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Thermal Conductivity of Nano ZnO Doped $CaFe_2O_4$

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The research objective of this study was to examine whether Zn was an effective doping element for thermal conductivity. $Ca_{1-x}Zn_xFe_2O_4$ ($x = 0.0–0.5$) were synthesized by solid state reaction method. The XRD results showed that all samples were mixed phase of $CaFe_2O_4$ and $ZnFe_2O_4$. The structure of $Ca_{1-x}Zn_xFe_2O_4$ ($x = 0.0–0.5$) belonged to a group of an orthorhombic system (space group: Pbnm). It was observed that all the samples of $Ca_{1-x}Zn_xFe_2O_4$ ($x = 0.0–0.5$) had positive Seebeck coefficient as shown on p-type semiconductor behavior. Thus thermal conductivity tended to decrease with increasing x value. The $Ca_{0.6}Zn_{0.4}Fe_2O_4$ showed lowest thermal conductivity of 6.52 W m^{-1} K^{-1} at 473 K, which was lower than 50.81% of $CaFe_2O_4$. These results suggested that Zn was an effective doping element for improving the thermal conductivity of $Ca_{1-x}Zn_xFe_2O_4$.

Key words $Ca_{1-x}Zn_xFe_2O_4$; thermal conductivity; solid state reaction method; orthorhombic

1. Introduction

Good thermoelectric materials should have large thermoelectric power and high electrical conductivity as well as low thermal conductivity. The thermoelectric materials could be evaluated by the figure of merit, ZT, which is defined as $ZT = \frac{S^2\sigma}{\kappa}T$, where S is the thermoelectric power, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature. Much research have focused on materials with special structure that are filled with atoms to scatter phonons and then reduce the lattice thermal conductivity [1–2].

The prototype of $CaFe_2O_4$ (Calcium ferrite) crystallization in an orthorhombic structure with lattice constants a = 9.238Å, b = 10.716Å, and c = 3.023Å (the space group is Pnma No.62[3], JCPDS Card No. 32-0168) is built up of eight-fold coordinated Ca atoms, and distorted FeO_6 octahedra. The electrical conductivity of $CaFe_2O_4$ has low 3–210 S cm^{-1} at 1123–1273 K in air. Z is in the range (12.0–13.9) 10^{-6} K^{-1}[4].

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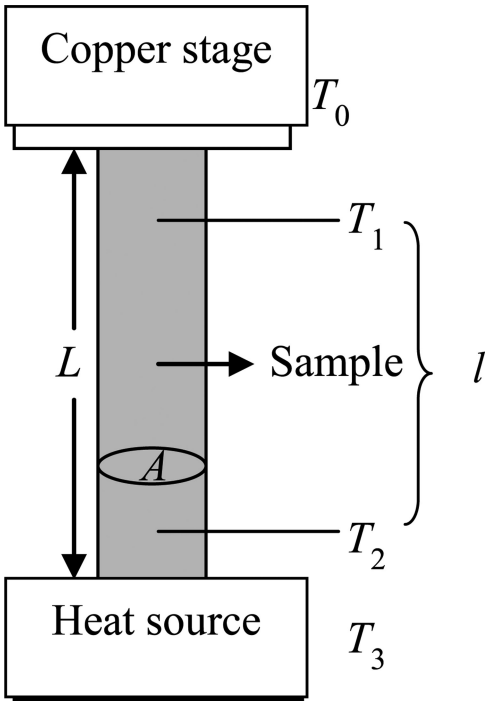

Figure 1. Steady state (Nolas et al, 2001).

ZnO (Zinc oxide) crystallization showed hexagonal structure with lattice constants a = b = 3.2495Å and c = 5.2069Å (the space group is $P6_3mc$). It is characterized by two interconnecting sublattices of Zn^{2+} and O^{2-} such that each Zn ion is surrounded by a tetrahedral of O ions.

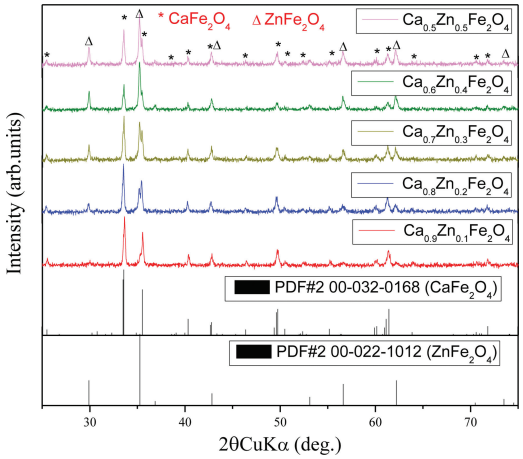

Figure 2. XRD patter of the $Ca_{1-x}Zn_xFe_2O_4$ (where x = 0.0–0.5).

Table 1
The physical of bulk $Ca_{1-x}Zn_xFe_2O_4$ (x = 0.0–0.5)

Order	Samples	Color	Bulk material
1	$CaFe_2O_4$	Black	
2	$Ca_{0.9}Zn_{0.1}Fe_2O_4$	Black	
3	$Ca_{0.8}Zn_{0.2}Fe_2O_4$	Brown	
4	$Ca_{0.7}Zn_{0.3}Fe_2O_4$	Auburn	
5	$Ca_{0.6}Zn_{0.4}Fe_2O_4$	Auburn	
6	$Ca_{0.5}Zn_{0.5}Fe_2O_4$	Crimson	

The thermal conductivity, κ(W cm^{-1} K^{-1}) of a semiconductor is an important property when considering high-power/high temperature devices. It is a kinetic property influenced by the vibrational, rotational and electronic degrees of freedom and is predominately limited by phonon-phonon scattering in a pure crystal. ZnO, like most other semiconductors, contains a large number of point defects, which have a significant effect on the thermal conductivity. The highest measured values of thermal conductivity come from a study done on vapour-phase grown samples which measured the conductivity on the polar faces of ZnO [5]. This study gives the values of $\kappa = 1.02 \pm 0.07$and 1.16 ± 0.08W cm^{-1} K^{-1} from the Zn face of two different samples, and $\kappa = 1.10 \pm 0.09$ and 0.98 ± 0.08W cm^{-1} K^{-1} from the O face of the two samples. These values are considerably higher than other values measured from ZnO which typically falls in the range $\kappa = 0.6 - 1.0$W cm^{-1} K^{-1} [6].

In this work we investigated thermal conductivity of $CaFe_2O_4$ doped ZnO nanopowder prepared by solid state reaction method.

Table 2
Shows the lattice parameter, unit cell volume and density of $Ca_{1-x}Zn_xFe_2O_4$ (x = 0.0–0.5)

Sample	Lattice	a (Å)	b (Å)	c (Å)	Unit cell volume (Å)^3	Measured density (g/cm^{-3})	Relative density %
$CaFe_2O_4$	Orthorhombic	9.238	10.716	3.023	299.260	4.51	94.41
$Ca_{0.9}Zn_{0.1}Fe_2O_4$	Orthorhombic	9.232	10.707	3.018	298.320	4.30	90.52
$Ca_{0.8}Zn_{0.2}Fe_2O_4$	Orthorhombic	9.224	10.701	3.020	298.092	4.34	92.34
$Ca_{0.7}Zn_{0.3}Fe_2O_4$	Orthorhombic	9.221	10.699	3.021	298.038	4.36	93.69
$Ca_{0.6}Zn_{0.4}Fe_2O_4$	Orthorhombic	9.218	10.699	3.022	297.941	4.47	97.38
$Ca_{0.5}Zn_{0.5}Fe_2O_4$	Orthorhombic	9.218	10.699	3.463	341.532	4.09	90.08

2. Experimental Details

$CaCO_3$ (95.0%, powder), ZnO (95.0%, powder), Fe_2O_3 (95.0%, powder) were used as the starting materials. The polycrystalline zinc substituted calcium ferrite having the compositional formula $Ca_{1-x}Zn_xFe_2O_4$ (where x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5). The preparation of $Ca_{1-x}Zn_xFe_2O_4$ (x = 0.0–0.5) started from calcined at 1073 K for 12 hr in air. The powder then was mixed and heat treated at 1173 K for 12 hr in air, and pressed at 14.70 MPa. The synthesized $Ca_{1-x}Zn_xFe_2O_4$-type powder was ground in an agate ball milling tank for 24 hr at a speed of 1,430 revolutions per minute (rpm).

The mixture transforms to mainly Calcium ferrite ($CaFe_2O_4$) were described by the following equation: $CaCO_3+Fe_2O_3 = CaFe_2O_4+CO_2$.The phase composition and morphologies of the products were analyzed through X-ray diffractometer and scanning electron microscope.

The thermal conductivity was calculated using the relation:

$$\dot{Q}_{\text{cond}} = \kappa \frac{A}{L} \Delta T$$

When κ is thermal conductivity (W m^{-1} K^{-1}), $A$is cross-sectional area of the sample (m^2), $L$is length of the sample (m), ΔTdenotes difference in temperature (K)

In a cross-sectional area of Fig. 1, A and the reference temperature is T_0 when the temperature high T_3 was calculated using the relation as follows:

$$\kappa = \frac{\dot{Q}}{A} \frac{l}{(T_2 - T_1)}$$

When $\dot{Q}$ is amount of heat transmitted of the sample, l is the distance between the measured temperature T_1 and T_2.

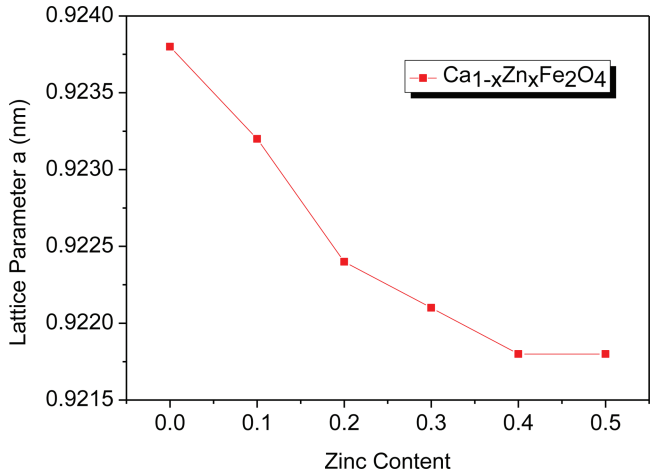

Figure 3. The relationship of lattice parameter a with zinc content: $Ca_{1-x}Zn_xFe_2O_4$ (where x = 0.0–0.5).

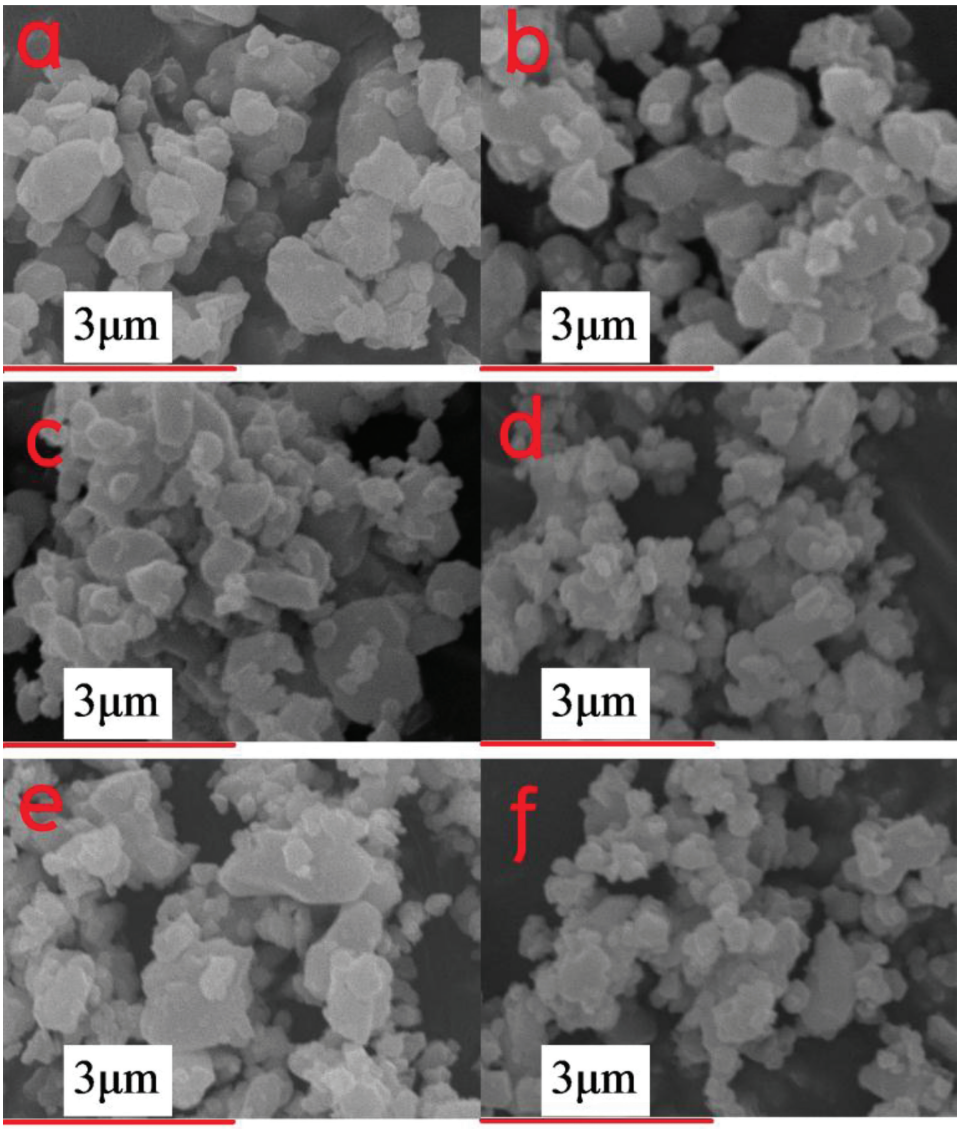

Figure 4. The microstructure of powder material. (a) $CaFe_2O_4$ (b) $Ca_{0.9}Zn_{0.1}Fe_2O_4$ (c) $Ca_{0.8}Zn_{0.2}Fe_2O_4$ (d) $Ca_{0.7}Zn_{0.3}Fe_2O_4$ (e) $Ca_{0.6}Zn_{0.4}Fe_2O_4$ (f) $Ca_{0.5}Zn_{0.5}Fe_2O_4$.

3. Results and Discussion

Bulk material when replacing Ca with Zn sintering and Ca with Zn 0.1 turned black color. When replacing Ca with three different Zn compositions, namely, Zn 0.2, Zn 0.3–0.4, and Zn 0.5, the bulk material turned into brown, auburn, and crimson color respectively.

Figure 2 shows the X-ray diffraction (XRD) patterns of the $Ca_{1-x}Zn_xFe_2O_4$ $x = 0.0, 0.1, 0.2, 0.3, 0.4$, and 0.5, after sintering from 1173 K for 12 hr. In these diffraction patterns it was clear that the characteristic diffraction was peaks. The obtained phase had orthorhombic

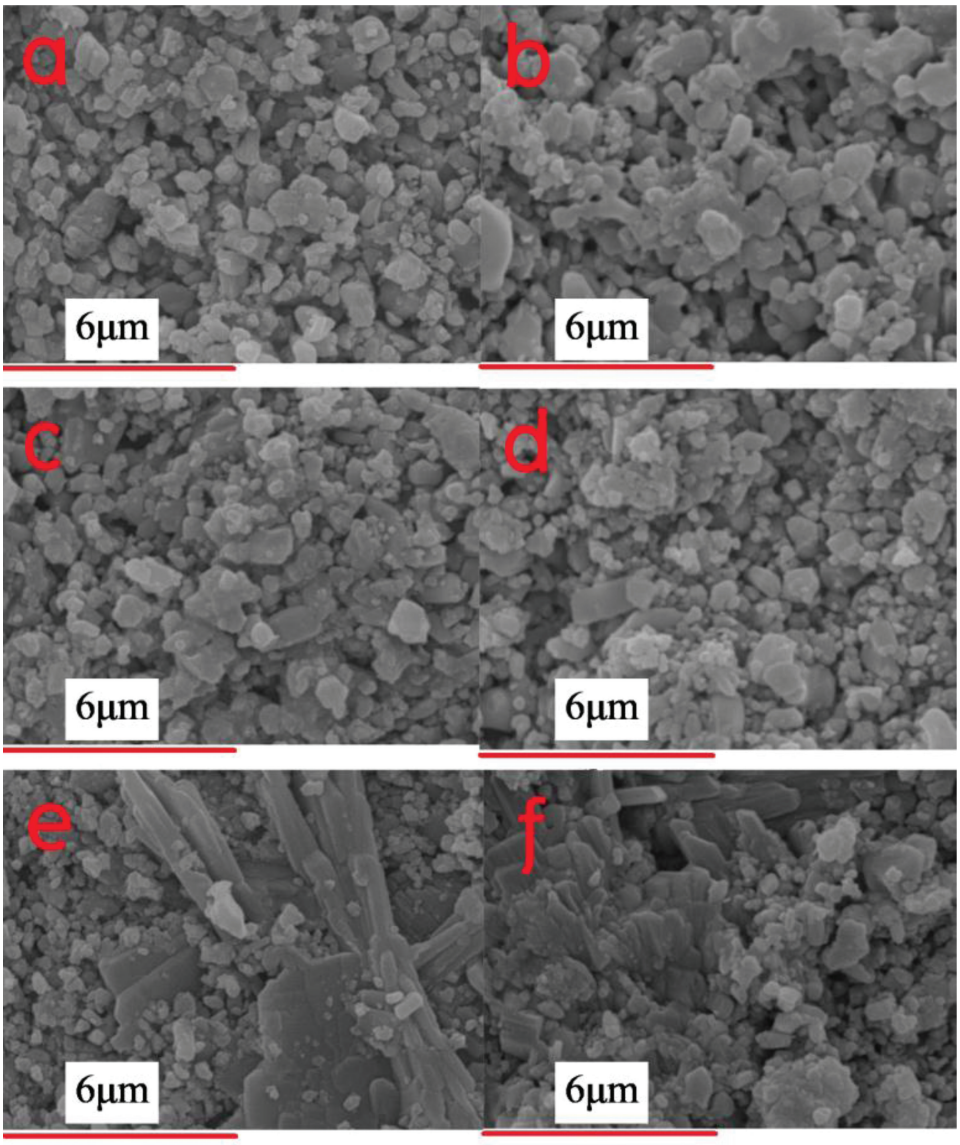

Figure 5. The microstructure of bulk material (a) $CaFe_2O_4$ (b) $Ca_{0.9}Zn_{0.1}Fe_2O_4$ (c) $Ca_{0.8}Zn_{0.2}Fe_2O_4$ (d) $Ca_{0.7}Zn_{0.3}Fe_2O_4$ (e) $Ca_{0.6}Zn_{0.4}Fe_2O_4$ (f) $Ca_{0.5}Zn_{0.5}Fe_2O_4$.

structure. The experiment lattice parameters were given in Table 2. The variation in the lattice parameter with zinc content was shown in Fig. 3.

Figure 4 shows the scanning electron microscopy (SEM) of $Ca_{1-x}Zn_xFe_2O_4$ with x = 0.0–0.5. From the images, it was noticed that there were formation of spherical and uniform particles. The average particle size was found to be in the range of 1–2 μm. With increase in ZnO doping, the spacing between the particles were expected to become narrower and also there was a decrease in particles size.

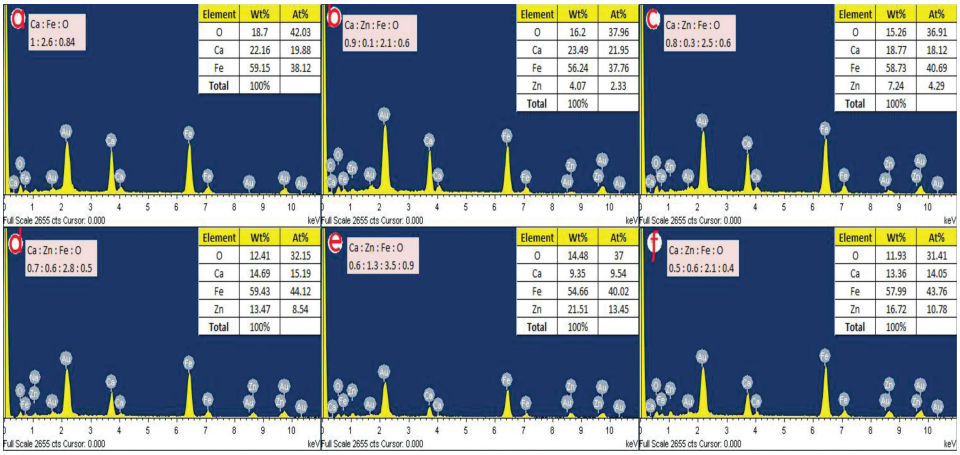

Figure 6. EDX of bulk material. (a) $CaFe_2O_4$ (b) $Ca_{0.9}Zn_{0.1}Fe_2O_4$ (c) $Ca_{0.8}Zn_{0.2}Fe_2O_4$ (d) $Ca_{0.7}Zn_{0.3}Fe_2O_4$ (e) $Ca_{0.6}Zn_{0.4}Fe_2O_4$ (f) $Ca_{0.5}Zn_{0.5}Fe_2O_4$.

Characterizations of the microstructure through SEM magnification zoom as 10,000. The crystal size of $Ca_{1-x}Zn_xFe_2O_4$ (x = 0.0–0.5) appeared about 1–2 μm and dispersed as shown in Fig. 4 (a) (b), (c), (d, (e) and (f) when a large amount of Ca and Zn increased at 0.1–0.5. Fig. 5 Crystallite sizes about 5 μm and grain size increased with Zn substitution increasing.

Figure 6(a) shows the peaks of the elements Ca, Fe and O in pure $CaFe_2O_4$. Fig. 6(b–f) shows the peaks of the elements Ca, Zn, Fe and O for Zn-doped $CaFe_2O_4$ samples. The observed percentage of Ca/Zn value matched well with the amount of Ca/Zn used in the respective precursors (inset of Fig. 6(a–f)), which indicated that no loss of element occurred during the synthesis. Measurements EDS or EDX bulk of material revealed that amount of

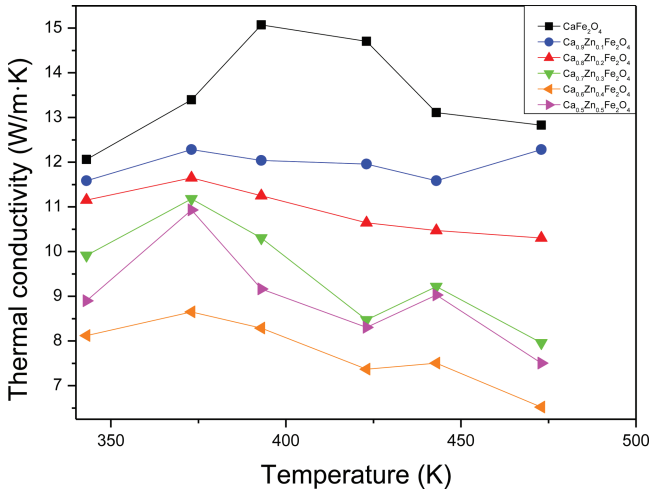

Figure 7. The relationship of thermal conductivity and temperature for $Ca_{1-x}Zn_xFe_2O_4$ (where x = 0.0–0.5).

Ca decreased with Zn increasing.

$$\kappa = \frac{1}{3}\frac{C_v}{V} v_s l$$

Where κ is thermal conductivity, C_v is lattice heat capacity, V is volume, V_s is effective sound speed and l is phonon mean free path

Figure 7 shows the thermal conductivity dependence on temperature of $Ca_{1-x}Zn_xFe_2O_4$ with x = 0.0–0.5. The thermal conductivity decreased with increasing x value. The $Ca_{0.6}Zn_{0.4}Fe_2O_4$ reported lowest thermal conductivity of 6.52 W m^{-1} K^{-1} at 473 K, which was lower than 50.81% of $CaFe_2O_4$. These results suggested that Zn was an effective doping element for improving thermal conductivity of $Ca_{1-x}Zn_xFe_2O_4$.

4. Conclusion

Thermal conductivity of $Ca_{1-x}Zn_xFe_2O_4$ with x = 0.0–0.5 were prepared by conventional solid state reaction methods. The XRD patterns revealed that all the samples were mixed phase of $CaFe_2O_4$ and $ZnFe_2O_4$. Thermal conductivity decreased with increasing Zn content up to x = 0.1–0.4 while x = 0.5 had an inconsistent result.

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