

## SYNTHESIS OF SODIUM-ZINC SPINEL FERRITES

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The synthesis of spinel ferrites with composition  $Zn_{1-2x}Na_xFe_{2+x}O_4$  has been performed and the composition range in which single phase samples are obtained has been defined. The characterization of the samples has been carried out from atomic absorption and X-ray fluorescence analyses, X-ray diffraction patterns, Mössbauer spectroscopy and thermomagnetic measurements. It is shown that significant loss of Na does exist when the synthesis is performed at high temperatures. When the Na volatilization is avoided spinel oxides with Na content up to 0.25 atoms per unit formula can be obtained. In this case the increase of the interatomic distances leads to differing fundamental magnetic properties as compared to the equivalent lithium-zinc ferrites.

Introduction

Lithium-zinc spinel ferrites are a wide class of ferrimagnetic materials with interesting magnetic characteristics in view of microwave applications [1]. In the same way, sodium-zinc spinel ferrites could be good candidates for these technological applications. As a matter of fact, due to the different ionic radii of Na and Li atoms the distances between magnetic ions will be very different in both cases. In this way, according to previous studies on spinel ferrites [2], a change of the fundamental magnetic properties may be expected.

The first report on the synthesis of sodium-zinc spinel ferrites was done by Mones and Banks [3]. From this study it seemed clear that a wide range of solid solutions could exist between  $ZnFe_2O_4$  and the hypothetical  $Na_{0.5}Fe_{2.5}O_4$  spinel. However, the composition and magnetic properties of their samples remain unclear. Therefore, we decided to undertake a full study of the synthesis conditions of  $Zn_{1-2x}Na_xFe_{2+x}O_4$  spinels in order to define their composition range. Some preliminary results concerning their magnetic properties are presented as well.

Experimental

The syntheses of all compounds, with nominal composition  $Zn_{1-2x}Na_xFe_{2+x}O_4$ , were performed in air from a high temperature solid state reaction of  $\alpha$ - $Fe_2O_3$ , ZnO and  $Na_2CO_3$

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stoichiometric mixtures. Before being introduced in the furnace the samples were homogenized in an agate mortar and pelletized. Different firing temperatures and cooling rates were used. X-ray diffraction patterns were obtained with a Siemens D-500 powder diffractometer using  $Cu K\alpha$  as incident radiation and a graphite monochromator. Lattice parameters were computed with the aid of a least squares program from X-ray patterns containing Si powder as internal standard. The Na content of the samples was determined by the atomic absorption technique while the Fe and Zn contents were determined by X-ray fluorescence. Mössbauer spectra were obtained with a conventional spectrometer by using a 10 mCi  $^{57}Co:Rh$  single line source. Velocity calibrations were made via  $\alpha$ -Fe spectra. Isothermal magnetization measurements were performed by the axial extraction technique in fields up to 55 KOe by using a superconductor solenoid and up to 150 KOe with a water cooled Bitter magnet of the Service National des Champs Intenses at Grenoble.

Results and discussion

The firing temperatures during the synthesis, together with the results of the chemical analyses for all the single phase samples obtained are indicated in Table 1. The samples corresponding to the M and A series have been slowly cooled at a rate of 50°K/hour from the synthesis temperature up to 473 K and then removed from the furnace and allowed to cool until room temperature. The B samples, instead, were cooled by immersing them in liquid nitrogen from the synthesis temperature.

Under our experimental procedure it has been not possible to obtain single phase samples with higher Na contents than those indicated in Table 1. The samples with higher nominal Na content showed after the synthesis process additional Bragg reflections, corresponding to  $\alpha$ - $Fe_2O_3$ , in the X-ray patterns.

The composition dependence of the cubic lattice parameters in the different series compounds are shown in figure 1.

From the results reported in Table 1 it becomes clear that an important loss of Na does exist in the M series compounds which allows to understand the invariance of their lattice parameters (fig.1). As a consequence of the Na volatilization, and taking into account that only the spinel phase is observed in the X-ray patterns, we can conclude that a mixture or a solid solution of different spinels, such as  $ZnFe_2O_4$  and  $Fe_3O_4$ , does exist. For example, in lithium spinel ferrite the loss of lithium or oxygen results in the formation of  $Fe_3O_4$  or  $\delta$ - $Fe_2O_3$ , depending on the synthesis temperature and oxygen pressure [4]. Due to the similarity of the lattice parameters of these solid solutions it is very difficult to

x	% Na weight		theoretical %Na weight
	M(T <sub>s</sub> =1653K)	A,B(T <sub>s</sub> =1273K)	
0.05	0.29	0.44	0.48
0.10	0.49	0.85	0.98
0.15	--	1.34	1.48
0.20	--	1.91	1.99
0.25	--	2.40	2.51

Table 1. Sodium content for the samples corresponding to the different solid solutions  $Zn_{1-2x}Na_xFe_{2+x}O_4$

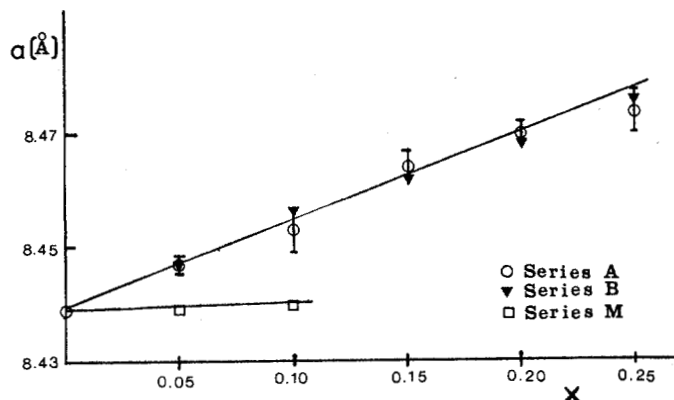


Fig.1. Lattice parameter as a function of the Na content, x, for the different series.

distinguish them in the X-ray diffraction patterns. Nevertheless, the different magnetic characteristics of these spinels enable us to distinguish them by using Mössbauer spectroscopy and thermomagnetic measurements. A typical Mössbauer spectrum of a M series compound is shown in figure 2 where the coexistence of a magnetic and a paramagnetic component is evidenced. The hyperfine parameters of the magnetic phase observed in the Mössbauer spectra are indicated in Table 2. The best fit of the x = 0.1 spectra has been obtained by introducing two separate hyperfine fields while the spectra of the x = 0.05 compound have been fitted to a unique hyperfine field. The spectra obtained at T = 80K show that the intensity ratio of the magnetic to the paramagnetic component is invariant with temperature; thus any interpretation of these spectra in terms of a superparamagnetic relaxation can be excluded. The values the hyperfine fields correspond roughly to those found in  $Fe_3O_4$  or  $Fe_{3-x}Zn_xO_4$  spinels [5], supporting our conclusion about the formation of solid solutions or mixtures of  $ZnFe_2O_4$  and  $Fe_3O_4$ .

The isothermal magnetization curves of the M series compounds have been measured in fields up to 55 KOe at temperatures ranging from 4.2K until 300K. Above saturation the curves M(H) can be fitted by a law  $M(H) = M_0 + \chi H$ . In figure 3 we show the temperature dependence of the saturation magnetization  $M_0$  and of the inverse of the high field differential susceptibility  $\chi$ . If we take into account the amount of magnetic phase existing in the samples as deduced from the Mössbauer spectra, both the  $M_0$  and  $\chi$  values are compatible with the existence of a  $Fe_3O_4$

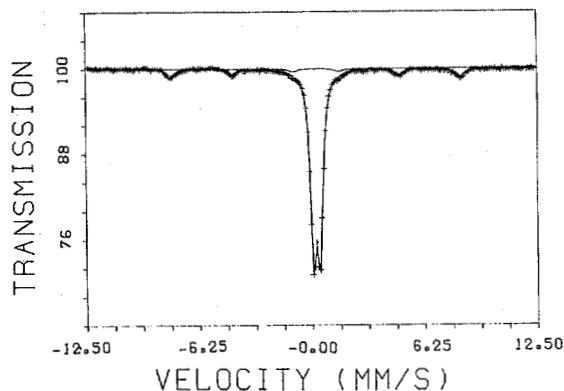


Fig.2. Room temperature Mössbauer spectra of the x = 0.05 M series compound

x	H <sub>hf</sub> (KOe)	IS (mm/s)	I <sub>s</sub> /I <sub>t</sub>	T (K)
0.05	493(2)	0.22(4)	0.15(2)	293
0.05	496(5)	0.30(7)	0.18(3)	80
0.10	479(5)	0.24(5)	0.10(5)	293
	445(16)	0.22(11)	0.10(5)	

Table 2. Hyperfine parameters of the Mössbauer spectra corresponding to the M series compounds

like ferrimagnetic component and a paramagnetic-antiferromagnetic  $Zn_{1-2x}Na_xFe_{2+x}O_4$  component. From the  $1/\chi$  versus T plot it can be seen that the Curie-Weiss law holds at high temperature. The effective paramagnetic moment per ion deduced from these data, assuming that only the paramagnetic component observed in the Mössbauer spectra contributes to the susceptibility, ranges from  $5.2 \mu_B$  to  $5.6 \mu_B$ . These values are compatible with those observed in  $ZnFe_2O_4$  [6]. At the same time,

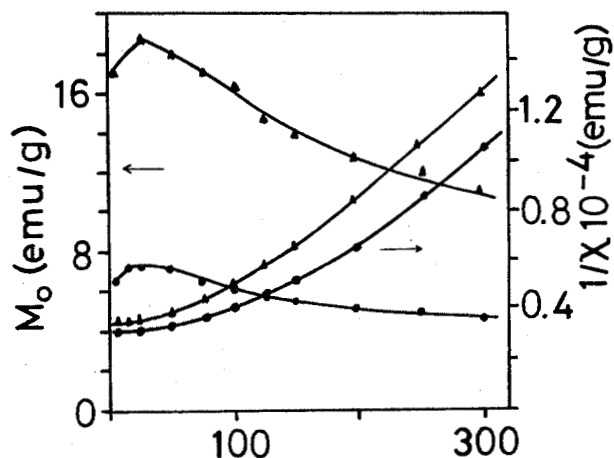


Fig.3 Temperature dependence of the saturation magnetization and the inverse of the high field differential susceptibility for the M series compounds; ● x = 0.05, ▲ x = 0.10

the measured  $M_0$  values correspond to values of  $M_0$  (OK) of the magnetic phase of about 100 emu/g, which are roughly those observed in  $\text{Fe}_{3-x}\text{Zn}_x\text{O}_4$  [7]. Moreover the peak observed in the  $1/\chi$  versus  $T$  plot at  $T \approx 15\text{K}$  evidence the setting of the antiferromagnetic ordering of  $\text{ZnFe}_2\text{O}_4$  at this temperature [6].

Our final conclusion concerning the M series compounds, is that when the synthesis is performed at high temperatures a great deal of Na volatilization does exist, leading to the appearance of  $\text{Fe}_3\text{O}_4$  or  $\text{Fe}_{3-x}\text{Zn}_x\text{O}_4$  as a impurity phase.

In what it concerns the A and B series compounds, both the chemical analyses (Na, Zn and Fe contents) and the linear increase of the lattice parameters with the Na content (Vegard's law) show that the Na ions are effectively incorporated into the lattice. Because of the high ionic radius of Na ions

( $r^{\text{VI}} = 1.02 \text{ \AA}$  [8]) we may expect that they will occupy the octahedral sites of the spinel structure. In this way, the increase of the lattice parameters with  $x$  can be understood as an overall rise of the size of the spinel polyhedra. This effect is put in evidence in figure 4, where for comparison purposes, the values corresponding to lithium-zinc ferrites are included as well.

Some preliminary high field (150 KOe) magnetic measurements of these samples show that saturation magnetizations as high as 72 emu/g ( $2.9 \mu_B$  /f.u.) can be obtained ( $x = 0.25$ ,  $T = 4.2\text{K}$ ). This magnetization curve shows as well a superposed high field differential susceptibility of  $\chi = 13.7 \cdot 10^{-5}$  emu/g which can be interpreted, as for lithium-zinc spinel ferrites [9], as arising from localized random canting of the spins. Nevertheless, if we compare these values with those representing the lithium compound with the same Zn content, we find that higher  $M_0$  values

( $4.3 \mu_B$  /f.u.) and lower  $\chi$  values ( $7 \cdot 10^{-5}$  emu/g) are obtained in the Li-Zn spinels, indicating that a higher degree of canting does exist in the Na-Zn spinels. Finally, the room temperature Mössbauer spectra of the A and B series samples show a progressive evolution from a typical quadrupole splitted paramagnetic spectra to spectra showing features characteristics of the spin-spin relaxation phenomenon which is well known to exist in Zn substituted spinels [10,11].

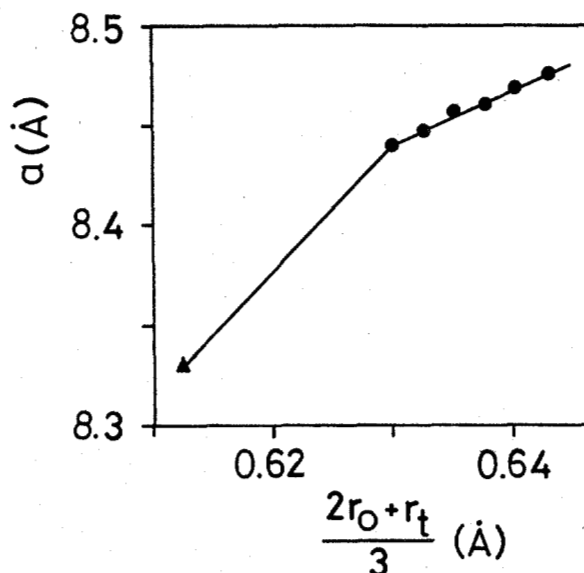


Fig.4. Lattice parameter  $a$  versus the mean ionic radius of metallic ions in the spinel polyhedra. ●  $\text{Zn}_{1-2x}\text{Na}_x\text{Fe}_{2+x}\text{O}_4$ , ▲  $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$

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