Role of Silica Addition on Thermal Transport Properties of Strontium Hexa-Ferrites

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Abstract

A series of Sr-hexa ferrite with the addition of SiO2 (wt % = 0.5, 1.0, 1.5, 2.0) has been prepared by the solid state reaction method. The structural characterization of all the samples confirmed the major phase of hexa structure and minor amount of hematite and Sr-silicate. The lattice parameters, bulk density, X-ray density and porosity have no significant change, ensuring the unchanged crystal structure of Sr hexa-ferrite system. Scanning electron micrographs show the details of grains of the Sr hexa-ferrite system. Thermal conductivity, thermal diffusivity and heat capacity per unit volume of these samples are measured by the Gustafsson probe as a function of temperature range from 303K to 473K. It has been noted that both thermal conductivity (λ) and thermal diffusivity (κ) increase whereas heat capacity per unit volume (ρCp) decreases with temperature.

Key words: Densities; Heat Capacity; Magnetic Properties; Scanning Electron Microscopy; Thermal Conductivity; Thermal Diffusivity, X-Ray Diffraction.

Introduction

M-type hexagonal ferrites, such as $Sr(Ba)Fe_{12}O_{19}$ have been intensively investigated as a material for permanent magnets, high-density recording, magneto-optic media, and microwave devices [1, 2]. In recent years, a few investigators have attempted to determine the thermal conductivity of ferrites as a fundamental material constant. Since thermal conductivity is a structural sensitive property, the constant obtained from measurements of polycrystalline aggregates are not generally applicable unless the effects of the microstructures on these values are known. In the dielectric materials, heat is transferred by thermal vibrations of the lattice. Thermal conductivity of the body is determined by inelastic collision and the scatter of phonons, or in analogy with kinetic theory, by the mean free path of the phonons. The factors which may affect thermal conductivity in ferrites are grain boundaries, pores, lattice imperfections, impurities and radiation through the material. The theory of thermal conductivities discussed earlier predicts that the conductivity of an ideal dielectric above its Debye temperature is inversely proportional to the absolute temperature. At lower temperatures, the conductivity increases more rapidly, supporting the theoretical expectation that the Debye relationship will not hold below, Debye temperature. The aim of present work is to characterize the material by thermal conductivity, thermal diffusivity and specific heat per unit volume using the Gustafsson probe. It is expected that the knowledge of thermal transport data on this important material will be useful in thermo-technological applications such as fire forewarning or as an integrating dosimeter.

Experimental

All the samples of Sr hexa-ferrites system with the addition of SiO_2 (0.5, 1.0, 1.5, 2.0 wt %) namely A-1, A-2, A-3 and A-4 were prepared by the standard solid state reaction method. The preparation details are already published by our research group [4]. X-Ray diffraction of the samples confirmed the formation of hexagonal structure with few peaks of Hematite (α-Fe_2O_3) and Sr-silicate as a second phase in a minute quantity.

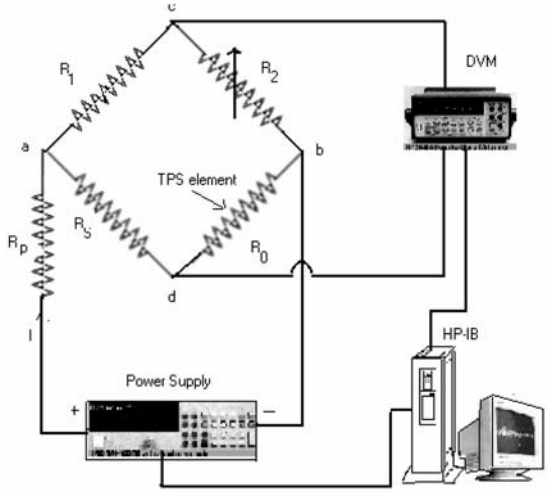

Fig. 1. Bridge circuit diagram for TPS technique: R_s= Standard resistance, R_o= Resistance of sensor [3]

The physical and mechanical properties are strongly influenced by their microstructure, so their studies are essential to understand the relationship between the processing parameters as well as the behavior of the materials when used in practical application. In the present study, a JEOL 2000CX Scanning Electron Microscope (SEM) equipped with energy dispersive spectra (EDS) was employed to examine the micro structural features such as

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grain size and porosity. The magnetic properties of the samples, using vibrating sample magnetometer at room temperature with maximum applied field of 10kOe was carried out.

The transient plane source (TPS) technique known as Gusstafsson probe [5] was utilized to measure the thermal transport properties of the samples, because it allows the measurements without any disturbance form the interfaces between the sensor and the bulk samples. Also, simultaneous measurement of thermal conductivity (λ), thermal diffusivity (κ), is possible and then heat capacity per unit volume (ρC_p) can be obtained [5]. In this technique, a TPS-element (Fig.2) made of 10 μm-thick nickel foil with an insulating layer made of 50 μm-thick mica, on each side of the metal pattern, is used both as constant heat source and a sensor of temperature.

For data collection, the TPS element of (20mm diameter) sandwiched between two halves of the same samples in a bridge circuit (Fig.1) [6, 7]. The TPS-element had a resistance of 5.00605 Ω at room temperature and a temperature coefficient of resistance (TCR) of around 4.87×10^{-3} $K^{-1.}$ The sample holder (Fig.2) containing these samples is placed in an oven having sensitivity of 1 K. The size of the samples was around 25 mm dia and 12 mm in height.

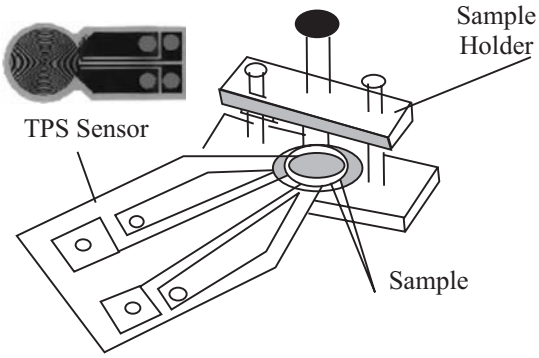

Fig. 2. TPS sensor and sample holder

After achieving the isothermal condition in the sample, a constant current pulse of width 28 s and a height 0.19 mA is passed through the heating element. The element owing to the change in average temperature of the sensor, the potential difference across changes. The transient potential difference across the terminals is recorded by a digital multimeter and the current through the TPS sensor with the digital power supply. The current in circuit is adjusted according to the nature of the sample material. Multiple readings at appropriate intervals are taken to ensure the accuracy of the results. The TPS programme used here is capable of recording the temperature of the sample through the TPS sensor itself. In addition to this a sensitive Pt-100 thermometer is kept just above the sample pieces inside the furnace to monitor the temperature of the sample. By recording the voltage drop for a particular time interval, detailed information about the thermal conductivity and thermal diffusivity of the test specimen is obtained. The heat capacity per unit volume is then calculated form the relation

$$\rho C_p = \frac{\lambda}{\kappa} \quad (1)$$

Where 'ρ' is the mass density of sample. For thermal conductivity measurements, each sample consisted of two identical circular tablets of the same specimen. The surfaces of the samples were made smooth to have a good thermal contact with TPS-element and to minimize thermal contact resistance. The thicknesses of the samples were chosen so as to satisfy the probing depth criteria [8]. Taking into consideration the errors of technique [7, 9], standard deviations of the measurements and the sampling errors, the thermal conductivity and thermal diffusivity data contain errors of 5% and 7%, respectively. The errors in volumetric heat capacity are around 10%.

Results and discussion

Material characterization

Lattice parameters were calculated by indexing XRD pattern at room temperature. The results showed the formation of main phase of Sr hexa-ferrite with Hematite (α-Fe_2O_3) as second phase [10].

X-ray densities of the samples were calculated using the relation

$$D_x = \frac{2M}{N_a V} \quad (2)$$

Here 'M' is molecular weight; 'N_a' is Avogadro's number and 'V' is the volume of the unit cell of hexagonal system given as

$$V = 0.866\, a^2 c \quad (3)$$

Where 'a' and 'c' are the lattice constants and '2' in Eq.2 is multiplied due to the fact that elementary cell contains two molecules [11].The material is also checked at the micro scale [4].

Porosities of the samples are determined from the equation,

$$P = \frac{D_x - D_B}{D_x} \quad (3)$$

Where 'P' is porosity, 'D_x' and 'D_B' are the X-ray and bulk densities respectively.

The values of lattice constants, X-ray densities, bulk densities and porosities as a function of SiO_2 wt % are shown in Table 1.

It is evident that lattice constants, X-ray density, bulk density and porosity have no significant changes. These confirm that SiO_2 did not enter into the Sr hexa-ferrite structure but only made wetting of grain boundaries with Sr-silicate which resulted from the reaction of Sr and SiO_2.The role of SiO_2 as an additive for micro-structural control of hard ferrite magnets has been explained as liquid phase forming agent [13, 14]. According to the proposed phase diagram Sr-SiO_2-Fe_2O_3 at 1250 ^oC the addition of SiO_2 causes the appearance of liquid or solid minority phases depending on the SiO_2 and Sr-excess concentration. This liquid phase of Sr-silicate significantly suppress the

abnormal grain growth and act as grain growth inhibitor [15] which can be seen from the Scanning Electron Microscopic (SEM) micrographs [4].

Table 1. Physical and Structural Properties of $SrFe_{12}O_{19}$ System with SiO_2 (0, 0.5, 1.0, 1.5. 2.0) wt %. 'S' refers to the values of Muller and Collomb [12]

S. No	S	A-1	A-2	A-3	A-4
SiO_2 wt %	0.0	0.5	1.0	1.5	2.0
a (Å)	5.882	5.87(4)	5.86(5)	5.85(8)	5.80(2)
c(Å)	23.023	23.0(2)	23.0(3)	22.9(2)	23.0(3)
Vol. $(Å)^3$	690(1)	686(1)	684(1)	679(1)	670(1)
D_B gm/cm^3	-	4.52	4.57	4.55	4.51
D_x gm/cm^3	5.11	5.14	5.15	5.19	5.26
Porosity P (%)	-	12	11	12	14

Magnetic properties

The magnetization parameters were determined from M-H loops by the application of 10 kOe as maximum field. The magnetic properties of hexa-ferrites are determined by its chemistry and microstructure. The coercivity H_c of the system increased from 4615 Oe to 4750 Oe with the addition of SiO_2 up to 1.5 wt % and decreased to 4236 Oe for 2.0 wt % of silica. The remanence M_r showed drastically increasing trend with the increase of silica addition. For detail the reader is referred to our earlier [4].

Thermal transport properties

Thermal transport properties of ferrites depend upon their structure, density, porosity, composition, temperature and pressure, etc. The temperature dependence of thermal conductivity, thermal diffusivity, and heat capacity per unit volume was measured from room temperature 303K to 473K with 25K intervals and the results are shown in Fig.3.

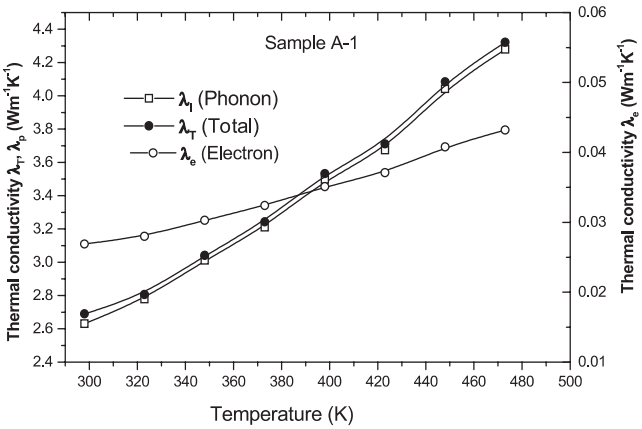

Fig. 3. Temperature dependence of the thermal conductivity of Sr-hexa ferrite contribution from electrons and phonons

It was observed that thermal conductivity of all the samples increased in the mentioned temperature range, as reported in literature [16, 17], indicating that behavior might be intrinsic.

Thermal conductivity can be expressed as a sum of lattice component (λ_l) and electronic component (λ_e) as

$$\lambda = \lambda_l + \lambda_e \quad (4)$$

The λ_e values can be estimated from Weidman-Franz's law as

$$\lambda_e = LT\sigma \quad (5)$$

Where *'L'* is Lorentz number (2.45×10^{-8} $W\Omega K^{-2}$ for free electrons), *'T'* temperature in K and *'σ'* is electrical conductivity at given temperature. Hence λ_l can be obtained from λ- λ_e [17, 18]. This is analogous with the electrical behavior in the semi conducting materials [18], in which by increasing temperature, free electrons are jumping from valance band to the conduction band in order to increase the electrical conductivity. But at low temperature electronic contribution to the thermal conductivity is very low as shown in Fig. 3.

A similar behavior is observed with conduction of heat in ferrites and alloys as reported earlier [19-21]. Another factor to increase in thermal conductivity is attributed to the increase in number of phonons with the rise in temperature which is the major portion. i.e. about 90% of total thermal conductivity due to phonon at low temperature [19, 20]. The increase in thermal conductivity with addition of SiO_2 is also observed at room temperature as shown in Fig. 4.

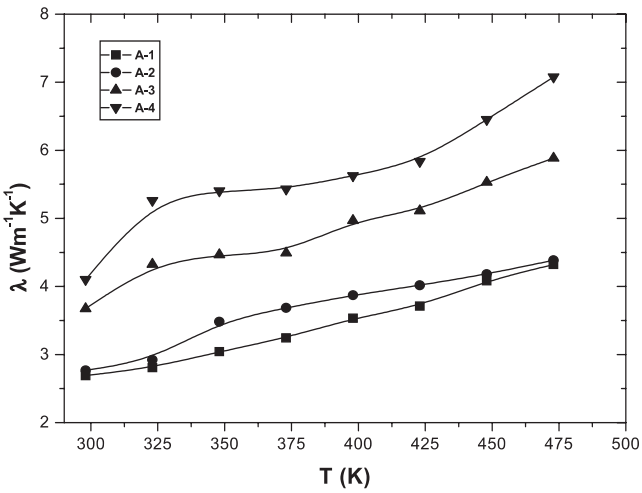

Fig. 4. Temperature dependent thermal conductivity for all samples

This may be due to the fact that the thermal conductivity of Si (1.480 $Wcm^{-1}K^{-1}$) is greater than the Fe (0.802 $Wcm^{-1}K^{-1}$) and Sr (0.353 $Wcm^{-1}K^{-1}$) at 20 ^oC [22]. Another increasing factor may be due to the fact that SiO_2 is grain growth inhibitor, results the denser structure [15]. The same behaviour was observed with the thermal diffusivity as shown in Fig. 5, which has the direct relation with the thermal conductivity. Heat capacity per unit volume of the studied samples has the inverse relation with

λ and κ. Thus it has decreasing trend with the rise in temperature from 303K to 473K as shown in Fig. 6.

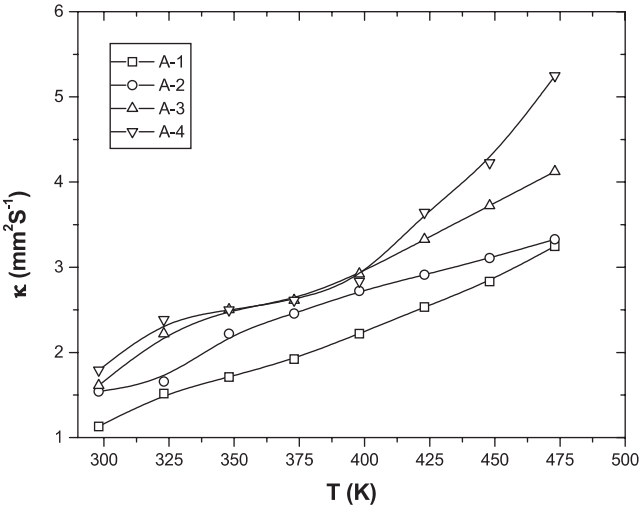

Fig. 5. Temperature dependent thermal diffusivity of the studied samples

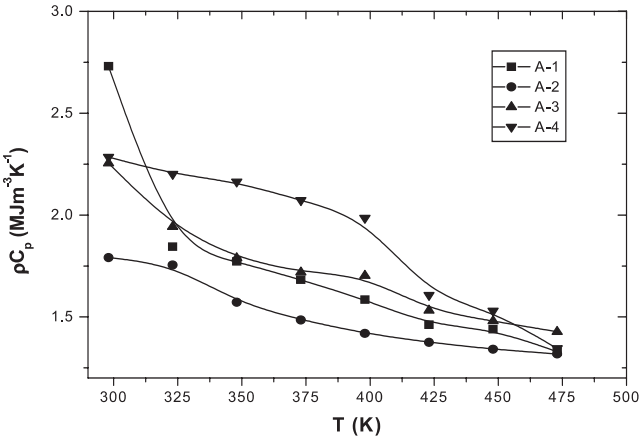

Fig. 6. Variation of heat capacity per unit volume with temperature for all samples

Since good thermal conductor will conduct maximum heat to the surroundings and have less capacity to store heat.

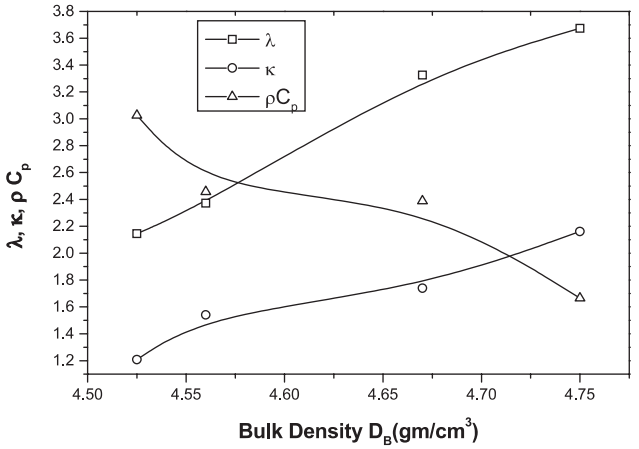

Fig. 7. Variation of thermal conductivity λ, thermal diffusivity κ, and heat capacity per unit volume ρC_p with density at normal temperature and pressure

Variation of thermal transport properties with density is shown in Fig 7. Density has direct relationship with thermal conduction phenomenon [23] and beneficial in the studied Sr-hexa ferrites for its permanent magnet application at high temperature. In case of high heat capacity, its temperature will rise quickly and which intern magnetic moments will misaligned and loss its magnetic properties.

Conclusion

To summarise the current study, it was noticed that by the addition of SiO_2 in the Sr-hexa ferrite system, thermal conductivity increases from 2.7 $Wm^{-1}K^{-1}$ to 4.1 $Wm^{-1}K^{-1}$ not only at room temperature but also with increase in temperature. The increase in λ with rise in temperature due to free electron and lattice vibrations (phonons). Thermal diffusivity also increases from 1.13 mm^2S^{-1} to 1.79 mm^2S^{-1} by the addition of SiO_2 at room temperature. Maximum measuring temperature was 473K due to the setup limitations, it is expected that this increase in thermal conductivity and thermal diffusivity would be upto transition temperature Tc, after that these should fall. Heat capacity per unit volume decreased from 2.73 MJ $m^{-3}K^{-1}$ to 2.29 $MJm^{-3}K^{-1}$ at normal temperature and pressure.

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