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THERMAL CONDUCTIVITY OF THE FERRITES $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$

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A series of samples of the type $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ (x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) were prepared by a ceramic technique. The existence of a single phase was confirmed by X-ray studies. The thermal conductivity and specific heat were measured at 53°C. The thermal conductivity had a minimum value at $x = 0.3$, due to the maximum porosity at this composition. The phonon frequency was estimated to have an optimum value at $x = 0.3$, due to the increase in phonon scattering.

Introduction

In recent years, a number of investigators have attempted to determine the thermal conductivity of ceramics as a fundamental material constant [1]. Since thermal conductivity is a structure-sensitive property, the constants obtained from measurements of polycrystalline aggregates are not generally applicable unless the effects of microstructure on these values are known.

The situation for the Mn ferrites is that the actual fraction of Fe^{2+} at the octahedral sites may be estimated from the thermoelectric power. In concert with the assumption that electron transport proceeds by a small polaron process, i.e. the hopping of localized electrons from an occupied Fe site to an adjacent occupied Fe site, the following expression is applied for the thermoelectric power Q [2, 3], defined as $Q = \frac{d\Phi}{dT} \approx \frac{\Delta\Phi}{\Delta T}$:

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$$Q = \frac{K}{e} \cdot \left[\ln\beta \cdot \left(\frac{1-c}{c} \right) + \frac{S_{T*}}{K} \right] . \tag{1}$$

Here, $c = \left[\mathrm{Fe}^{2+}_{\mathrm{oct}}\right] / \left[\mathrm{Fe}^{\mathrm{tot}}_{\mathrm{oct}}\right]$, $(1-c) = \left[\mathrm{Fe}^{3+}_{\mathrm{oct}}\right] / \left[\mathrm{Fe}^{\mathrm{tot}}_{\mathrm{oct}}\right]$ and β is a degeneracy factor involving the spin and orbital degeneracy of the carrier. S_{T*}, the vibrational entropy, is estimated to contribute 10 μV/K or less to the thermoelectric power.

Values for c and the effective carrier density are found to be substantially in excess of the values calculated by Pelton *et al.* [4] for both stoichiometric $MnFeO_4$ and that in which there is a slight Fe excess, implying that at least the Mn ferrites are significantly reduced or oxygen-deficient over their entire range of existence at high temperatures. This finding is of special significance as regards the accessible resistivities attainable for these materials under ambient conditions.

A combination of carrier density with electrical conductivity allows determination of the electron mobility [5]:

$$\mu = \sigma / ne \tag{2}$$

and further the optical phonon frequency ν_0 may be estimated from the small polaron mobility expression

$$\mu = \left[(1-c) \cdot e^2 a^2 \nu_0 / KT \right] \cdot \exp(-E_H/KT) \tag{3}$$

where a is the jump distance between conduction sites and E_H is the activated hopping energy.

The goal of the present program is to examine the thermal properties of the ferrites $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$, including the thermal conductivity, specific heat, velocity and mean free path of the phonons in these samples.

Experimental

Sample preparation

Samples in the system $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ ($x = 0$, 0.1, 0.2, 0.3, 0.4 and 0.5) were prepared by using the usual ceramic technique. The pure oxides were mixed and then ground to a very fine powder in an agate mortar made of carborundum. The samples in the form of discs were sintered at 1200°C for 8 hours and slowly cooled to room temperature. The samples were polished to produce uniform parallel surfaces. Contacts on the sample surface were made with silver paste for thermal measurements.

Thermal measurements

The apparatus used for the measurements is shown in Fig. 1. It consists of a sample holder (1) held on three iron rods (2). The sample holder consists of a stainless steel bar (3) fixed in the central axis of a tubular stainless steel furnace (4) and (5). The two heaters and the stainless steel bar are fixed to the holder base. The central steel bar, copper leads, thermocouple wires and heater connections are insulated from the holder base plate by a ceramic disc (6). Connecting wires and thermocouples pass through ceramic tubes and lead to the outside through Teflon tubes (7) in the apparatus base plate by means of copper leads (8). The sample S is tightly pressed between two copper electrodes by means of the pressure of the load (9) screwed to the rods. The base plate is surrounded by a metal jacket (10), which rests on an annular vacuum rubber ring (11). The cooling copper coil (12) is sealed on the surrounding of the metal jacket. For measurement stability, the system is provided with a connection to the vacuum system.

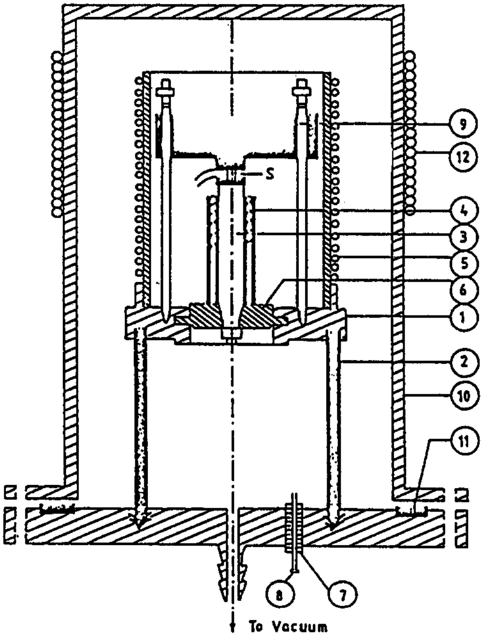

Fig. 1 Cross-section of the apparatus used for the measurements

For each sample, it was required to measure the thermal conductivity at a temperature of 53°C. This was achieved by controlling the external and internal heaters. The external heater was used to keep a constant temperature around the sample, and for measuring the thermal conductivity (*K*), while the internal heater was used to maintain a temperature gradient across the sample.

Results and discussion

Effect of Cu additions on thermal conductivity of $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ *ferrites*

The coefficient of thermal conductivity of the samples was estimated via the formula

$$Q = IV/J = KA \cdot \frac{dT}{dX}$$

where Q is the quantity of heat transferred through the sample per unit time, and I, V, T and X are the current in amperes, the voltage across the internal heater in volts, the temperature, and the sample thickness in cm, respectively.

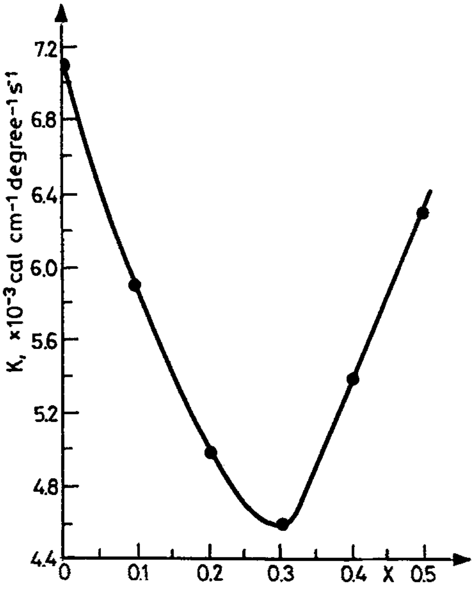

Fig. 2 Variation of thermal conductivity K with copper additions x

The variation in the coefficient of thermal conductivity K with Cu additions x is shown in Fig. 2. The pronounced decrease in K had a minimum value at $x = 0.3$. The explanation of these results is as follows: It has been suggested that doping increases the concentration of lattice vacancies [6]. The formation of excess vacancies enhances the volume of diffusion mechanism. However, if excess vacancies are formed, these would be anion vacancies rather than cation vacancies since the Cu^{2+} ion has a lower charge than the Fe^{3+} ion. These vacancies act as centres of phonon scattering, causing a decrease in the coefficient of thermal conductivity. For $x>0.3$, the introduction of Cu^{2+} ions at the octahedral sites creates Fe^{2+} ions, and the hopping electrons between Fe^{2+} and Fe^{3+} are the predominant carriers of the thermal phonons which give rise to the coefficient of thermal conductivity.

Effect of Cu^{2+} additions on specific heat of $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$

The effect of Cu additions on the specific heat of NiZn ferrite is shown in Fig. 3. It is observed that the Cu additions decrease the specific heat (c) to give a minimum value at $x = 0.3$. Above this value of x, the specific heat increases. This behavior may be discussed as follows:

Doping is another mechanism for introducing vacancies [7]. When an ion with an incorrect valence enters the lattice, charged vacancies may form to maintain local electroneutrality. These phenomena are established when Cu^{2+} is substituted for Fe^{3+}, and are assumed to create charged vacancies. These vacancies decrease the thermal conductivity and also the specific heat by inelastic collisions of the phonons. For $x>0.3$, the excess vacancies which are formed reduce the phonon scattering and the porosity and enhance sintering [8], leading to a noticeable increase in the specific heat.

Variation of phonon frequency with x

The phonon frequency ν_o is estimated via Eq. (3). The effect of copper additions x on the phonon frequency is shown in Fig. 4. The frequency increased with x to attain a maximum value at $x = 0.3$. Above this addition, the frequency decreased. These results can be explained as follows: The thermal conductivity of a material determined by the umklap process may be considered a fundamental property of the material, and is called the lattice conductivity. Imperfections and inhomogeneities in a body also act as centres of phonon scattering, and thus further reduce their mean free path. It is convenient to consider imperfections on the atomic scale (e.g. impurity atoms,

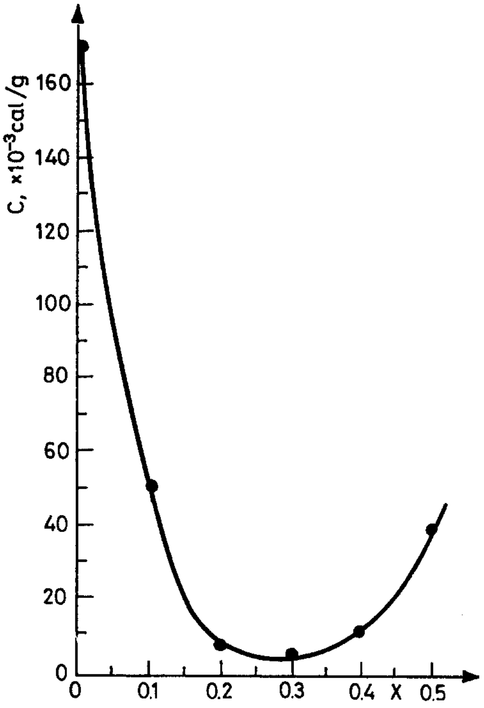

Fig. 3 Variation of specific heat *c* with *x*

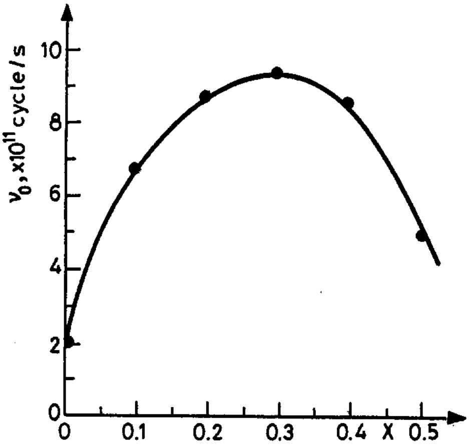

Fig. 4 Variation of phonon frequency ν with copper additions *x*

dislocations and pores). In our case, the lattice vacancies (cation vacancies) generated give rise to porosity, as shown in previous work [8]. The increase in the pores decreased the thermal conductivity (Fig. 5) and increased the phonon frequency. These pores scattered the phonons and reduced the mean free path, causing the increase in the phonon frequency to a maximum value at $x = 0.3$. For higher additions, oxygen vacancies would be generated, allowing stress relaxation and decreasing the internal stresses, with decreases in the number and size of the pores [1]. This markedly increases the thermal conductivity, leading to a decreased phonon frequency.

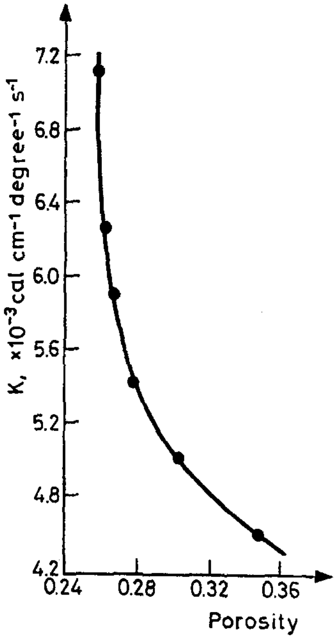

Fig. 5 Thermal conductivity *vs.* porosity of $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$

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Zusammenfassung — Mittels keramischer Techniken wurde eine Reihe von Proben des Types $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ mit (x = 0, 0.1, 0.2, 0.3, 0.4 und 0.5) hergestellt. Mittels Röntgendiffraktion wurde die Existenz einer Single-Phase bestätigt. Die Wärmeleitzahl und spezifische Wärme wurden bei 53°C gemessen. Hinsichtlich der maximalen Porösität dieser Zusammensetzung hatte die Wärmeleitzahl einen Mindestwert von x = 0.3. Hinsichtlich der Phononenstreuung wurde für die Phononenfrequenz ein Optimum für x = 0.3 geschätzt.