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Simultaneous Enhancement in the Electrical Conductivity and Reduction in the Lattice Thermal Conductivity Leading to Enhanced Thermoelectric ZT Realized by Incorporation of Metallic Nanoparticles into Oxide Matrix

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Abstract: Nanoporous Fe₃O₄ composites containing metallic Cu nanoparticles were synthesized by reducing-leaching treatment of CuFe₂O₄ precursor. Thermoelectric properties of the composites sintered at 1270 °C greatly improved compared with Fe₃O₄ without Cu, presumably due to a nanoporous structure and the Cu nanoparticles remaining in the Fe₃O₄ matrix after acid leaching. The electrical and thermal conductivity indicate that Cu in the matrix promotes the electron conduction and suppresses the phonon conduction, improving the dimensionless figure-of-merit, ZT.

Keywords: thermoelectrics; nanocomposites; metallic nanoparticles; nanoporous structure; phonon scattering; oxides

1. Introduction

Global energy consumption increasing year by year requires a technique development of renewable energy source such as wind and solar energy.¹-²) Thermoelectrics, a class of materials utilized to convert heat directly into electricity by the Seebeck effect, is also expected to be another source of renewable energy. Thermoelectric materials are evaluated by the dimensionless figure-of-merit,

\[
ZT = \frac{S^2 \sigma}{\kappa T} = \frac{S^2 \sigma}{\kappa_{el} + \kappa_{ph}} T
\]

where \( \sigma \) is the electrical conductivity, \( S \) is the Seebeck coefficient, \( T \) is the absolute temperature, \( \kappa \) is the thermal conductivity, \( \kappa_{el} \) is the electron thermal conductivity, and \( \kappa_{ph} \) is the phonon thermal conductivity. Good thermoelectric materials should have high \( \sigma \) and \( S \) with low \( \kappa \) simultaneously. However, \( \sigma \), \( S \) and \( \kappa_{el} \) are all a function of the carrier concentration and hence interdependent each other, making good materials difficult to develop. On the other hand, \( \kappa_{ph} \) is associated with crystal lattice vibrations, and the only parameter insensitive to the carrier concentration, being independent of other parameters in ZT. Therefore, an approach to selectively decrease \( \kappa_{ph} \) is one of the most prospective way to improve \( ZT \).³-²⁰)

Recent studies showed that nanostructure control in materials is an efficient way to decrease the phonon thermal conductivity.²¹) Coarse porous structure can decrease \( \kappa \), while \( \sigma \) is also suppressed equally or more strongly due to the reduction of the cross-sectional area for the electron conduction.²²) Meanwhile, nanocomposite structure can selectively reduce \( \kappa \), specifically \( \kappa_{ph} \), because of phonon scattering by nanopores and nanoparticles.²³) This specific decrease in \( \kappa_{ph} \) is governed by the composite structure, particularly the size of the pore and the particles.

In this paper, we report novel synthesis of nanoporous oxide containing metallic nanoparticles and investigation of a relation between the structure and the thermoelectric properties of the oxide composites. A copper spinel Cu₂M₄O₈ (M = Fe, Al, Mn, Ni) has been reported to form metallic Cu nanoparticles in M-oxide matrix by heating in a reducing atmosphere.²⁴-²⁶) If the Cu nanoparticles in the matrix can be selectively removed, nanosized pores will remain in the oxide. Here, we focused on CuFe₂O₄, which is expected to form Fe₃O₄ composite containing Cu nanoparticles after H₂ reduction, because the iron oxide is more electrically conductive than aluminum or manganese oxides to be obtained as a matrix by reducing CuAl₂O₄ and CuMn₂O₄. Finally, we aim to establish an innovative nanostructure-control approach to achieve high thermoelectric performance.

2. Experimental

2.1 Sample preparation
CuFe₂O₄, a precursor of the nanocomposites was prepared by calcining a mixed powder of α-Fe₂O₃ (99%, Kishida Kagaku) and CuO (99.9%, Wako) at 1000 °C for 4 h in air. The copper spinel oxide thus formed was ground in a mortar and heated in a reducing atmosphere (5%H₂/N₂) at 270 °C for 14 h. After the reduction, the sample powder was washed with 69% nitric acid for leaching of metallic copper. The reducing and leaching processes (denoted as R-L cycle hereafter) were repeated under the same conditions for some samples. These powders were finally sintered at 1270 °C for 3 h in an N₂ atmosphere. For comparison, a reagent grade Fe₃O₄ (95%, Wako) was also sintered under the same conditions.

2.2 Characterization

Powder x-ray diffraction (XRD) measurements were performed using a PANalytical EMPYREAN diffractometer with Cu-Kα radiation. The surface structures of the samples were observed on a scanning electron microscope (SEM, Hitachi S-4800). The amount of copper and iron after each treatment were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Jobin Yvon Horiba, ULTIMA 2C). The thermal conductivity was obtained from the thermal diffusivity and the specific heat measured on a Kyoto Electronics LFA-502 laser flash measurement system and a Netzsch DSC404F3 Pegasus, respectively.

The electrical conductivity and the Seebeck coefficient were measured under Ar atmosphere simultaneously on an Ozawa Science RZ2001i apparatus.

3. Results and Discussion

3.1 Nanocomposite Structure

Figure 1 shows the XRD patterns of the copper ferrites after each treatment. These patterns indicate that the precursor consisted mainly of CuFe₂O₄ (Fig. 1(a)), and metallic Cu and Fe₃O₄ formed after the reduction (Fig. 1(b)). After leaching with 69% HNO₃, the Cu peaks at 43.3, 50.4 and 74.1° disappeared (Fig. 1(c)). These results demonstrate that 69% nitric acid can preferentially remove the metallic Cu from the reduced CuFe₂O₄ leaving Fe₃O₄ as a matrix. Table 1 summarizes the results of ICP-OES analysis for the samples. The amount of Cu in the samples after the reducing-leaching (R-L) cycles of 1 and 5 times decreased to 20% and 11% of the initially charged Cu, respectively. These results suggest that the copper amount remaining in the Fe₃O₄ matrix can be controlled by the R-L cycles.

Table 1. The Cu amount in the samples after each treatment relative to the nominal Cu amount in CuFe₂O₄.

| Treatment     | Relative Cu amount / CuFe₂O₄ u.f. |
|---------------|-----------------------------------|
| only reduction| 1.03                              |
| 1 R-L cycle   | 0.20                              |
| 3 R-L cycle   | 0.13                              |
| 5 R-L cycle   | 0.11                              |

Figure 2 shows the surfaces of the samples after each treatment. Whereas the surface of the copper spinel before the reduction is dense and smooth (Fig. 2(a)), a number of Cu nanoparticles were observed on the surface of the reduced CuFe₂O₄ (Fig. 2(b)). A nanoporous structure formed after leaching Cu nanoparticles (Fig. 2(c)), and the pore diameter was similar to the size of the Cu nanoparticles observed prior to the leaching treatment. These results indicate that the nanoporous structure was formed by selective leaching of copper nanoparticles from the reduced CuFe₂O₄. After the R-L cycles for 5 times, the pore size increased, from 50 nm to more than 100 nm (Fig. 2(d)).

These observation suggests that the structural transformation proceeds as depicted in Fig. 3. The nanoporous
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Fe$_3$O$_4$ composite powders containing Cu nanoparticles were thereby synthesized by selective leaching of the Cu nanoparticles from the reduced CuFe$_2$O$_4$.

3.2 Thermoelectric properties

In order to investigate thermoelectric properties of the Fe$_3$O$_4$ nanocomposites thus obtained, we sintered the nanocomposite powders at 1270 °C in N$_2$. Sintered bodies of the Fe$_3$O$_4$ nanocomposites after 1 and 5 R-L cycles will be denoted as 1RL and 5RL, respectively. Fe$_3$O$_4$ represents the reagent grade Fe$_3$O$_4$ sintered under the same conditions. The relative densities of 1RL, 5RL, and Fe$_3$O$_4$ were 96, 94, and 99%, respectively. The nanoporous structure disappeared from the surface of the sintered bodies (Fig. 4), while the main phase of the samples remained Fe$_3$O$_4$ with a small XRD peak of Cu at 2θ = 50.4 ° (Fig. 5), being consistent with the ICP results (Table 1). Therefore, it is plausible that the Cu nanoparticles remaining in the Fe$_3$O$_4$ matrix would influence the thermoelectric properties.

Figure 6 shows the temperature dependence of the electrical conductivity, $\sigma$. All the samples exhibited the semiconducting behavior, in which $\sigma$ increases with increasing temperature. The $\sigma$ values of 1RL and 5RL were about 10 times higher than that of Fe$_3$O$_4$ without Cu. Since the CuFe$_2$O$_4$ phase is much less conductive (~10$^{-1}$ S cm$^{-1}$ at 300 °C) than Fe$_3$O$_4$, even if CuFe$_2$O$_4$ remained in the samples, it cannot rationalize the much higher $\sigma$ of 1RL and 5RL. Therefore, only possible reason of the markedly increased $\sigma$ would be the metallic Cu nanoparticles remaining in the Fe$_3$O$_4$ matrix. Figure 7 shows the temperature dependence of the Seebeck coefficient, $S$, which was almost the same for all the samples. This implies that the Cu nanoparticles remaining in the matrix has negligible influence on $S$.

The electrical conductivity, $\sigma$, is given by the following equation:

$$\sigma = ne\mu,$$  \hspace{1cm} (2)

where $n$, $e$, and $\mu$ are the carrier concentration, electrical charge of the carrier, and the carrier mobility, respectively. For degenerate semiconductors, the Seebeck coefficient is given by:

$$S = \frac{8\pi^2k_B^2}{3e^3h^2}m^*T\left(\frac{m^*}{3e^2}\right)^{2/3} \propto n^{-2/3}$$  \hspace{1cm} (3)

![Fig. 3: Schematic diagram for synthesis of nanoporous Fe$_3$O$_4$ containing Cu nanoparticles.](image)

![Fig. 4: SEM images of the surfaces of (a) 1 RL and (b) 5RL.](image)

![Fig. 5: XRD patterns for 1RL and 5RL (a, b) before and (c, d) after sintering.](image)
where $k_B$, $h$, and $m^*$ are the Boltzmann constant, the Plank constant, and the effective mass of the carrier, respectively. These equations show that $\sigma$ and $S$ are oppositely dependent on $n$, while our results are inconsistent with this relation. It is therefore implied that the Cu nanoparticles provide an additional conduction path with higher carrier mobility, giving negligible influence on the overall carrier concentration.

Figure 8 shows the temperature dependence of the thermal conductivity of the samples. The thermal conductivity of the samples containing Cu was significantly lower than that of the Cu-free Fe$_3$O$_4$. Moreover, the more Cu remained in the samples, the more $\kappa$ decreased. To investigate the carrier and phonon thermal conduction, we calculated the electron thermal conductivity, $\kappa_{el}$, and the phonon thermal conductivity, $\kappa_{ph}$, using the following equations:

$$\kappa_{ph} = \kappa - \kappa_{el} \tag{5}$$

where $L_0$ is the Lorentz number, $2.45 \times 10^{-8}$ V$^2$ K$^{-2}$. Equation (4) is the Wiedemann-Franz law. Figure 9 shows the temperature dependence of $\kappa_{el}$ and $\kappa_{ph}$ of the samples. The electron thermal conductivity of all samples was very small. Although $\kappa_{el}$ of 1RL and 5RL was slightly higher than that of Cu-free Fe$_3$O$_4$, the maximum $\kappa_{el}$ was just 0.20 W m$^{-1}$ K$^{-1}$ at 289 ºC for 1RL. On the other hand, $\kappa_{ph}$ is strongly dependent on the Cu amount remaining after the leaching. The $\kappa_{ph}$ values substantially decreased with increasing Cu amount, and the lowest $\kappa_{ph}$ was obtained for 1RL containing 20% of initial amount of Cu. These results clearly indicated that the Cu nanoparticles remaining in the Fe$_3$O$_4$ matrix increased $\sigma$ (and hence $k_B$), and decreased $\kappa_{ph}$ simultaneously, successfully decoupling electrical and thermal conductions.

In order to evaluate influence of the Cu nanoparticles on the thermoelectric properties, we have
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Figure 10: The normalized $\kappa_{el}/\kappa_{ph}$ ratios of the samples at 100 ºC.

![Graph showing normalized $\kappa_{el}/\kappa_{ph}$ ratios at 100 ºC.](image)

Figure 11: Temperature dependence of dimensionless figure-of-merit of the samples.

![Graph showing temperature dependence of ZT.](image)

As shown in eq. (6), if $\kappa_{el}<<\kappa_{ph}$ and $S$ is almost unchanged, we can use the ratio, $\kappa_{el}/\kappa_{ph}$, as an indicator of selective phonon scattering or decoupling of the electron and phonon conduction. Figure 10 compares the $\kappa_{el}/\kappa_{ph}$ ratios at 100 ºC normalized by that of Fe$_3$O$_4$, and indicates that the samples containing the Cu nanoparticles have more than 30 times larger $\kappa_{el}/\kappa_{ph}$. It is therefore presumable that the Cu nanoparticles in the Fe$_3$O$_4$ matrix can simultaneously enhance the electron conduction and suppress the phonon conduction.

4. Conclusions

Nanoporous Fe$_3$O$_4$ composite powders containing Cu nanoparticles were synthesized by selective leaching of the Cu nanoparticles from reduced CuFe$_2$O$_4$ matrix. The porous structure and the amount of Cu remaining in the Fe$_3$O$_4$ matrix can be controlled by reducing-leaching cycles. After sintering, the porous structure disappeared, whereas the left-over Cu nanoparticles improve the thermoelectric properties. The more Cu remained in the Fe$_3$O$_4$ matrix, the higher electrical conductivity and the lower thermal conductivity were obtained. These results suggested that the Cu nanoparticles remaining in the Fe$_3$O$_4$ improved the thermoelectric properties by the provision of carrier conduction path and the enhancement of phonon scattering, making the ZT about 10 times higher than that of the Fe$_3$O$_4$ without Cu. Furthermore, all the results mean that we therefore established nanostructure-control approach to increase electrical conductivity and decrease thermal conductivity simultaneously. We can expect the introduction of nanocomposite structure to some good thermoelectric materials such as SrTiO$_3$ and ZnO by using this approach, and improve their thermoelectric properties further.

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