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High Thermal Insulation Properties of $A_2FeCoO_{6-\delta}$ (A = Ca, Sr)

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Abstract: *Materials with low thermal conductivity are essential to providing thermal insulation to many technological systems, such as electronics, thermoelectrics and aerospace devices. Here, we report ultra-low thermal conductivity of two oxide materials.* $Sr_2FeCoO_{6-\delta}$ *has a perovskite-type structure with oxygen vacancies. It shows a thermal conductivity of 0.5* $Wm^{-1}K^{-1}$*, which is lower than those reported for perovskite oxides. The incorporation of calcium to form* $Ca_2FeCoO_{6-\delta}$*, leads to a structural change, and formation of different coordination geometries around transition metals. This structural transformation results in a remarkable enhancement of thermal insulation properties, showing the ultra-low thermal conductivity of 0.05* $Wm^{-1}K^{-1}$*, which is one of the lowest values found among solid materials to date. A comparison to previously reported perovskite oxides, which show significantly inferior thermal insulation compared to our materials, point to the effect of oxygen-vacancies and their ordering on thermal conductivity.*

Thermally insulating materials are vital for safety purposes and for the longevity of equipment or life span in high-temperature processes; be it as a surface coating or as a bulk insulator. In land-based gas turbines or airplanes or aerospace turbines, the combustion chamber, blades, and vanes constitute hot-section components. Land and aero-based gas turbines are coated with thermal insulating materials as a thermal barrier coating (TBC) for protecting metallic components. Materials with low thermal conductivity are also important for thermoelectric devices.[1] So, there are numerous studies that attempt to lower the thermal conductivity of different materials.[1]There are different oxide materials studied for their low thermal conductivity. Some examples of the studied oxide materials are VO_2, $La_2Zr_2O_7$, $La_2Ce_2O_7$, ZrO_2, Y_2O_3-ZrO_2, $SrTi_{0.9}Ta_{0.1}O_3$ etc.[1-3] One of the oxide materials is perovskite oxide. Some examples of the perovskite oxides studied for low thermal conductivity are $Sr_{0.85}La_{0.15}TiO_3$, $Sr(Ti_{0.8}Nb_{0.2})O_3$, $SrTi_{0.9}Ta_{0.1}O_3$ etc.[1] However, oxygen-deficient perovskite demonstrates better functional properties compared to fully occupied perovskites.[4] There has been evidence for the improvement of the functional properties in the perovskite oxides by generating oxygen vacancies and changing the crystal structures. For example, Oxygen vacancy was created in $CaMnO_3$ to get $CaMnO_{2.5}$ to study the effect of vacancy generation on electrocatalytic activity toward oxygen evolution reaction.[4] $CaMnO_{2.5}$ (also written as $Ca_2Mn_2O_5$ demonstrated much better catalytic activity compared to fully occupied $CaMnO_3$ toward oxygen generation from alkaline water.[4] Similarly, $SrMnO_3$ is a material without oxygen vacancy and that can be found with more than one crystal structure.[5] Some of the oxygens can be removed from the crystal to get the formula $SrMnO_{2.6}$ and $SrMnO_{2.5}$. They were studied for their electrocatalytic activity of oxygen evolution reaction. The catalytic activity was found improved as the number of vacancy increases. The catalytic performance was reported in the order as $SrMnO_{2.5} > SrMnO_{2.6} > SrMnO_3$.[5] So, ODPs have attracted more attention in the study of functional properties.[6-8] Thus, we are motivated to focus on oxygen deficient perovskites for their thermal insulation properties.

Oxygen deficient perovskites have a general formula, $ABO_{3-\delta}$. Here, A, B and δ usually stand for lanthanide/alkaline earth metal, transition metal and oxygen vacancy, respectively. When there is more than one crystallographic site for A or B, the general formula can be expressed as $AA'BB'O_{6-\delta}$. An ideal parent perovskite has cubic structure with full oxygen occupancy where A cations are surrounded by BO_6 octahedra, B cations are at the centers of octahedra, and O anions at the corners of the octahedra. Due to the oxygen vacancies in Oxygen-deficient perovskites (ODPs), they offer much structural flexibility. The vacancies can arrange in an ordered or disordered fashion in the crystal system. The ODP can resemble the fully occupied parent perovskite structure of the cubic system when the oxygen-vacancies are disordered. However, when ordered, the vacancies can arrange in several ways resulting in different structures and functional properties.[6] When vacancies are generated, they may result in various coordination geometries such as tetrahedra or square pyramids.[9] When tetrahedra are formed, they share corners with one another forming a layer that shares apexes with octahedral layers above and below. The overall structure will contain alternating octahedra and tetrahedra. Such type of arrangement produces the brownmillerite-type structure. [6]

Though there are numerous studies of different oxides and perovskites,[1, 10] much attention has not been found yet on ODPs for thermal insulation properties. Here in this report, the thermal insulation property of ODPs $Sr_2FeCoO_{6-\delta}$ (δ =0.5) and $Ca_2FeCoO_{6-\delta}$ (δ =0.9) are investigated where the thermal conductivity is found to vary with the vacancy concentration and order/disorder. Our compounds are not new. They have been extensively studied for their structures and other properties as discussed.[6] The focus of this article is to show the correlation between the oxygen vacancy (defect) and the thermal insulation property. These materials were synthesized by solid state reaction at high temperature in the same way and environment of the other previously reported perovskite oxides.[11-13] Our materials were sintered at 1200 ^{0}C in air. The detailed synthesis conditions and techniques are described in the supplementary information. The phase purity was confirmed by Rietveld refinement of powder X-ray diffraction data.[14, 15] Detailed XRD refinement profile and parameters are given in supporting information. The crystal structures of these materials have already been reported.[6] As discussed earlier, these two materials show different types of oxygen vacancy distributions. The Sr-based material has random distribution of vacancies, and its structure resembles the structure of a fully occupied perovskite (figure S1 of supporting information), while the Ca-based material has ordered vacancy distribution. The arrangement of vacancies in Ca-based material forms tetrahedral layers alternating with octahedral layers, similar to the so-called called brownmillerite structure. The Ca-based compound has *Pbcm* space group with double the unit cell size than that of a typical brownmillerite (refer the supporting information, figure S2). Thus, vacancies are created only in the tetrahedral layers but alternating with the octahedral layers. The vacancies are arranged in such a way that each tetrahedral chain is oriented opposite to its all nearest neighbors. Many functional properties have been reported for oxygen deficient perovskites associated with their structural difference.[6-8, 16] Therefore, an effect on thermal conductivity is anticipated.

The thermal conductivity data of the materials are collected using circular pellets of 13 mm diameter and 3 mm thickness. Similar dimensions have already been reported for thermal conductivity measurement of other materials which were also synthesized by solid state reactions.[11, 13] The detailed thermal conductivity measurement method and conditions for our materials are described in the supporting information. Our materials, which are oxygen deficient perovskites, have shown thermal conductivities lower than those of the reported fully occupied perovskite oxides. $Sr_2FeCoO_{6-\delta}$ (δ =0.5) and $Ca_2FeCoO_{6-\delta}$ (δ =0.9) have thermal conductivities of 0.5 and 0.05 W/m/K, respectively, at room temperature. Figure 1 shows the thermal conductivity vs temperature relation. The Thermal conductivity increases uniformly with temperature in both materials. However, vacancy disordered material $Sr_2FeCoO_{6-\delta}$ with smaller vacancy concentration does not only show higher thermal conductivity at room temperature but also the slope of conductivity increment increases with temperature in this material. The value for thermal conductivity of $Ca_2FeCoO_{6-\delta}$ is lower by more than an order of magnitude at room temperature. This is unprecedented among oxide systems. It indicates that oxygen vacancies can affect the thermal conductivity. Greater oxygen vacancy concentration and ordering are associated with lower thermal conductivity.

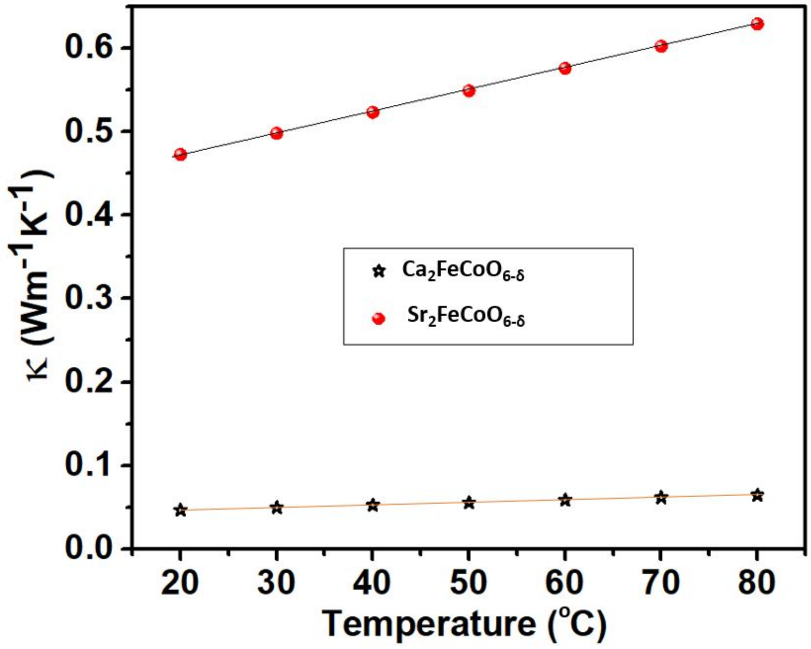

Figure 1. Thermal conductivity (κ) vs Temperature

The lowest reported thermal conductivity for fully occupied perovskite oxides are often near 1 W/m/K.[1] However, the thermal conductivity was reduced in $La_{1-x}Ba_xCoO_3$ to 0.5 – 0.6 W/m/K by partial substitution of A-site cation.[1, 17] La has +3 oxidation state and Ba has +2 oxidation state. Though the material was formulated as fully occupied perovskite oxide, the crystal lattice may have some oxygen deficiency due to Ba doping.

Thermal conductivity (K) is expressed as

$$K = \frac{Q}{A} \cdot \frac{L}{\Delta T}$$

Where *Q, A, L and* ΔT are heat flow, area of a sample, thickness of sample and temperature gradient, respectively. To validate our data, a standard sample of polystyrene was used for thermal conductivity measurement. Its thermal conductivity was found as 0.03 $Wm^{-1}K^{-1}$ which is a universally accepted value for this material,[7] and validates the thermal conductivity data of our materials.

Perovskite oxides are polycrystalline materials. In such materials, the heat flow takes place through a spectrum of phonons with different wavelengths and mean free paths.[18, 19] The interference on thermal phonons slows the propagation of heat.[19] It is well understood that local lattice distortions, vacancies, etc. can act as sites for phonon scattering, resulting in reduced thermal conductivity. Thus, different factors play a role in the reduction of thermal conductivity of perovskite oxides. Widely discussed factors are crystal structure variation, grain size[20], grain boundary[11, 21] and oxygen vacancy, which are associated with the increased phonon scattering, resulting in reduced thermal conductivity of the lattice. Many of the previous studies on polycrystalline materials, such as perovskite oxides, discuss oxygen vacancies or defect generation that increase the phonon scattering, resulting in the thermal conductivity reduction. One example is the study of $(Ca_{0.25}Sr_{0.25}Ba_{0.25}RE_{0.25})TiO_3$ ceramics, which showed the reduction of thermal conductivity with increase in oxygen vacancies. It also reported that the oxygen vacancy increment led to the phonon scattering.[11] There have been many other examples that attempt to lower the thermal conductivity of fully oxygen-occupied perovskite oxides by A-site or B-site cation substitution. For example, the thermal conductivity was suppressed by Ca and rare earth elements substitution in A-site in $Sr_{0.9-x}Ca_xLa_{0.1}TiO_3$ ($0 < x < 0.6$).[1, 22] The substitution lowered the thermal conductivity from 4.7 to 3.3 $Wm^{-1}K^{-1}$ when x increased from 0 to 0.6. In another example, $La_{1-x}Ba_xCoO_3$, the thermal conductivity decreased more and more as the value of x increased.[17] Similarly, the thermal conductivity diminished with the increase of x in $La_{1-x}Sr_xCoO_3$.[1, 23] The increase in Sr and Ba concentrations in these examples can lead to the formation of oxygen vacancies in the crystal lattice because La (+3 oxidation state) is partially substituted by Sr and Ba (+2 oxidation state). The decrease in thermal conductivity is due to the oxygen-vacancy formation.[1, 17, 23] Some reports attributed this effect to the point defect scattering and the lowered symmetry.[1, 22] Some reports clearly discussed the oxygen vacancy generation and its effectiveness in reducing thermal conductivity.[11] [12] Some reports considered the reduction of mean free path of phonons as a responsible factor for thermal conductivity reduction.[1, 22, 24] All those reports discussed that oxygen vacancies acted as strong scattering centers for phonons. Some researchers tried to create lattice distortions to increase phonon scattering.[24] The study of thermal conductivity in $CaMnO_3$ and $Ca_{0.9}R_{0.1}MnO_3$ revealed the dominant role of lattice distortion on phonon scattering, and the resulting reduction in thermal conductivity.[24] Thus, the thermal conductivity reduction was attributed to lattice distortion and phonon scattering.[25, 26] But in our materials, not the lattice distortion but the structural transformation takes place with the result of great variation of oxygen vacancy concentration. For many inorganic thermoelectric materials to improve the performance, the thermal conductivity was reduced by increasing the phonon scattering to reduce the lattice contribution.[27, 28] The reduction of thermal conductivity by B-site cation substitution has also been discussed based on phonon scattering and suppressing the lattice thermal conductivity. These were studied on $CaMnO_3$ where Mn was partially substituted by different elements.[1, 21, 29-31] In addition, phonon scattering was sometimes realized by the introduction of grain boundary.[1, 21] The greater in number and more random the grain boundaries are, the higher is the effect on the phonon scattering, and the lower is the thermal conductivity.[1, 21, 32] If grain size is different, it may also affect the phonon scattering and thermal conductivity. The lower the grain size, the higher the phonon scattering and the lower the thermal conductivity.[20, 32]

The total thermal conduction is generally considered as the sum of the contributions from phonons and photons (radiations)

$$K = K_p + K_R$$

where K_p is the thermal conductivity contribution of phonon scattering by lattice, grain boundaries and point defects and K_R is the thermal conductivity contribution by radiation.[33] For example, the phonon scattering in porous yttria stabilized zirconia was considered due to (i) lattice anharmonicity, (ii) oxygen vacancies, and (iii) oxygen vacancy jumping. [33]

SEM images of our materials illustrate the grains and boundaries, showing the well sintered materials. Grain size difference is not clear between these two materials. The average grain size looks similar for both materials. In such a case, the grain size contribution can be ignored for their thermal conductivity difference, as reported in a previous work.[20] In SEM images of both compounds, boundaries are observed, separating the grains. There is not a major difference in the grain boundaries of these two materials. So, grain boundary contribution to thermal resistance can be considered insignificant though it could still influence thermal conductivity/resistance.[1, 11, 21, 34]

Co^{2+}, Co^{3+} and Co^{4+} spins may play a role in the thermal conductivity because these cations act as electron holes, and electrons are, in most cases, considered the thermal energy carrier. However, this is not the only factor that controls thermal conductivity. In the case of electron doped $CaMnO_3$ or $Ca_{0.9}R_{0.1}MnO_3$, phonon scattering becomes more dominant than the contributions of electrons and spins.[24] Similarly, a $SrTiO_3$-related oxygen deficient compound demonstrated the dominant effect of phonon scattering over electronic contribution.[13] The experiment patterns and result patterns of our materials are similar to those previous reports. $Ca_2FeCoO_{6-\delta}$ has one more type of cobalt ion, Co^{2+} which $Sr_2FeCoO_{6-\delta}$ does not possess. If the electronic or spin contribution is dominant, $Ca_2FeCoO_{6-\delta}$ could have higher thermal conductivity compared to $Sr_2FeCoO_{6-\delta.}$ The decreasing tendency of thermal conductivity with increase in oxygen deficiency (void spaces) indicates that oxygen vacancies act as phonon scattering centers in our materials, which suggests that the role of Co^{2+}, Co^{3+} and Co^{4+} spins is insignificant in our materials as well.

Overall, oxygen-vacancies play an essential role in increasing the phonon scattering and lowering the thermal conductivity in our materials. The suppression of thermal conductivity by introduction of small amount of oxygen vacancy has already been reported.[1, 35] Phonon scattering becomes disproportionately dominant over contributions of other factors discussed above (grain size, boundary, and spins) for thermal wave propagation.[13, 24] Our materials are oxygen deficient, with $\delta = 0.5$ and 0.9 for $Sr_2FeCoO_{6-\delta}$ and $Ca_2FeCoO_{6-\delta}$, respectively. Since phonon scattering is importantly considered to be responsible for lowering the thermal conductivity in the above discussions, the very low thermal conductivity of our materials may also be ascribed to phonon scattering due to oxygen-vacancies.[22, 23, 26, 36]

In addition to the concentration of oxygen-vacancies ($\delta = 0.5$ for $Sr_2FeCoO_{6-\delta}$ and $\delta = 0.9$ for $Ca_2FeCoO_{6-\delta}$), the ordering of vacancies may also play an important role. A comparison of thermal conductivities of our materials to those of previously reported perovskite oxides, such as those described above, points to a possible trend in thermal conductivity:

ABO_3 perovskite (no oxygen vacancies) > $ABO_{3-\delta}$ (vacancy disorder) > $ABO_{3-\delta}$ (vacancy order)

Thus, we can propose an additional factor, namely oxygen-vacancy order, that may have an impact on thermal insulation properties.

Conclusion

Oxygen-deficient perovskites are an interesting class of ceramic materials, that have not been widely explored for thermal insulation properties. Here, the thermal conductivities of $Sr_2FeCoO_{6-\delta}$ and $Ca_2FeCoO_{6-\delta}$ are studied. Both compounds have oxygen deficiency in their structure and show excellent thermal insulation properties. In particular, $Ca_2FeCoO_{6-\delta}$ exhibits thermal conductivity of 0.05 $Wm^{-1}K^{-1}$ which is the lowest thermal conductivity for a ceramic material reported to date. Though different factors may impact the thermal conductivity, the dominant factor that contributes to the lowering of thermal conductivity in these systems, as reported previously for some other materials, is the phonon scattering due to oxygen vacancies. In addition, the ordering of vacancies appears to be a parameter that affects the thermal conductivity. Therefore, thermal insulation properties can be enhanced by oxygen-vacancies and their ordering.

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