Journal of Thermal Analysis, Vol. 37 (1991) 241-248

SINTERING BEHAVIOUR OF THE SPINEL FERRITE SYSTEM $Ni_{0.65}Zn_{0.35}Fe_{2-x}Cu_xO_4$

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(Received June 6, 1990)

A series of samples of the system $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) are prepared by the usual ceramic technique. X-ray analysis shows that they are cubic spinel (single phase). The lattice parameter, theoretical density (D_x), bulk density (D) and the porosity (P) are measured for the samples. The vacancy concentration of oxygen is an important parameter in the sintering process of spinel ferrites. The decrease in the population of Fe^{3+} ion in the octahedral sites with the introduction of Cu^{2+} results in the decrease of lattice parameter. The DTA tracing shows a strong exothermic peak at 90°C.

The recent development of a high-magnetization nickel-zinc ferrite with stress-intensitive square hysteresis loop achieved through substitution of MN^{3+} ions has prompted a study of the family $Fe^{3+}_{0.65}Zn^{2+}_{0.35}[Ni^{2+}_{0.65}Fe^{3+}_{1.35-x}Mn^{3+}_x]O_4$ [1]. The magnetic and dielectric properties of compositions with x ranging from 0 to 0.4 were measured to determine the effects of the manganese substitutions over this concentration range. As anticipated, the saturation magnetization decreased gradually with increasing x because of reduced magnetic moments in the B sublattice. Of greater importance, however, was the observation that maximum hysteresis loop squareness and minimum stress sensitivity occurred with $x \sim 0.2$. A single-ion magnetization model is used to interpret this result. Since the electrical resistivity remained above 10^6 Ω cm and the dielectric loss tangent stayed below 10^{-3} for the entire series, Fe^{2+} ion formation is probably negligible.

A series of samples of the system $Co_{1-x}Zn_xFe_2O_4$ (x = 0, 0.3, 0.4, 0.6, 0.8 and 1) are prepared by the usual ceramic technique. X-ray analysis shows that they are cubic spinel (single phase). The lattice parameter, theoretical density D_x, bulk density D, and the porosity P are measured for the samples

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[2]. Thermopower and *dc* resistivity measurements are carried out and the drift mobility μ at different temperatures is calculated. The activation energies and the *dc* conductivity σ for different samples in the system $Co_{1-x}Zn_xFe_2O_4$ (x = 0.3, 0.4, 0.6 and 0.8) are presented. As expected, the activation energies are lower for higher conductivity samples.

The aim of this paper is to study the effect of copper doping on the sintering behaviour of the spinal cubic ferrites. For this purpose, X-ray density, measured density and the lattice parameter (a) measurements are presented for $Ni_{0.65}Zn_{0.35}Fe_{2-x}Cu_xO_4$ where x ranging from 0 to 0.6.

Experimental

Sample preparation

Samples of the system $Ni_{0.65}Zn_{0.35}Fe_{2-x}Cu_xO_4$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) were prepared using the usual ceramic technique. The pure oxides were mixed and then ground to a very fine powder by using an agate mortar made of carborundum. The samples in form of discs were sintered at 1200° for two hours and slowly cooled to room temperature. The samples were polished to have uniform parallel surfaces.

Lattice parameter and density measurements

The X-ray diffraction pattern for each sample was recorded by using Shimadzu X-ray diffractometer (Model X D-3). The powder specimens were exposed to CuK_α radiation. The lattice parameter and X-ray density D_x (true density) were calculated according to the formula

$$D_x = \frac{8M}{Na^3}$$

where M is the molecular weight, N Avogadro's number, and a the lattice parameter which was calculated from the X-ray diffraction pattern.

The bulk density D is determined by using Archimedes principle in toluene according to the following formula

$$D = \frac{W_s}{W_t}\rho_t$$

where W_s denotes the weight of the specimen in air, W_t the apparent weight loss in toluene, and ρ_t the density of toluene.

The DTA patterns were obtained using DTA thermal analyzer (DuPont Instruments 990 thermal analyzer) from room temperature to 900°.

Results and discussion

Lattice parameters of Cu-doped $Ni_{0.65}Zn_{0.35}Fe_2O_4$

The following relation gives the interplanar for a certain series (hkl)

$$d_{hkl} = 1/\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}$$

In the case of cubic system, the lattice parameter a can be calculated directly using the following relation and Table (1).

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2}$$

The lattice parameter value of $NiZnFe_2O_4$ is determined to be 8.385 Å which compared favorably with value of previous work [3]. The variation of lattice parameter a as a function of copper addition x in $Ni_{0.65}Zn_{0.35}Fe_{2-x}Cu_xO_4$ is represented in Fig. 1. It shows that the lattice parameter decreases with the increase of copper content. The lattice constant values are in the expected range with the lattice constants of spinal cubic ferrites [4, 5]. Our results are explained on the assumption that the presence of small amount of Fe^{2+} in one site in the lattice is sufficient enough to ionize Fe^{3+} in the adjacent site and the resulting electron is used by an adjacent Fe^{3+}, i.e. $Fe^{3+} + e \rightleftarrows Fe^{2+}$ and the propagates. The introduction of Cu^{2+} to the lattice of $NiZnFe_2O_4$ results in the decrease in the number of Fe^{3+} ions in the octahedral sites. The decrease in the population of Fe^{3+} in the octahedral sites with the introduction of Cu^{2+} results in the decrease of the lattice parameter a. This is because Fe^{2+} has a much smaller ionic radius than Fe^{3+}, it is estimated to have a radius of about 0.59 Å. Since Fe^{3+} have ionic radius of 0.69 Å. Little change in the lattice parameter was expected with direct substitution.

Table 1 X-ray analysis for $Ni_{0.65}Zn_{0.35}Fe_{2-x}Cu_xO_4$

Plane	ASTM card for cubic system		The prepared sample		a,
hkl	d, Å	I/I_o, %	d, Å	I/I_o, %	Å
			$x = 0$		
220	2.968	30	3.028	27.0	8.564
311	2.531	100	2.578	100.0	8,550
222	2.424	8	2.462	7.5	8,529
400	2.099	20	2.127	25.0	8.508
422	1.713	10	1.728	16.0	8.465
511	1.615	30	1.629	51.0	8.465
440	1.483	40	1.492	67.0	8.440
			$x = 0.1$		
220	2.968	30	3.018	25.0	8.536
311	2.531	100	2.564	100.0	8.504
222	2.424	8	2.449	9.9	8.484
400	2.099	20	2.118	27.0	8.472
422	1.713	10	1.725	14.8	8.451
511	1.615	30	1.626	40.7	8.449
440	1.483	40	1.492	51.0	8.440
			$x = 0.3$		
220	2.968	30	3.008	27.0	8.508
311	2.531	100	2.557	100.0	8.481
222	2.424	8	2.449	9.2	8.484
400	2.099	20	2.113	21.0	8.452
422	1.713	10	1.722	16.9	8.436
511	1.615	30	1.623	43.0	8.433
440	1.483	40	1.490	0.55	8.429
			$x = 0.4$		
220	2.968	30	3.028	23.0	8.514
311	2.531	100	2.578	100.0	8.456
222	2.424	8	2.449	8.7	8.454
400	2.099	20	2.127	23.0	8.408
422	1.713	10	1.731	14.5	8.450
511	1.615	30	1.629	43.5	8.465
440	1.483	40	1.495	61.0	8.457
			$x = 0.6$		
220	2.968	30	3.028	21.8	8.564
311	2.531	100	2.578	100.0	8.550
222	2.424	8	2.449	12.5	8.484
400	2.099	20	2.122	26.5	8.488
422	1.713	10	1.731	15.6	8.480
511	1.615	30	1.629	46.9	8.465
440	1.483	40	1.495	53.0	8.457

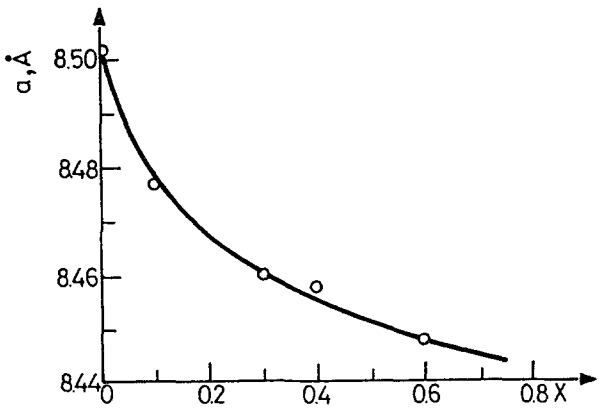

Fig. 1 Variation of lattice parameter (a) as a function of copper additions x

Effect of copper additions on the density and porosity of $NiZnFe_2O_4$

The X-ray density D_x is calculated. The results of calculation is shown in Fig. 2. It is noticed that the X-ray densities for all compositions of $Ni_{0.65}Zn_{0.35}Fe_{2-x}Cu_xO_4$ increase with copper additions to be optimized for $x = 0.3$ and then decreases with increasing x. The bulk density D for the specimens is determined also. The true densities D_x are higher than the bulk values D. This is attributed to the existence of pores which depend on sintering conditions and the kind of additions.

The porosity P is calculated from the following relation

$$P = 1 - \frac{D}{D_x}$$

The effect of copper additions on the porosity and the bulk density D for our compositions is observed also in Fig. 2. The copper additions decrease the density thus increasing the porosity of the samples up to $x = 0.3$. For additions higher than 0.3, a reduction in porosity is observed. This can be explained by the following.

It has been suggested that doping increases the concentration of lattice vacancies [6]. The substitution of Cu^{2+} into $NiZnFe_2O_4$ might cause the formation of excess vacancy. However, if excess vacancy is formed it would be cation vacancies rather than anion vacancies which reduces the concentra-

tion of anion (Oxygen vacancy) causing the decrease in oxygen ion diffusion. This behaviour retard the densification. For an addition higher than 0.3, the increasing of density and reduction of porosity may be due to the increase of the concentration of oxygen vacancies which increase the rate determining step in the sintering of ferrites. Thus the vacancy concentration of oxygen is an important parameter in the sintering process of spinel ferrite [7].

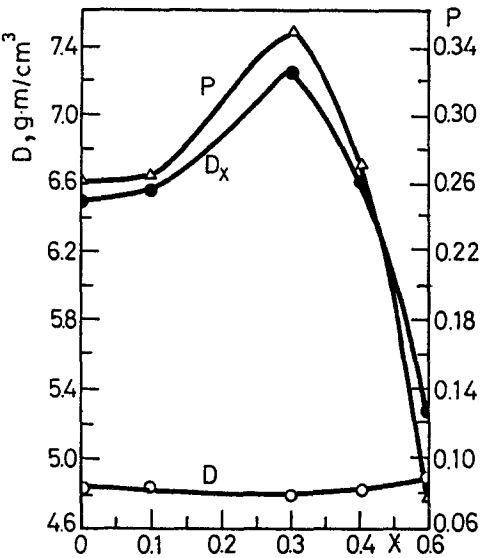

Fig. 2 Effect of copper additions on the X-ray density (D_x), experimental density (D) and porosity (P)

DTA for $NiZnFe_2O_4$ compositions

An exothermic peak is observed over a range of about 20-170° for all compositions as shown in Fig. 3. It is noticed that the sharpness of the peak increase with increasing x up to 0.3. A decrease of the sharpness of the peak is recorded for x higher than this value.

The results can be explained on the basis of slight change in the lattice parameter of the cubic lattice. The increase of the sharpness of the peak with x is due to more creation of lattice vacancies which give rise to lattice defects. The decrease of the sharpness of the peak for the ferrite composition containing Cu higher than 0.3 can be discussed by the decrease of the

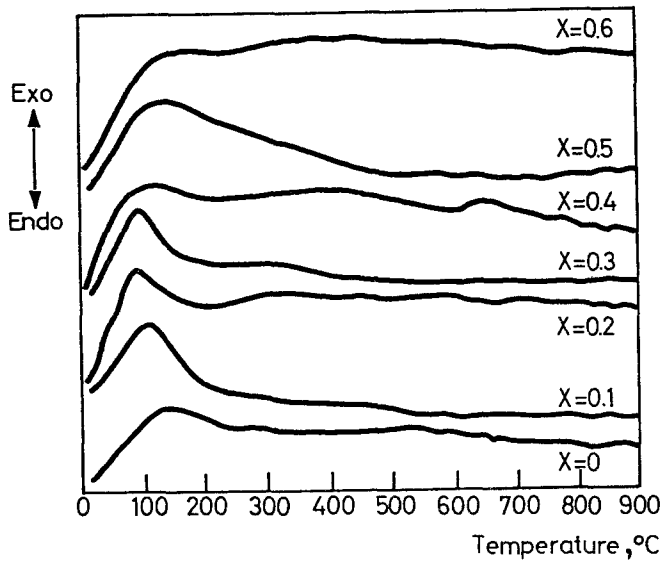

Fig. 3 DTA patterns for $Ni_{0.65}Zn_{0.35}Fe_{2-x}Cu_xO_4$

number of cation vacancies and increasing the oxygen vacancies which diffuse in the lattice. This diffusion increase the density of the specimen and decreasing the change in the lattice parameter.

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The measurements were carried out at the Solid-state Physics Laboratory, Faculty of Science, Tanta University.

The authors are grateful to the technical assistance of the Central Laboratory of Tanta and Manoufia University for X-ray and DTA facilities.

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Zusammenfassung – Mittels herkömmlicher keramikchemischer Verfahren wurde eine Reihe von Proben des Systemes $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ ($x = 0$, 0.1, 0.2, 0.3, 0.4, 0.5 und 0.6) hergestellt. Röntgendiffraktionsanalyse zeigt kubisches Spinell (eine Phase). Es wurden die Gitterkonstanten, die theoretische Dichte *Dx*, die Raumdichte *D* und die Porosität *P* dieser Proben gemessen. Die Gitterleerstellenkonzentration von Sauerstoff ist ein wichtiger Parameter beim Sintern von Spinellferriten. Die Abnahme der Besetzung mit Fe^{3+}-Ionen bei der Einbringung von Cu^{2+} führt zu kleineren Gitterkonstanten. DTA-Kurven zeigen einen starken exothermen Peak bei 90°C.