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Thermal diffusivity measurements for Mg–Mn ferrites ☆

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The thermal diffusivity of Mg–Mn ferrites is studied through a modified scheme of the photothermal deflection method able to derive the diffusivity of low-diffusivity samples and to avoid any influence of the vertical offset parameter. The examined samples have been realized under different preparation conditions producing different grain dimensions, and a negligible influence of the grain dimensions is found on the thermal properties.

1. Introduction

The importance of Mg–Mn ferrites lies in their magnetic properties and low electrical conductivity which allow electromagnetic waves to propagate in the medium and make them suitable for applications in microwave devices [1]. An "in transit" high-power microwave signal [2] causes heating of the material and the thermal drag problem arises. For this purpose both new stoichiometric compounds and sintering conditions have been developed.

The aim of this paper is to study the thermal diffusivity behaviour of ferrites prepared with different sintering conditions, giving rise to different grain dimensions and to try to correlate the latter with the thermal behaviour. The experimental method empoyed to measure the thermal diffusivity is the photothermal deflection method, used in the transverse configuration, but adopting a modified technique of evaluation of experimental results, due to the low diffusivity of the ferrites (lower than that of air) and to avoid any influence of the surface treatment.

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2. Sample preparation

The samples of $Mg_1Mn_{0.1}Fe_{1.55}Al_{0.35}O_4$ are obtained with the standard ceramic procedure which starts with mixing of the constituent oxides (Fe_2O_3, MgO, MnO_2 and Al_2O_3) taken in their stoichiometric proportions. After mixing and drying, the oxide mixture is subjected to a prefiring step in fireclay crucibles at temperatures of about 80% of the final sintering temperature for about 1 h. During this reaction, sintering also takes place and results in very hard aggregates. In order to homogenize the dimensions of the grains this product has to be ground. This is performed in a second cycle of ball milling with a binder addition. Due to the hardness of the reaction product there is some gain in iron, mainly from the steel ball of the mill, which changes the stoichiometry. This amount of iron wear has been determined empirically and compensated for by using a correspondingly lower Fe_2O_3 content in the starting mixture. After crushing and sieving, the powder is pressed in a hydraulic press at a pressure of about 100 nPa. The organic binder has been eliminated from the pressed pieces to prevent their cracking during the subsequent sintering cycle and to avoid the carbonization of the polymers with its reduction and damaging effects.

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The sintering step has been performed under four different conditions: 1320°C for 5 and 10 h, and 1360°C for 5 and 10 h. The quenching conditions are the same for all samples (i.e. free descent in a closed kiln). The samples, with dimensions of tens of millimeter were mechanically finished to the required sizes.

From the SEM photographs [3] for the samples heated at different temperatures (first column, table 1) and for different times (second column, table 1), we can deduce the average dimensions for the grains (third column, table 1).

3. Thermal diffusivity measurements

The method used to determine the thermal diffusivity is the photothermal deflection method in its transverse configuration [4]. This essentially involves the detection of the deflection caused to a probe-laser beam travelling in the air layer near the sample surface by a gradient in the air refractive index produced by heating the sample with a pump-laser beam, modulated in time at a frequency ν through a chopper.

The experimental arrangement is shown in fig. 1, where the Ar laser is the pump and the He–Ne laser acts as a probe beam. The probe beam is detected through a position detector and the signal is sent to a lock-in amplifier. The deflection angle ϕ is related to the temperature gradient perpendicular to the probe beam by the expression

$$\phi = \frac{1}{n}\frac{\partial n}{\partial T}\int_{\text{path}} \nabla T(r, t)\,\mathrm{d}s\,, \qquad (1)$$

where $T(r, t)$ is the temperature at point r and time t in air, n is the refractive index of air, $\partial n/\partial T$ is the change of n with respect to the temperature and the integral is performed over the probe path s.

Table 1
Experimental data for the samples studied. Sintering was performed at the temperature T for t hours. The grain dimension is d and χ is the measured thermal diffusivity

T (°C)	t (h)	d (μm)	χ (cm²/s)
1320	5	5.8	0.0159
1360	5	6.7	0.013
1320	10	9.3	0.02
1360	10	13.2	0.013

The deflection signal has one parallel (ϕ_t) and one normal (ϕ_n) component with respect to the sample surface. Usually the normal component of the deflection signal is measured [4,5]. In our case since the sample thermal diffusivity was very low in comparison with air, the normal component was subject to considerable noise; this was very much decreased by measuring the parallel component ϕ_t.

The amplitude and phase of the deflection signal is obtained from a position sensor whose signal is sent to a lock-in amplifier, and is related to the deflection signal $\Delta V/V$ by the equation

$$\Delta V/V = (4/\sqrt{2\pi})(4\pi w n/\lambda)\phi\,, \qquad (2)$$

where w is the probe beam spot size and λ the wavelength. The pump laser used was an Ar laser with input power $P = 4$ mW, focused to a spot size of 60 μm; the probe was a He–Ne laser with a spot size of 20 μm.

In our setup we measured the deflection signal phase as a function of the offset x between the probe and pump beam. In fact, at a suitable offset distance of the probe from the center of the pump beam ($x > a$, where a is the pump-beam spot, i.e. approximating to a point heating source), the deflection signal can be written as [5]

$$\phi = \phi^0 \exp(-x/l_t)\exp\{\mathrm{i}[\nu t - \Theta(x)]\}\,, \qquad (3)$$

where $\Theta(x)$ is a phase term given by

$$\Theta(x) = -x/l_t + f(z)\,, \qquad (4)$$

where l_t is the thermal diffusion length given by $l_t = (2\pi\chi/\nu)^{1/2}$, and $f(z)$ is an arbitrary function depending on the vertical offset z. Therefore, the slope of the curve of the phase signal as a function of x (in the linear region of this phase signal) gives directly a value of l_t, from which, knowing the chopper frequency ν, the thermal diffusivity χ can be calculated. An example of phase signals as a function of offset is shown in fig. 2, for different z values. From the figure one can see how the different values of z affect the amplitude of the phase signal but in all cases a linear region exists in which the phase signal is proportional to the offset x. Moreover, the absence of a change of slope in the linear part of the signal means

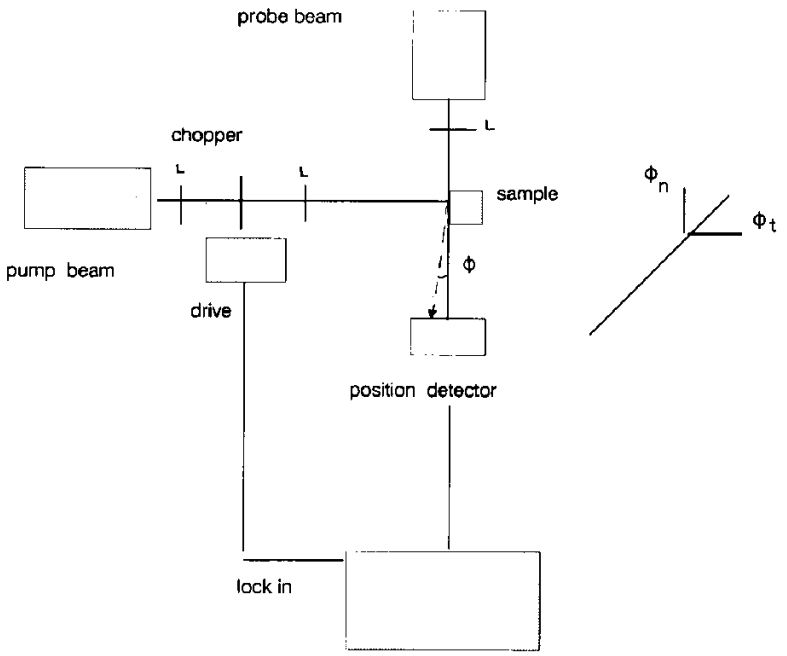

Fig. 1. Experimental arrangement.

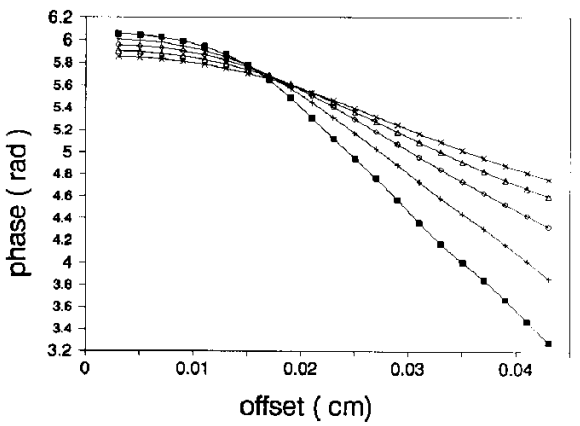

Fig. 2. Phase signal as a function of the offset between pump and probe, for different z values, (■) $z=0$, $\chi=1.3\times10^{-2}$ cm^2/s; (+) $z=25$ μm, $\chi=2.3\times10^{-2}$ cm^2/s; (◇) $z=50$ μm, $\chi=4\times10^{-2}$ cm^2/s; (△) $z=75$ μm, $\chi=6\times10^{-2}$ cm^2/s; (×) $z=100$ μm, $\chi=9\times10^{-2}$ cm^2/s.

the absence of a surface layer [6] with thermal properties different from the bulk.

Applying this method to ferrites, we found that the thermal diffusivity was frequency dependent (as shown in fig. 3). Of course this result is not correct; on changing the frequency the derived value of thermal diffusivity must remain the same. Fig. 4 shows the thermal diffusivity length l_t plotted as a function of the inverse square root of frequency for one of the samples. For the other samples, similar results were obtained; simple inspection shows that for high fre-

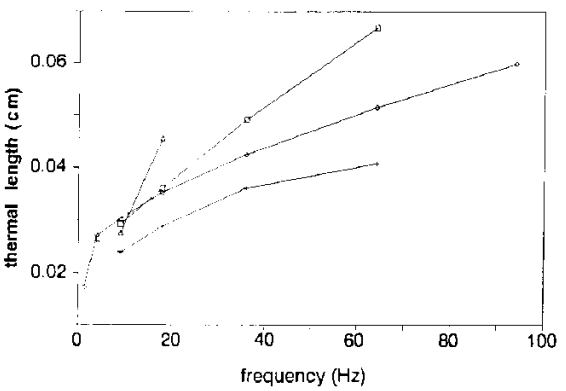

Fig. 3. Thermal diffusion length as a function of the chopper frequency: (△) sample 1, (□) sample 2, (◇) sample 3, (+) sample 4.

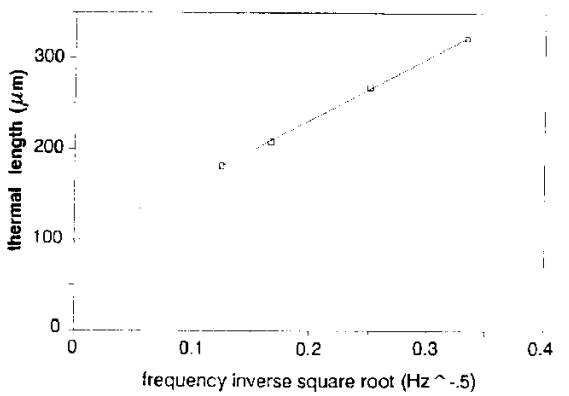

Fig. 4. Thermal diffusion length as a function of the inverse square root of the chopper frequency.

quencies the extrapolated l_t value does not go to zero as one should expect. The thermal diffusivity length rather exhibits a behaviour given by

$$l_t = A + C/\nu^{1/2}, \qquad (5)$$

where $A = l_t$ at $\nu \to \infty$, and $C = (\chi/\pi)^{1/2}$ as expected from the theory, and where all the measured $l_t(\infty)$ values fulfill the condition of $l_t > a$, a being the spot size of the heating laser. A simulation made with different values of z has verified the validity of the empirical relation (5), showing that the coefficient A changes by changing the z value.

It is therefore very important to take into account correctly the value of the vertical offset in all the cases in which the thermal diffusivity of the sample is lower or of the same order of magnitude as the thermal diffusivity of the air [7]. The ideal situation could be the one of zero vertical offset, which is of course not practically possible.

Otherwise by using the empirical relation (5), the correct value of diffusivity can be obtained as

$$\chi^{cor} = \pi (l_t^{measured} - A)^2 \nu .$$

Table 2 gives, for four different samples, the relevant parameters. The wrong diffusivity derived by the relation $\chi^m = \nu\pi\ (l_t^{measured})^2$ is also given for comparison in column 3.

The corrected values for χ are also given in table 1. No clear relation is found between grain dimensions and thermal diffusivity.

Table 2
Thermal length and diffusivity at different frequencies for four samples

Sample no.	ν (Hz)	$l_t^{measured}$ (μm)	χ^m (cm²/s)	χ^{cor} (cm²/s)	$l_t^{effective}$ (μm)	$\Delta\chi/\chi$ (%)
1	9	322	0.0293	0.0152	232	−4.7
	16	268	0.036	0.0159	178	−0.93
	36	208	0.0492	0.0159	118.6	−0.93
	64	182	0.067	0.0172	92.4	+7.2
2	4	456	0.0261	0.0182	381	
	9	291	0.0241	0.0132	216	+2.3
	16	240	0.029	0.0137	165	+6.2
	36	179	0.036	0.0122	104	−5.4
	88	142.5	0.056	0.0126	67.5	−2.3
3	4	465	2.66	0.0206	405	+2
	9	328	0.0305	0.0203	268	+1
	20	237	0.035	0.0197	177	−2.5
	36	194	0.0425	0.0203	134	+1
	64	160	0.0513	0.0201	100	+1
	88	142.5	0.06	0.0201	82.5	+1
4	9	312	0.0274	0.0134	217	+3
	36	200	0.0455	0.0126	105.6	−3

4. Conclusions

The thermal diffusivity of Mg–Mn ferrites has been measured, indicating anomalous behaviour of this parameter which came out to be a function of the chopper frequency. To correct for this clearly unrealistic behaviour, a phenomenological equation has been used which gives reasonable values of diffusivity, in agreement with expected values. The anomalous behaviour is associated with the low diffusivity of the samples and with the influence of the vertical offset parameter. The measurements performed for samples prepared under different conditions so as to give different grain dimensions do not show clear evidence of any relation between thermal diffusivity and grain size.

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