Evaluation of The Sinterability of Copper-Substituted Ferrites by Means of Dilatometric Thermal Analysis

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Abstract. Cobalt and cobalt-manganese spinel ferrites have magnetostrictive properties suitable for application in magneto-electric and magneto-mechanical transducers. In this work, copper-substituted ferrites of these compositions were processed by means of the ceramic method and their sinterabilities were evaluated by dilatometric thermal analyses. The results obtained suggest that copper affects the solid-state reactions for the spinel formation and lowers the required sintering temperature for the ferrites. However, the densification obtained with sintering of the copper-substituted ferrites at 950 °C for 6h was only 64%, which indicates that further adjustments on the processing route must be made in order to obtain higher densities.

Introduction

Ferrites are magnetic ceramics that have a wide range of application in electronics, such as in magnetic sensors for temperature, electric current, magnetic field, and mechanical stresses.

Ferrites with cobalt in composition have potential application in magneto-mechanical sensors for torque, compressive stresses, hydrostatic stresses, and magnetic field. Literature also shows a large number of works about the use of magnetostrictive ferrites in magneto-electric composites, which are applicable in advanced electronic devices and magnetic field sensors.

Cobalt ferrite ($CoFe_2O_4$) present relatively high magnetostriction values and its magnetoelastic sensitivity may be enhanced by means of substitutions for other elements, such as Mn, Ga, Al, Ge, and Cr [1]. Bhame and Joy [2] demonstrated that the magnetostrictive properties of $Co_{0.7}Mn_{0.3}Fe_2O_4$ are suitable for applications in magneto-mechanical sensors.

Sintering of dense ferrites normally requires temperatures between 1300-1450 °C. Copper substitution has been successfully used for lowering the sintering temperature of ferrites, allowing the fabrication of dense samples with sintering temperatures as low as 1050 °C [3]. The aim of this work is to study the sintering behavior of the $CoFe_2O_4$ and $Co_{0.7}Mn_{0.3}Fe_2O_4$ magnetostrictive spinel ferrites, using dilatometric thermal analysis, and to verify the effect of copper substitution when their chemical composition are changed to $Co_{0,8}Cu_{0,2}Fe_2O_4$ and $Co_{0,6}Mn_{0,2}Cu_{0,2}Fe_2O_4$.

Experimental procedure

$CoFe_2O_4$, $Co_{0.7}Mn_{0.3}Fe_2O_4$, $Co_{0,8}Cu_{0,2}Fe_2O_4$ and $Co_{0,6}Mn_{0,2}Cu_{0,2}Fe_2O_4$ ferrites were processed by means of the ceramic method, using Fe_2O_3, MnO_2, Co_3O_4, and CuO as raw materials. These compositions will be referred as Co, Co-Mn, Co-Cu and Co-Cu-Mn ferrites hereafter. The oxides were manually dry-mixed in a mortar and calcined at 850 °C for 4h.

The crystal structures of the calcined powders were evaluated by means of X-ray diffraction (XRD), with CuKα radiation. Samples of calcined powders were heat-treated at 950 ^{o}C for 6h and their crystal structures were also evaluated by means of X-ray diffraction; the lattice parameters (a) were measured and the theoretical densities (d_t) of the ferrites were calculated by means of eq. 1, as in Smit and Wijn [4]. In (1), M is the molar mass of the ferrite and N is the Avogadro's number.

$$d_t = \frac{8M}{Na^3}$$ (1)

The calcined materials were wet milled in an eccentric mill. Carbon steel balls and nylon jars were used as milling media and the powder to liquid volume ratio was 0,15.

Samples of the milled calcined powders were uniaxially compacted under 50 MPa, followed by isostatic compaction under 200 MPa in 6mm diameter / 9mm length. These samples were used for dilatometry experiments in a Netzsch DIL402-E7 dilatometer, with a heating rate of 10 ^{o}C/min. The maximum test temperatures used were 1400 ^{o}C for the non-substituted ferrites and 1050 ^{o}C for the copper substituted; a lower temperature was used in the latter in order to avoid the possibility of liquid phase formation and damage of the equipment.

Ferrite samples were sintered under different conditions and their densities (d) were measured by means of the Archimedes' method. The percent densifications were estimated, taking the calculated d_t values as reference. The samples used in this experiment had been uniaxially compacted in 8-mm diameter circular shape, under 50 MPa, and subsequently compacted under 300 MPa in an isostatic press. The sintering conditions used were:

- Copper-substituted ferrites: 950 ^{o}C for 6h and 1050 ^{o}C for 12h.
- Non-substituted ferrites: 1300 ^{o}C for 2h, 1350 ^{o}C for 6h, and 1400 ^{o}C for 6h (for compositions that had not attained 90% densification with the two previous sintering conditions).

Results and discussion

The results of powders' X-ray analysis are shown on Figs. 1-4. The calculated values of lattice parameter and d_t of the sintered powders are shown on Table 1.

Peaks corresponding to Fe_2O_3 were found in the X-ray diffractograms of the Co-Cu and Co-Cu-Mn calcined powders (Figs. 1 and 2), which usually indicates that the reactions to form the spinel phase weren't completed during calcining [5]. The presence of Fe_2O_3 was more evident in the Co-Mn-Cu composition. Fe_2O_3 peaks were not detected in the Co and Co-Mn calcined samples, which leads to the conclusion that the copper substitutions may have retarded the spinel formation in these ferrites.

There are some possible explanations for the broad peaks observed near 2θ=36.8^{o} in the X-ray diffractograms of the copper-substituted calcined powders:

- presence of unreacted Co_3O_4;
- formation of cobalt-copper oxides.

Table 1: Lattice parameters (a) and calculated theoretical densities (d_t) of the ferrites.

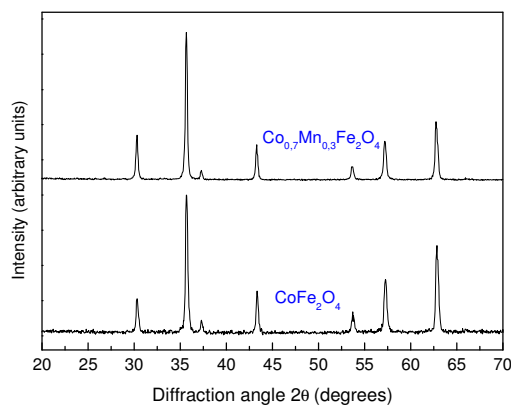| Ferrite	a (Å)	d_t (g/cm^3)
Co	8.35	5.35
Co-Cu	8.33	5.41
Co-Mn	8.37	5.29
Co-Mn-Cu	8.39	5.29

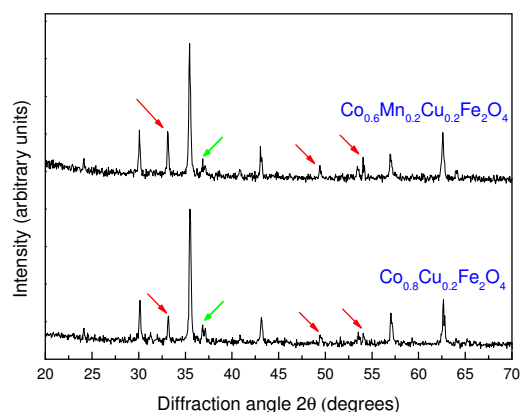Fig. 1: X-ray diffractograms of the calcined non-substituted ferrites.

Fig. 2: X-ray diffractograms of the copper-substituted calcined powders. The peaks that correspond to Fe_2O_3 (JCPDS #89-0599) are indicated by red arrows. We suggest that the peaks indicated by green arrows may correspond to Co_3O_4 (JCPDS #78-1970), or cobalt-copper oxide (JCPDS #76-1887).
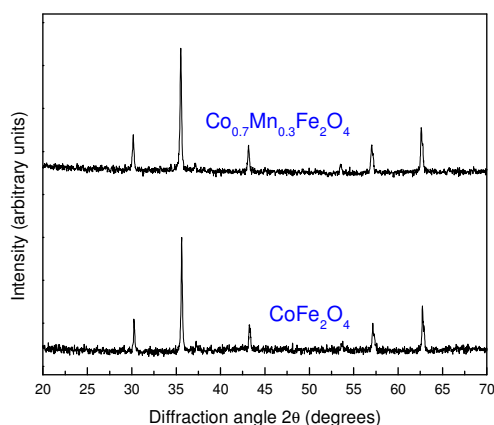

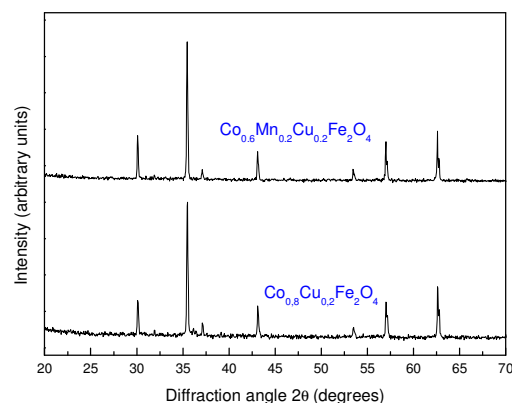Fig. 3: X-ray diffractograms of non-substituted ferrites, heat-treated at 950 ^{o}C for 6h.

Fig. 4: X-ray diffractograms of the copper-substituted powders heat-treated at 950 ^{o}C for 6h.

The lattice parameters obtained for the Co ferrite is similar to the ones reported in literature [6]. The changes in the lattice parameter of this ferrite, after copper substitution, may be explained with basis on the differences between the ionic radii of the previous ions and their substitute. Table 2 shows the ionic radii of some ions, considering that their coordination number is 4.

The typical lattice parameter in literature [7-8] for the Co-Mn ferrite is around 5.40Å, value that is larger than the one obtained in this work. In the Co-Cu-Mn ferrite, the Cu^{2+} ions were supposed to substitute both Mn^{2+} and Co^{2+}. The ionic radius of Cu^{2+} is very close to Co^{2+} but it is considerably shorter than Mn^{2+}. Thus, it was expected that the copper substitution would reduce the lattice parameter, which was not observed. The lattice parameter of ferrites is determined by the cation distribution in the crystalline structure which, in turn, is affected by the processing and sintering conditions, as well as the cooling rate after sintering [6, 10]. In addition, the lattice parameter calculations were made based on XRD data from powders that were heat-treated at a relatively low temperature (950 ^{o}C), and they may not be constituted of ferrite phases with the targeted stoichiometry but of a mixture of intermediate spinel phases.

Table 2: Ionic radii of the cations that are present in the ferrites of this work [7].

Ion	Ionic radius (Å)
Cu^{2+}	0.57
Mn^{2+}	0.66
Co^{2+}	0.58
Fe^{2+}	0.63
Fe^{3+}	0.49

Figs. 5-8 show the results from the thermal analyses. The initial portions of all shrinkage curves approximate a linear thermal expansion: it may indicate low reactivity of the calcined powder, which was expected to happen in tests below the calcining temperature (850 ^{o}C). The shrinkage curves obtained by Fonseca [11], for alumina samples of different particle size distributions, showed that the initial thermal expansion was reduced as the fractions of nanoparticles in the samples were increased. This happens because smaller particles are more reactive and may favor shrinkage. Thus, it is expected that the reactivity of the materials studied here may be increased by means of particle size reduction, favoring the sinterability and allowing higher densifications.

The expansion and its corresponding increase in the shrinkage rate of the Co-Cu-Mn ferrite around 720 ^{o}C indicates phase transformation. Sale [12] compared the shrinkage characteristics of calcined and non-calcined oxide mixtures and observed a similar behavior occurring only in the non-calcined material. The author attributed the observed expansion to the spinel formation.

The shrinkage rate of the Co and Co-Mn ferrites clearly increases at a certain temperature between 1100-1200 ^{o}C (see green arrows in Figs. 5 and 7). Below this temperature and above the calcining temperature (850 ^{o}C) it is possible that the formation of spinel phases still occurred and that the corresponding expansion of these reactions retarded shrinkage.

In temperatures higher 990 ^{o}C, the shrinkage values of the cobalt ferrite are increased with copper substitution (Fig.5), which means better sinterability. The trend presented by the shrinkage curve of the Co-Mn-Cu ferrite (Fig. 7) allows one to predict that the shrinkage values in temperatures higher than 1050 ^{o}C would be larger than in the Co-Mn ferrite. In this case, the copper substitution would favor the sinterability of the Co-Mn ferrite.

Bhame [19] made dilatometry tests, in $CoFe_2O_4$ and $Co_{0.7}Mn_{0.3}Fe_2O_4$ ferrrites, in temperatures up to 1350 ^{o}C. In his work, the shrinkage of the $CoFe_2O_4$ ferrite at 1350 ^{o}C was around 9%, while the shrinkage obtained here at 1250 ^{o}C was 15%. The Co-Mn ferrite tested by the author attained a shrinkage lower than 10% at 1300 ^{o}C, while the same ferrite in the present work had a 17% shrinkage at that temperature. Since the processing route used by Bhame differs in many aspects from the one used in this work, this comparison illustrate that the sinterability of these ferrites are very sensitive to the parameters employed in the ceramic processing route.

The measured density values of the samples sintered under different conditions are shown on Table 3. None of the copper-substituted ferrites reached 90% densification with a sintering temperature of 950 ^{o}C. Although the results suggest that the copper substitution may favor densification of the ferrites, the characteristics of the calcined powder (such as particle size distribution and composition homogeneity) must be adjusted in order to obtain high densification values after sintering.

The relatively low density values obtained in the Co-Mn ferrite, even with sintering temperatures as high as 1400 ^{o}C, suggest that attaining higher densification of this ferrite wouldn't depend only on increasing the sintering temperature but also on adjusting the processing parameters. This conclusion is also supported by the expansion observed in Fig. 7 in temperatures higher than 1300 ^{o}C.
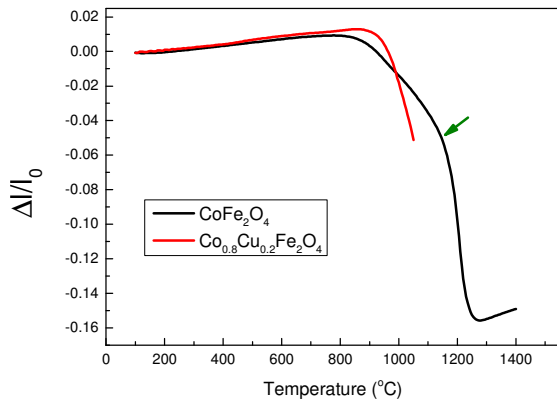
Fig. 5: Shrinkage curves of the Co and Co-Cu ferrites. The arrow indicates a change in the shrinkage rate.
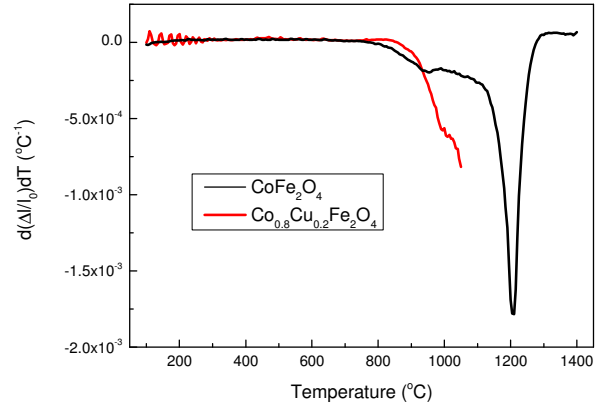
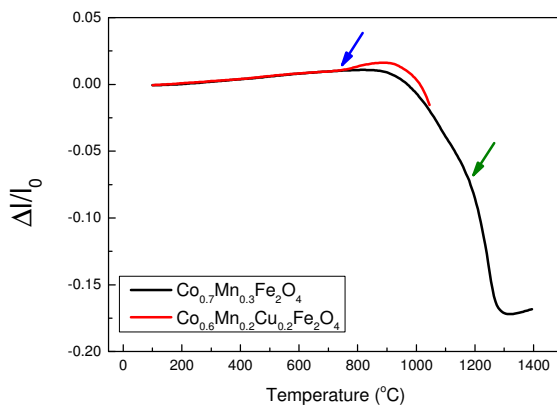Fig. 6: Shrinkage rate curves of the Co and Co-Cu ferrites.

Fig. 7: Shrinkage curves of the Co-Mn and Co-Mn-Cu ferrites. The blue arrow indicates a point that corresponds to spinel formation and the green arrow indicate the change in shrinkage rate.
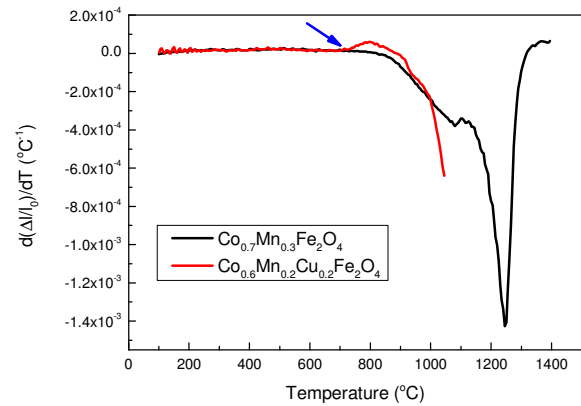
Fig. 8: Shrinkage rate curves of the Co-Mn and Co-Mn-Cu ferrites. The arrow indicates a point that corresponds to a phase transformation.

Table 3: Densities of the sintered ferrite samples.

Composition	Sintering parameters	Density (g/cm^3)	Densification (%)
$CoFe_2O_4$	$1300^oC/2h$	4.85	91
	$1350^oC/6h$	4.92	92
$Co_{0.7}Mn_{0.3}Fe_2O_4$	$1300^oC/2h$	4.67	88
	$1350^oC/6h$	4.64	88
	$1400^oC/6h$	4.63	87
$Co_{0.8}Cu_{0.2}Fe_2O_4$	$950^oC/6h$	3.48	64
	$1050^oC/12h$	4.08	75
$Co_{0.6}Mn_{0.2}Cu_{0.2}Fe_2O_4$	$950^oC/6h$	3.41	64
	$1050^oC/12h$	3.92	74

Conclusions

The results obtained suggest that the copper substitution retarded the spinel formation in the cobalt and cobalt-manganese ferrites. The proposed copper substitution may favor the sintering of the ferrites studied but none reached a densification higher than 90% with a sintering temperature of 950 ^oC. The use of more reactive calcined powders, obtained by other processing methods such as

high energy milling, is proposed to favor the attainment of higher densities at low sintering temperatures.

Acknowledgments

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