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Effect of Low Cost Iron Oxide with Si Additive on Structural Properties of Ni-Zn Ferrite

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Abstract. Mixed Ni-Zn ferrites (x = 0.66, 0.77, 0.88, 0.99) were prepared by double sintering ceramic method using locally available low cost Fe_2O_3 with 0.5% (by wt) of Si additive. The chemical phase analysis, carried out by X-ray powder diffraction method, confirms the major phase of Ni-Zn ferrite. Study of the effect of composition on structural properties of ferrite system revealed a decreasing trend of lattice parameters with increasing Ni content. X-ray density and mass density increase with increasing Ni content, which in turn decreases the porosity due to successive presence of Si in Fe_2O_3. This decrease in porosity along with chemical homogeneities, distribution of phases and grain formation were also observed in scanning electron micrographs.

Keywords: Ni-Zn ferrites; Si additive; iron oxide; ceramics

Introduction

Ferrites, being ceramic materials formed by sintering, have mechanical properties similar to those of pottery. In particular the properties depend on the sintered density. It was reported by Costa *et al.* (2003) and Snelling (1988), that during sintering, oxides react to form crystallites or grains which, nucleating at discrete centres, grow outwards until the boundaries meet those of neighbouring crystallites. During this process, the density rises; if this process were to yield perfect crystals meeting at perfect boundaries, the density would rise to the theoretical maximum, i.e., the X-ray density.

In practice, imperfections occur and the sintered mass has microscopic voids, both within the grains and at the grain boundaries. The resulting density is referred to as the sintered density. In normal production, the sintered density for Ni-Zn ferrite, suggested by Snelling (1988), is 4600 kg/m^3 (pressed), and porosity is 13.5%. It is a well-known fact that the properties of ferrite materials are strongly influenced by the materials composition and microstructure. But according to He *et al.* (2003), Da silva and Mohallem (2001), Heck (1974) and Von Aulock (1965), properties can also be changed by the sintering conditions employed and the impurity levels present in or added to these materials. The density and porosity can be improved further by using different techniques, like special sintering conditions and selecting suitable composition with addition of small amount (a few mols %) of metal oxide to ferrites. Researchers like, He *et al.* (2008), Goldman (1990), Heck (1974) and Von Aulock (1965), indicated that optimum properties of Ni-Zn ferrites were obtained when sintered at 1200-1250 °C. The sintering temperature 1200- 1250 °C proved to be the most appropriate condition to obtain Ni-Zn ferrites and gave satisfactory values of density and other parameters comparable with the theoretical values reported for ferromagnetic Ni-Zn ferrites. In addition to this, He *et al.* (2008), Wu *et al.* (2006; 2004) and Goldman (1990), investigated the effect of Si, which improved the properties of ferrite products.

The present work was aimed at sintering Ni-Zn ferrite using low cost iron oxide, having 0.5 wt % of Si additive, and studying its effect on improvement of the properties of ferrite samples and overcoming the cost of finally achieved ferrite products. The presence of Si improves density, but the amount must be low enough to prevent growth of large grains, which is confirmed through scanning electron micrographs.

Materials and Methods

Ferrite samples with compositions $Ni_xZn_{1-x}Fe_2O_4$, (x = 0.66, 0.77, 0.88 and 0.99) were prepared in polycrystalline form through high temperature solid-state reaction method. The compositions, $Ni_xZn_{1-x}Fe_2O_4$, were prepared from powder mixture of NiO, ZnO, of purity better than 99% along with locally available low cost Fe_2O_3 with 0.5 wt% of Si as an additive. The powder mixture were pressed into pellets of 16 mm diameter under a uni-axial pressure of 2.5 tons. Initially the samples were sintered in a muffle furnace at 1000 °C for prolonged period and finally heated for 6 h at 1200 °C for making a homogenous product. The samples were quenched in air and X-ray diffraction (XRD) patterns were taken by Rigaku XRD D/MAXIIA diffractometer using CuKá radiations with

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scanning speed of 1° (2è/min) to identify the phases formed and to confirm the completion of the chemical reaction. In the present work, the surface of the pellets were cleaned with SiC grinding paper in order to remove any contamination and used to study structural properties.

Results and Discussion

All the four compositions of $Ni_xZn_{1-x}Fe_2O_4$ ferrite, sintered at 1200 °C, were analyzed by XRD. The XRD pattern of these samples confirmed the completion of major phase of ferrite structure, (Ni-Zn ferrite) with few peaks of zinc silicate (Zn_2SiO_4) as an additive, as shown in Fig. 1. The lattice constant values were compared with values reported in JCPDS cards by Bayliss *et al.* (1986). These values of the lattice constant as a function of Ni-concentration are plotted in Fig.2a. It was observed in the graph that the lattice constant decreases linearly with the nickel content, x, in Ni-Zn ferrite system because the Ni^{2+} ions have a marked preference for octahedral sites due to their favourable fit of charge distribution of these ions in the crystal field of the octahedral site. On the other hand Zn^{2+} ions have preference for tetrahedral site because of their readiness to form covalent bonds involving sp^3 hybrid orbital. So the linear decrease of lattice constant with Ni content can be attributed to the smaller ionic radius of Ni^{2+}(0.74 A°) as compared to the ionic radius of Zn^{2+}(0.84 A°) (Hossain *et al.,* 2007; El-Sayed, 2002).

The X-ray densities were calculated using the following relation used by Islam *et al.* (1999), in his work;

$$dx = 8M/Na^3 \quad \text{.....(i)}$$

where 8 represents the number of molecules in a unit cell of spinal lattice, M is the molecular weight of the sample; a, is the lattice constant and N is the Avogadro's number.

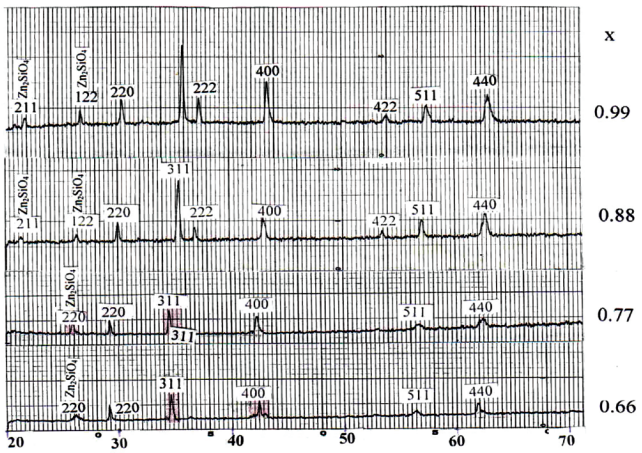

Fig. 1. XRD patterns of Ni-Zn ferrites ($Ni_x Zn_{1-x}Fe_2O_4$) with x= 0.66, 0.77, 0.88,0.99.

The X-ray density depends on the lattice constant and molecular weight of the sample and the mass density calculated from the geometry and mass of the samples. Both the densities dx and ds (plotted in Fig. 2b, as a function of Ni concentration) were found to increase with increase in the Ni content, x. Increase in mass density can be attributed to the difference in specific gravity of the ferrite components, since NiO (6.72 g/cm^3) is heavier than ZnO (5.60 g/cm^3), as mentioned by Lide (1995). The increase in X-ray density is because of the decrease in lattice constant with the increase of Ni content, x, as predicted from the above equation (i). For each concentration, mass density and X-ray density were calculated to obtain the porosity, P by the following equation used by Hossain *et al.* (2007):

$$P = (1\text{-}ds/dx) \quad \text{.....} \quad \text{(ii)}$$

Porosity *vs.,* Ni-concentration has been plotted in Fig. 2c, which shows that porosity decreases with increasing Ni con-

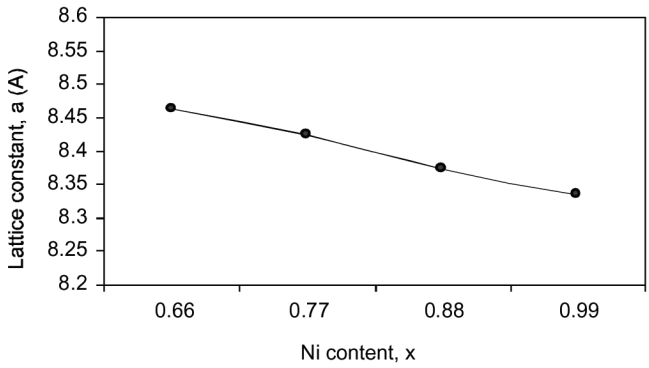

Fig. 2(a). Plot showing lattice parameters *vs.* Ni concentration for Ni-Zn ferrite system.

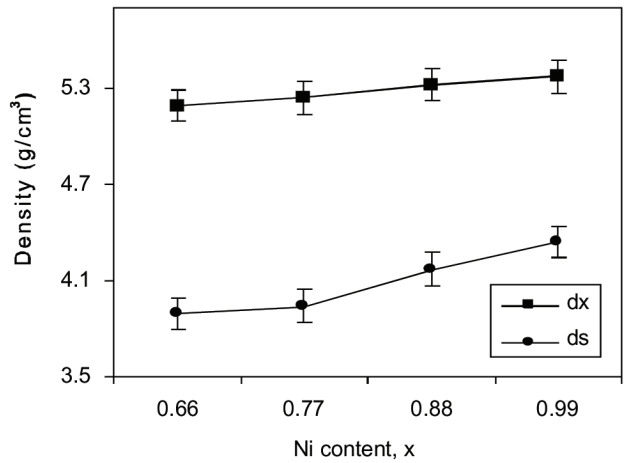

Fig. 2(b). Plot showing X- ray and bulk densities *vs.* Ni concentration for Ni-Zn ferrite system.

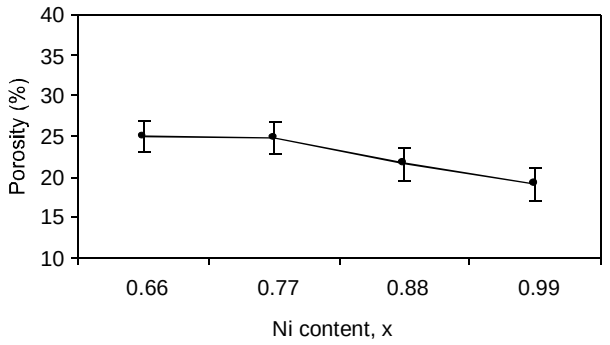

Fig. 2(c). Porosity plotted against Ni concentration for Ni-Zn ferrite system.

tent, x, from 0.66 to 0.99. It can be observed that the value of X-ray density is increasing because the lattice constant is decreasing with the increase of Ni content. Hence the ratio ds/dx decreases which leads to the decrease in porosity. The other reason is that porosity depends on different factors, like sintering temperature, quality of the oxide used and somehow on melting points of the oxide used. Sintering at higher temperature generally brings about reduced porosity and an improvement in the homogeneity.

Hu *et al.* (2005), suggest that at a higher sintering temperature, the number of pores is reduced, as a result of which individual grains come closer to each other and the effective area of grain to grain content increases. This, in turn results in greater densification or less porosity, as Ni content, x, was increased having melting point of NiO (1955 °C) less than ZnO (1975 °C) used. The XRD data were supported by observations from scanning electron micrographs. The microstructure analysis of these samples was carried out using the high resolution scanning electron microscope operated at 25 kV in the secondary electron image mode. It is useful to study the microstructure and to identify the phases formed during sintering. It is also useful to interpret the amount of porosity and find out the size of grains and their positions in the crystal. The morphology of grain structure of $Ni_xZn_{1-x}Fe_2O_4$, as seen from the scanning electron microscopy in Fig.3, shows maximum of cellular type particles with major phase of NiZn ferrite and minor phase of Zn_2SiO_4 (zinc silicate) due to its less energy of formation (Gibb's energy) as mentioned by Smithells (1967). It also shows an average grain size of 3-7 µm. It is to be noted that small grains due to Si are preferred in ferrites as it shows better microstructure and chemical homogeneity. It is also interpreted from the micrograph of this series of Ni-$ZnFe_2O_4$ (Fig. 3), that second phase (zinc silicate) dominates more for x = 0.88 and x = 0.99, which is also clear through XRD patterns.

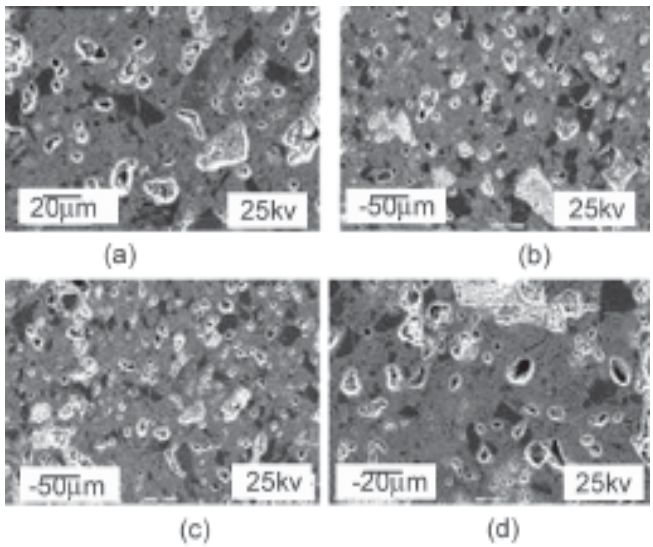

Fig. 3. SEM micrographs of Ni-Zn ferrite system for x = (a) 0.66, (b) 0.77, (c) 0.88, (d) 0.99.

Conclusion

The aim of the present study was to produce homogenous ferrite having small average grain size. Use of low cost Fe_2O_3 with 0.5 wt% Si as an additive in the system was considered in order to improve the properties of the samples and control the process economics. The presence of Si was found to suppress the ceramic grain growth, which further confirms that the formation of major phase of Ni-Zn ferrite structure with lattice content decreases linearly to the nickel content, x, due to the difference in ionic radius. There is increasing trend of dx and ds with the increase in Ni concentration, x, but porosity decreases with increase in Ni concentration, x.

Scanning microscopy was used to observe the distribution of phases, chemical homogeneities and porosity along with grains formation. It was observed that all the samples of ferrite were sound, homogeneous and free from any sort of macro porosity and in agreement with XRD results.

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