Green density effects on the structural and magnetic properties of (Cd, Zn)$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ ferrites produced by combustion technique

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Abstract. We present results of structural and magnetic measurements derived from x-ray diffraction, magnetization and Mössbauer spectroscopy for (Cd, Zn)$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ ferrites prepared by combustion technique. The changes in properties are investigated as a function of pressure or green density used to compact the pellets before sintering. Information on lattice parameters, grain sizes, porosity, coercive fields, saturation magnetization, Curie points and hyperfine field distributions are correlated with the pressure effect, bulk densities of the samples and differences in ionic sizes of Cd and Zn atoms. Evidence of trapped porosity and optimum sample preparation conditions are also deduced from the data.

1. Introduction

Ni-Zn ferrites are amongst some of the well-studied and used ferrites. They are characterized by soft magnetic properties and high resistivity. The desired phase is easy to form and materials produced have the advantage of high stability and low cost. This accounts for the wide use of Ni-Zn ferrites in magnetic and electrical applications. The research interest in these materials is aimed at improving the quality, reliability and consistency in the material properties. A good understanding of the evolution of properties imposed by the methodology and sample preparation conditions is therefore critical. The techniques used to arrive at the final product are known to influence the properties. However, it is expected that better techniques for sample preparation in different places under similar conditions should produce samples with greater consistency because of the use of common raw materials of similar or identical purity. The conventional technique used to produce ferrites is the ceramic technique, which involves at least two stages of grinding of the starting oxides. Here the final level of homogeneity depends on the type and duration of grinding process and the initial particle size of the oxides. Hence the same level of homogeneity every time and in different places is harder to achieve when samples are produced by mechanical methods. There is also greater chance of contamination and sample loss during milling operations [1-3]. Prolonged heating of the samples at high temperature also gives rise to further mass loss.

In materials produced by wet chemical methods a higher degree of homogeneity of the starting solution can be achieved. The samples produced by these techniques should demonstrate a higher degree of consistency. Unfortunately, this appears not to be the case when two sets of data are compared in two recent reports [2, 3]. It is therefore important to develop firm criteria that can be used to compare properties of samples from different sources. We have employed the combustion technique [1-3] to produce samples of high quality from a well-homogenized mixture of starting nitrates and urea. The main interest was to investigate the extent to which material properties evolve from samples prepared from the same homogenized and ignited mixture under different conditions of applied pressure (related to the green density) in the production of sample pellets. The effect of totally replacing Zn^{2+} ions by the larger Cd^{2+} in the $Zn_{0.5}Ni_{0.5}Fe_2O_4$ compound was also investigated.

2. Experimental details

The nominal compositions of $(Cd, Zn)_{0.5}Ni_{0.5}Fe_2O_4$ ferrites were prepared from a mixture of stoichiometric amounts of $Cd(NO_3)_2 \cdot 4H_2O$ or $Zn(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$) and NH_2CONH_2 (synth.). The quantity of urea used was such that it matched the number of N atoms in the nitrate mixture [3]. The mixture was then dissolved in some distilled water and well homogenized in a vitreous porcelain basin placed on a cold plate of a heater inside a fume cupboard. The mixture was then gradually heated until self-ignition of the mixture was finally completed at about 600 °C in a period of about an hour. This process of heating ensured a very high degree of homogeneity of the mixture and minimized the likelihood of spillage if the mixture had been placed on a preheated plate at 600 °C. The final product was homogenized by using an agate mortar and pestle. The powder was then pressed into pellets of almost the same mass at different pressure for about two minutes to produce pellets of different compaction or states of green density. The samples were finally sintered in air in a preheated tube furnace at 1210 °C for about 6 hours. A typical sintered pellet was roughly about 0.4 grams with diameter of about 7 mm and 2 mm thickness. The diameters increased while the thickness of the sintered pellets decreased with increase in green density. Bulk density measurements of the sintered pellets were performed on small mass fragments using Archimedes principle. This involved direct measurement of the buoyant force on solid fragments in a suitable oil medium using a Mettler AT261 Delta Range electronic balance with precision of 0.00001 grams [4]. Density measurements based on the geometry of the pellets were found to be unreliable. The structure of the samples produced was determined by x-ray diffraction (XRD) using a DRX-HGZ/Herzog model 1D 3000 unit with CuKα(1) radiation ($\lambda = 1.5418$ Å). The angle 2θ was varied by 0.2° intervals. The magnetic measurements were performed at room temperature using a ^{57}Fe Mössbauer spectrometer and vibrating sample magnetometer (VSM). The accuracy of the VSM measurements was counter checked by a Quantum Design MPMS XL squid magnetometer.

3. Results and discussion

Typical XRD spectra for $(Cd, Zn)_{0.5}Ni_{0.5}Fe_2O_4$ compounds are presented in Figure 1. Virtually all the significant peaks are indexed. Hence all the samples produced had single-phase formation. The spectra are consistent with the spectrum published by Costa et al [3] on similar compounds produced by the combustion technique. In Table 1 we present results of bulk density, lattice parameter, grain size and porosity as a function of applied pressure (or green density). Slight but definite changes with pressure are observed. Zn- and Cd-based samples have comparable values of the lattice parameters, with those of Cd-based samples being slightly larger. We attribute this largely due to differences in ionic sizes because

$$\frac{(a)_{Zn}}{(a)_{Cd}} \approx \frac{r_{ionic, Zn}}{r_{ionic, Cd}}.$$

(1)

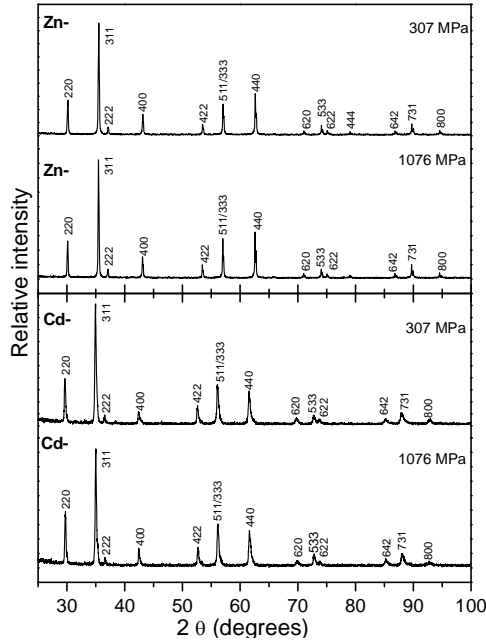**Figure 1.** Typical XRD spectra of sintered (Cd, Zn)$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ oxides. Pre-sintered pellets were formed at pressures of 307 and 1076 MPa.
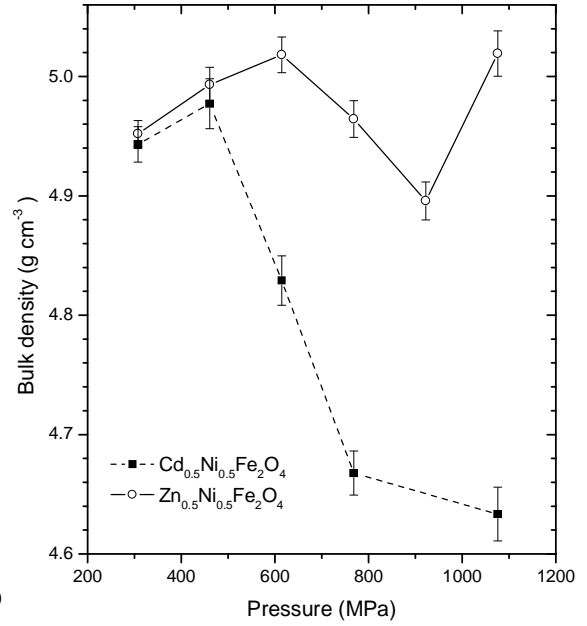
Figure 2. Bulk densities of sintered (Cd, Zn)$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ oxides plotted as a function pressure (or green density) of pre-sintered pellets.

Table 1. Bulk density ρ, lattice parameter a, grain size D and porosity P_o as a function of applied pressure (or green density) (P) for (Cd, Zn)$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$.

	P (MPa) ±10	ρ (g/cm^3) ±0.02	a (Å) ±0.001	D (nm) ±0.7	P_o (%) ±0.05
Zn	307	4.95	8.385	45.6	7.57
	461	4.50	8.384	49.1	6.83
	615	5.02	8.384	49.5	6.37
	769	4.96	8.391	51.2	7.15
	922	4.90	8.393	51.7	8.37
	1076	5.02	8.382	48.8	6.40
Cd	307	4.94	8.516	32.1	12.04
	461	4.98	8.504	39.4	11.79
	615	4.83	8.482	28.2	15.09
	769	4.67	8.508	30.9	17.17
	1076	4.63	8.505	35.7	17.87

The ionic sizes for Zn and Cd are 0.74 Å and 0.97 Å respectively [5]. The crystalline grain size D for each sample has been estimated using the Scherrer formula [3, 6, 7]

$$D = \frac{\lambda}{\beta \cos\theta} \tag{2}$$

where λ is the wavelength of the CuKα radiation and β is the full width at half maximum of the (311) intensity peak. The grain sizes are larger for Zn-based compounds reflecting the well-known tendency of Zn to enhance the desired phase formation. In addition there is a systematic increase of the grain size to a maximum value around 770 MPa in Zn-based compounds. Grain sizes are lower in Cd-based samples. We attribute this to the larger ionic size of Cd. This would tend to weaken inter-ionic interactions resulting in smaller crystallites. An important parameter that measures the average coordination of atoms in the entire sample is the bulk density. This parameter has information of the average compaction of the atoms and includes also the effect of the empty spaces (a measure of porosity). The results of bulk density measurements as a function of pelletizing pressure are presented in Figure 2. Costa et al [3] prepared a similar set of compounds by combustion technique but at a pre-sintering pressure of 392 MPa. They found a bulk density of 5.00 g cm^{-3} for the Zn-based sample sintered at 1200 °C. This is consistent with the present results. However, there is an apparent anomaly in the variation of the bulk density with pressure P. A slight increase in bulk density is observed initially which reduces with further increase in the green density. We believe that these results can be explained on the basis of a significant amount of trapped porosity. The pelletizing pressure can interfere with escape routes of excess gases from a pellet during sintering process. The porosity of the samples can be calculated from the knowledge of bulk density and x-ray density deduced from the size of the unit cell. The porosities are also given in Table 1. Cd-based samples with smaller particle sizes have higher porosity $(P_o)_{Cd} \approx 2(P_o)_{Zn}$.

The $(Cd, Zn)_{0.5}Ni_{0.5}Fe_2O_4$ samples were observed to have a ferromagnetic effect at room temperature in response to a small bar magnet. Isothermal magnetization $\sigma(H)$ measurements were performed at room temperature in the field range: $-6\,kOe \leq H \leq 6\,kOe$. The samples appear to have significant superparamagnetic character. Typical low field isothermal magnetization curves are given in Figure 3 for $Cd_{0.5}Ni_{0.5}Fe_2O_4$ sample. The hysteresis curve for the Ni calibration sample is also given in Figure 3 to illustrate the limit of the accuracy of our measurements. The results show very little hysteresis loss at room temperature. In Table 2 we show the data of coercive fields and saturation magnetization. There is no significant change in saturation magnetization as function of pressure. However, there appears to be a slight correlation between coercive and bulk density. Lower coercive field seems to be associated with higher bulk density in Zn-based samples.

Mössbauer spectroscopy measurements were performed at room temperature. Typical spectra spectra are given in Figure 4, which show ordered magnetic phase at room temperature. The spectra are characterized by broad peaks, which indicate a range of hyperfine fields. The appropriate analysis is therefore to deduce hyperfine field distributions from the spectra. Figure 5 shows such distributions. The plots clearly show systematic change of the hyperfine field distributions as a function of pelletizing pressure (green density). We can identify four principle gaussian peaks that make up the hyperfine distributions as illustrated in Figure 6 for the hyperfine distribution at 1076 MPa.

The Curie points of the samples were determined using the zero velocity Mössbauer technique, which is associated with the relative change of the transmission of gamma ray through an absorber in ordered and disordered states. No significant change of Curie points with green density was observed. The average Curie point was determined to be 554±4 K.

Table 2. Coercive field (H_C) and saturation magnetization (σ) as a function of applied pressure (or green density) (P) for $(Cd, Zn)_{0.5}Ni_{0.5}Fe_2O_4$.

	P (MPa) ± 10	H_C (Oe) ± 0.5	σ (emu/g) ± 0.2
Zn	307	3.7	74.2
	461	1.9	72.8
	615	2.2	73.5
	769	0.6	75.1
	922	4.5	74.1
	1076	2.7	75.3
Cd	307	3.4	56.1
	461	3.2	56.0
	615	3.4	56.9
	769	3.8	58.0
	1076	4.9	57.9
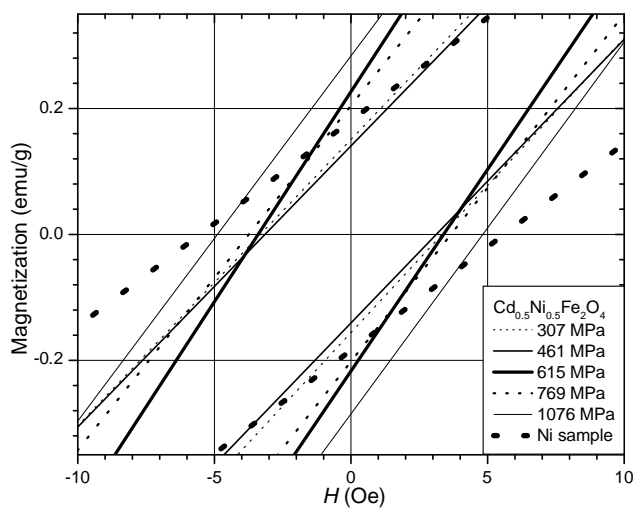
Figure 3. Isothermal magnetization curves in low magnetic fields. A saturating field is initially applied to the samples.
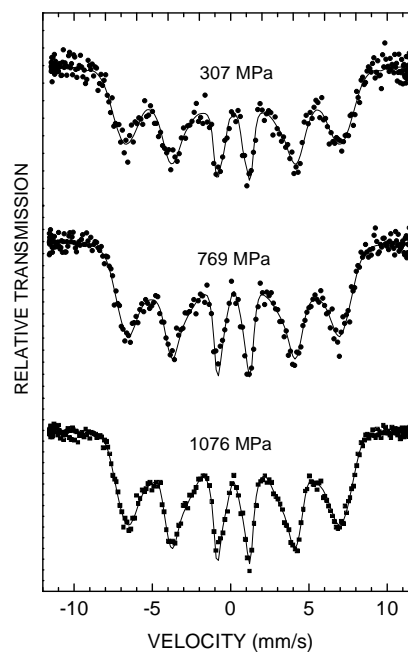
Figure 4. Typical Mössbauer spectra for $Cd_{0.5}Ni_{0.5}Fe_2O_4$ samples.

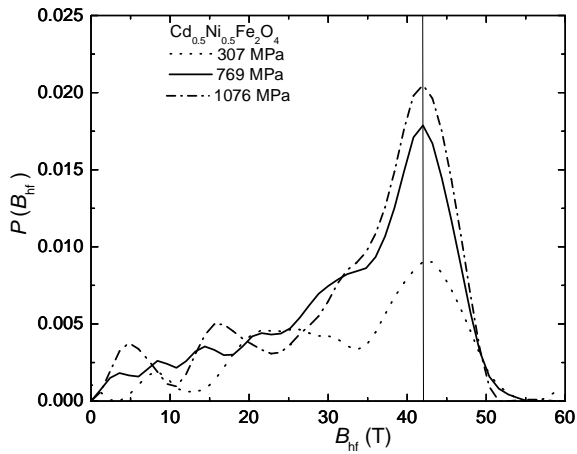**Figure 5.** Hyperfine field distributions for $Cd_{0.5}Ni_{0.5}Fe_2O_4$ samples.

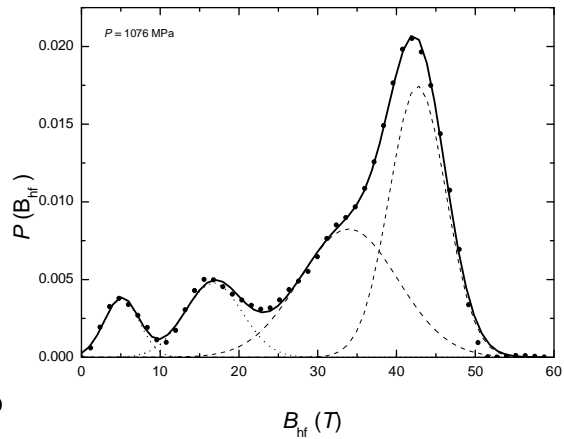**Figure 6.** Gaussian fits to the hyperfine field distribution for $Cd_{0.5}Ni_{0.5}Fe_2O_4$

4. Conclusions

Our results show a significant influence of the green density on the final bulk density of $(Cd, Zn)_{0.5}Ni_{0.5}Fe_2O_4$ ferrites investigated. The bulk density measurements are important because they can provide information of the quality of the materials and how their properties are influenced by the sample preparation conditions such as the pre-sintering green density. Our results show that a maximum bulk can be obtained for a pressure of about 600 MPa. Samples produced from different states of green density can easily be distinguished from the hyperfine field distributions. Other parameters like lattice constants, grain sizes, porosity, coercive fields and saturation magnetization are less significantly affected by the pelletizing pressure.

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