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SINTERING AND MAGNETIC PROPERTIES OF Co-Nb FERRITES

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A series of samples of the system Co $Nb_xFe_{2-x}O_4$ (x = 0, 0.2, 0.4, 0.6 and 0.8) 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 magnetic susceptibility is measured and conducted with the additions of niobia. Results were evaluated on the bases of the exchange electrons at the octahedral sites.

Oxides having the general formulae AB_2O_4 (A and B are transition metal ions) and crystallizing with spinel like structures ($Fd^3m\ O_h^7$) have been goining attention in the recent years. The interest in these oxides emerges from their versatile applicability in radio to microwave frequency regions. Among the various oxides studied, the spinel ferrites have been of interest owing to their interesting electrical and magnetic properties. Ferrites have vast applications from microwave to radio frequencies. The electric conduction mechanism of ferrites containing Fe^{2+} ions was explained by the hopping motion of electrons between Fe^{2+} and Fe^{3+} ions on the octahedral sites of the spinel lattice [1-2].

The activation energy, resistivity, and Seebeck coefficient were measured for a semiconducting $CoFe_2O_4$ [3].

The lattice constants of Co-Zn ferrites were studied [4] depending on the Co concentration. It was a linear relation. There are a number of reports concerning the effects of sintering aids on the magnetic properties of ferrites. The effect of Nb_2O_5 on the memory core characterestics of substituted lithium ferrites are reported [5, 6].

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The present study was directed towards determining the sintering behaviour and knowing the situation of magnetic susceptibility for the various compositions (x = 0, 0.2, 0.4, 0.6 and 0.8).

Experimental

Sample preparation

Samples of the system $\mathrm{Co\,Nb_x\,Fe_{2-x}\,O_4}$ (x = 0, 0.2, 0.4, 0.6 and 0.8) 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. Contacts on the sample surface were made by silver paste for electrical measurements.

Lattice parameter and density measurements

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

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

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 the Archimedes principle in toluene according to the following equation:

$$D = \frac{w_s}{w_t}\rho_t \quad ,$$

where w_s denotes the weight of the sample in air, w_t the apparent weight loss in toluene, and ρ_t the density of toluene. The measurements of magnetic susceptibility was carried out using spinner magnetometer type spinal spin (England). The experimental results were taken at room temperature (30°).

Results and discussion

Lattice parameters of Nb-doped $CoFe_2O_4$

The data of X-ray diffraction was represented in Table 1 and the lattice parameter value of $CoFe_2O_4$ is determined to be 0.8385 nm which compared favorably with the value of 0.8394 nm [7]. The variation of lattice parameter a as a function of Nb additions x in $Co\cdot Nb_xFe_{2-x}O_4$ is represented in Fig.1. It shows that the lattice parameter increases linearly with the increase of Nb content. The lattice constant values are in the expected range with the lattice constant of $CoFe_2O_4$ [8]. These results are in good agreement with the previous work [4]. Our results are explained on the assumption that the substituting Nb^{5+} ions instead of Fe^{3+} ions in the composition [9].

Table 1 X-ray data for $CoNb_xFe_{2-x}O_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8$)

2θ	d	sin 2θ	s	hkl	I/I_0	a	average
30.49	2.93	0.069	8	220	31.0	8.287	
35.79	2.51	0.094	11	311	100.0	8.324	8.31
43.48	2.08	0.137	16	400	29.5	8.320	
57.38	1.60	0.230	27	511	36.0	8.314	
$x = 0.4$							
30.55	2.92	0.0649	8	220		8.259	
35.92	2.497	0.0951	11	311		8.282	8.289
43.58	2.074	0.1378	16	400		8.296	
57.48	1.601	0.2310	27	511		8.319	
$x = 0.6$							
30.45	2.932	0.0689	8	220		8.293	
35.50	2.526	0.0929	11	311		8.378	8.346
43.27	2.088	0.1359	16	400		8.352	
57.18	1.609	0.2289	27	511		8.361	
$x = 0.8$							
30.30	2.946	0.0683	8	220		8.333	
35.30	2.539	0.0919	11	311		8.421	8.387
43.05	2.099	0.1346	16	400		8.396	
56.90	1.616	0.2269	27	511		8.397	
$x = 0$							
30.51	2.926	0.0692	8	220		8.276	
35.82	2.503	0.0945	11	311		8.302	8.302
43.56	2.075	0.1376	16	400		8.300	
57.40	1.603	0.2301	27	511		8.329	

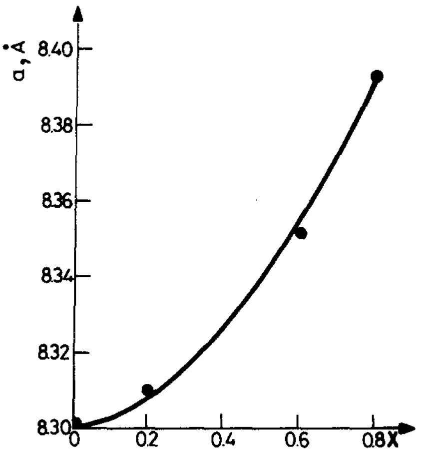

Fig. 1 Variation of lattice parameter a as a function of composition x

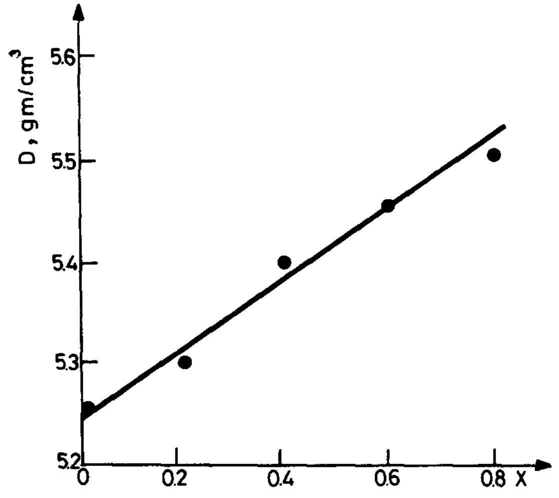

Fig. 2 Variation of X-ray density D_x as a function of composition x

It was confirmed that Nb^{5+} enters the lattice substitutionally for Fe^{3+} in octahedral sites for all concentrations in $CoNb_xFe_{2-x}O_4$. Nb^{5+} has a much larger ionic radius than Fe^{3+}, little change in the lattice parameter was expected with direct substitution. The introduction of Nb^{5+} to the lattice of $CoFe_2O_4$ results in the decrease in the number of Fe^{3+} ions in the octahedral sites which results in the increase of lattice parameter. The X-ray density D_x is calculated. The results of calculations is shown in Fig. 2. It is noticed that the true densities for all compositions of Co-Nb ferrites increase with niobium additions. The bulk density D for the specimens is determined also. The true densities D_x are higher than the bulk volumes D. This is attributed to the existence of pores which depend on the sintering conditions.

The porosity P is calculated from the following relation:

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

The effect of niobium additions on the porosity and the bulk density D for Co-Nb ferrites is observed in Fig. (3).

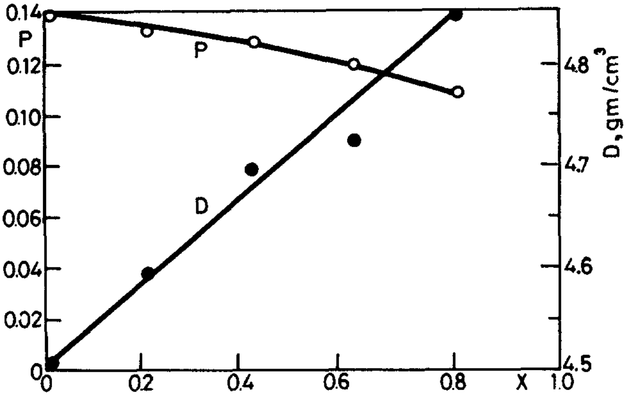

Fig. 3 Variation of porosity P and bulk density D as a function of composition x

The niobium additions reduce the porosity thus increasing the density of the sample. Niobium accelerates densification [10]. It has been suggested that the substitute of Nb^{5+} into cobalt ferrite might cause the formation of lattice vacancies and hence enhance the sintering of cobalt ferrites by an enhanced volume diffusion mechanism [12, 6]. Moreover the atomic weight of niobium is higher than the atomic weight of iron gaving rise to the increase of density.

Effect of niobium on the magnetic susceptibility of cobalt ferrite

The effect of niobium on the magnetic susceptibility of cobalt ferrite is shown in Fig. (4). The increase of magnetic susceptibility can be explained by the following:

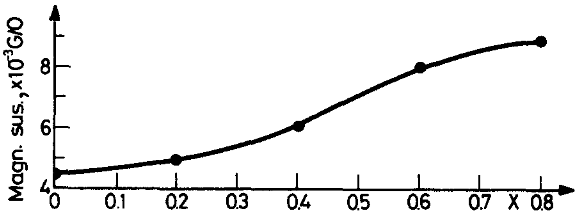

Fig. 4 Variation of magnetic susceptibility with increasing Nb addition (*x*)

It was observed from thermoelectric power measurements, $CoFe_2O_4$ are *n* type ferrites [13]. The most probable conduction mechanism could be the electron hopping between Fe^{2+} and Fe^{3+} ions as Fe^{3+} Fe^{2+} +e and will occur between two adjacent octahedral points in the spinel lattice [14, 15]. 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 chain propagates. The introduction of Nb^{5+} to the lattice of $CoFe_2O_4$ results in the decrease in the number of Fe^{3+} ions in the octahedral sites. This gave rise to the electron hopping which takes place between two adjacent octahedral sites. This mechanism had higher magnetic moment with increasing niobium addition which resulted the higher magnetic susceptibility.

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References

1 E. J. W. Werwey, P. W. Haaijman, F. C. Romeyn, and G. W. Vanoosterhout, Philips Res. Rep., 5 (1950) 173.
2 I. G. Austin and N. F. Mott, Adv. Phys., 18 (1969) 41.
3 F. G. Brockman and K. E. Matteson, J. Amer. Ceram. Soc., 53 (1970) 517.
4 O. S. Josyulu and J. Sobhanadri, Phys. Stat. Sol, (a) 59 (1980) 323.

5 H. B. Im in Proceedings on International Conference on Ferrite, Kyoto, Japan, (1980) 281.
6 H. T. Kim and H. B. Im, IEEE Trans. Magn. MAG - 18 (1982) 1541.
7 J. Smit and H. P. J. Wijy, Les Ferrites, Phil. Tech. Lib., Dunod, Paris (1959) 144.
8 ASTM Cards.
9 H. T. Kim, H. B. Im, J. Mat. Sc., 22 (1987) 1235.
10 E. C. Subbarao, J. Amer. Ceraur., 43(3) (1960) 119.
11 T. Ilmura, Jpn. Yogo Kyokaishi, 84 (1976) 34.
12 M. A. Ahmed, Phys. Stat. Sol., (a) 111 (1989) 567.
13 R. R. Heikes, J. Chem. Phys., 26 (1957) 582.
14 G. H. Jonker, J. Phys. Chem. Solids, 9 (1959) 165.

Zusammenfassung — Mittels herkömmlicher keramischer Verfahren wurde eine Reihe von Proben des Systemes Co $Nb_xFe_{2-x}O_4$ (mit x = 0, 0.2, 0.4, 0.6 und 0.8) gefertigt. Röntgenographische Untersuchungen zeigen ein kubisches Spinell (single-phase). Gitterkonstanten, theoretische Dichte D_x, Raumdichte D und das relative Porenvolumen der einzelnen Proben wurden bestimmt. Die magnetische Suszeptibilität wurde bestimmt. Die Ergebnisse wurden auf der Grundlage von Elektronenübergängen an den oktaedrischen Stellen gewertet.