INFLUENCE OF Ni/Zn RATIO VARIATION ON STRUCTURAL AND MAGNETIC PROPERTIES OF NiZn FERRITES

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Pure single phase polycrystalline NiZn ferrite materials with the chemical composition Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$, where $x = 0.30, 0.33, 0.36, 0.42$ and 0.50 were prepared by solid state reaction with a slow cooling from the sintering temperature 1200°C for 6 hours. The influence of Ni/Zn ratio in composition on structural and magnetic properties prepared ferrite samples was investigated. The structural properties were analysed using by the X-ray diffraction method, the particle size and shape were studied using by the Scanning Electron Microscope. Low-frequency magnetic properties of prepared NiZn ferrites were determined from the measured magnetisation curves. The results have confirmed known, a little bit surprising fact, that for $x > 0.3$ the addition of ferromagnetic metal (Ni) into the chemical composition deteriorates some magnetic properties (especially the permeability, coercivity, etc), meanwhile the Curie temperature increases.

Keywords: ferrites, structural properties, magnetic properties

1 INTRODUCTION

NiZn ferrites are widely used materials for various applications especially in electrical engineering. As such, they have attracted considerable research interest. However, the correlation between the microstructure and magnetic properties of this system is not yet obvious, [1]. Since pure nickel ferrite NiFe$_2$O$_4$ is an inverse spinel because Ni$^{2+}$ cations have a strong tendency to occupy octahedral B-sites, relatively larger Zn$^{2+}$ cations prefer smaller tetrahedral A-sites. Therefore pure zinc ferrite ZnFe$_2$O$_4$ crystalizes as a normal spinel. Ni-Zn ferrite solid solutions are characterised by cation distribution which is normal with respect to Zn and inverse for Ni according to the scheme (Zn$_{1-x}$Fe$_{x+1}$)$_3$[Ni$_x$Fe$_{1-x}$]$_2$. From point of view of the magnetic ordering the Curie temperature strongly increases with increasing content of Ni$^{2+}$ cations as the concentration of zinc ferrite characterised by antiferromagnetic behaviour decreases and ferrimagnetic ordering of nickel ferrite prevails. The ferrimagnetic ordering in ferrites is the result of super-exchange interactions. The 3d unpaired spins of transition metals exhibit an antiparallel arrangement which takes place through oxygen anions. The most important super-exchange interactions in spinels are the A-O-B and the B-O-B interactions [2].

In this paper we examine the influence of Ni/Zn ratio on magnetic properties of prepared NiZn ferrite materials at low frequencies. Basic magnetic properties that can be evaluated from magnetisation curves were studied. Polycrystalline NiZn ferrite materials with the chemical composition Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$, where $x = 0.30, 0.33, 0.36, 0.42$ and 0.50 were analysed.

2 SAMPLE PREPARATION

The samples were prepared by classical ceramic procedure utilising solid-state reaction method. As initial raw materials, the oxides of relevant metals (such as NiO, ZnO and Fe$_2$O$_3$) with the amounts corresponding to the required stoichiometric composition were used. After homogenisation by means of wet-milling, the semi-product was dried and subsequently sifting. Further, the raw materials were calcined in the furnace at the temperature of 950°C for 1 h. After repeated homogenisation and drying, the calcinate was mixed with binding material (polyvinyl alcohol), pressed to attain the shape of tablets with the diameter of 15 mm. The tablets were sintered at 1200°C for 6 h and a circular hole was drilled into the centre of the tablets by means of water-beam drilling machine. The ring-shaped samples with the outer diameter of about 12 mm and inner diameter of 6 mm have been obtained and used for the measurement of magnetic properties.

3 STRUCTURAL PROPERTIES

The powder samples prepared by the same technology (sintering temperature 1200°C) using X-ray diffraction method (XRD) and Scanning Electron Microscope (SEM) were used to determine the structural properties of the ferrites. XRD measurements were carried out using CuK$_a$ radiation source for selected samples with the composition Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$, where $x = 0.30, 0.36$ and 0.42. XRD patterns of the ferrite samples characterised by sharp and narrow peaks are the evidence for well-crystallised single-phase ferrite having cubic spinel structure regardless of the composition (Fig. 1).

The dependence of the lattice parameter of measured ferrite samples on content of the Ni$^{2+}$ ion is shown in Fig. 2. The value of lattice parameter $a$ decreases nearly linearly with increasing content of Ni$^{2+}$ ions in the ferrite. This can be explained easily, since in the crystalline spinel structure relatively large Zn$^{2+}$ cations occupy smaller tetrahedral A-sites and smaller Ni$^{2+}$ cations prefer octahedral B-sites that are larger than A-sites. Therefore increasing Ni$^{2+}$ content along with decreasing Zn$^{2+}$ contents causes reducing of the lattice parameter. Similar behaviour of lattice parameter value in NiZn ferrites was reported in [2].

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from the hysteresis loops in Fig. 3) are given. One can see a linear dependence of $H_c$ upon Ni contents $x$, meanwhile

SEM analysis confirmed the presence of irregular polycrystalline particles with an average grain size less than 10 μm. SEM images of Ni$_{0.3}$Zn$_{0.7}$Fe$_2$O$_4$ ferrite powder, from which the morphology of the sample is visible, are shown in Fig. 3.

**4 MAGNETIC PROPERTIES**

The magnetisation characteristics were measured by means of computer controlled measuring set-up consisting of commercially available instruments. The controlling software fitted to particular needs was developed using commercially available graphical programming development environment. Further information on hardware and software is given elsewhere [3-5].

The families of measured minor loops were used to find various magnetic parameters. The loops of entire set of samples with all the studied material compositions were measured in a wide range of maximum applied fields ($H_{\text{max}} = 1$ to 200 A.m$^{-1}$, step 1 A.m$^{-1}$). In Fig. 4 minor hysteresis loops of the ferrite samples at $H_{\text{max}} = 80$ A.m$^{-1}$ are presented. The dependencies of relative amplitude permeability $\mu_r$ upon exciting field amplitude $H_{\text{max}}$ are shown in Fig. 5.

In Fig. 6 the dependencies of the coercive field $H_c$ and remanent flux density $B_r$ at $H_{\text{max}} = 80$ A.m$^{-1}$ (determined
sub-lattices (tetrahedral and octahedral) due to the fact that the occupation of the sub-lattices by Ni and Zn ions depends on their counts in the crystalline cell.

Moreover, the exchange interactions among the atomic magnetic moments in the sub-lattices are affected by the changes of the lattice parameter. A noteworthy aspect of spinel structure is that it can form an exceptionally large diversity of total solid solutions. In solid solutions, composition can be changed on a continuous basis, leading to continuous variations in the physical properties as well. This allows a very precise tailoring of magnetic properties, which is a key benefit for any application, [2].

5 CONCLUSIONS

After many years, NiZn ferrites continue to be an excellent system to study magnetic properties of solids. Significant influence of the chemical composition on the magnetic properties, which offers the potential for preparing of tailor-made materials for particular applications, is obvious. Thanks to their properties, these NiZn ferrite powders can also be used as magnetic fillers in the ferrite polymers composite materials for various applications, especially at higher (microwave) frequency range.

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