3$ materials, as indicated by the magneto-thermal conductivity measurements.

5 See footnote 3.
6 See footnote 3.
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