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Magnetic properties of selected substituted spinel ferrites

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ABSTRACT

Polycrystalline NiZn ferrites with the chemical formula $(Ni_{0.3}Zn_{0.7})_{1-x}Me_xFe_2O_4$ where Me is Cu^{2+} or Be^{2+} ion with $x=0.05$, 0.1 and 0.25 have been prepared by a ceramic method. Selected magnetic properties such as saturation magnetisation M_S, Curie temperature T_C, coercivity H_C and permeability of the ferrites have been measured and discussed to compare of the substituted $Li_{0.5-0.5y+0.5t}Zn_yTi_tFe_{2.5-0.5y-1.5t}O_4$ ferrites, when $y=0.1$, 0.2, 0.3, 0.4 and $t=0.35$, 0.45, 0.55. The samples have been prepared by a ceramic method and the samples $Li_{0.5-0.5y}Zn_yFe_{2.5-0.5y}O_4$ by a chemical way. Mössbauer spectra and crystallographic parameters of selected samples have been analysed as well.

1. Introduction

It is still a lack of detailed information on properties of the RF magnetic dielectrics and their practical applications. The magnetic properties of polycrystalline ferrites are determined by chemical composition and depend also on the ionic distribution and on the method of preparation. The way of preparation forms a grain size, grain boundaries and pores, and thus influences extrinsic properties. An adequate amount of substituents can greatly affect the magnetic properties due to the ionic distribution [1–2,4–12]. The additives could improve intrinsic magnetic properties (saturation magnetisation/polarisation and Curie temperature) and extrinsic magnetic properties of ferrites. The $Me'Fe_2O_4$ spinel ferrites, where $Me'=Ni^{2+}$ or $(LiFe)_{0.5}^{2+}$ are the divalent ion or appropriate combination of two (monovalent Li^+ and trivalent Fe^{3+}) ions are well known for their high frequency properties among the oxide-based materials applied in electronics. As will be shown the magnetic properties depend not only on the ionic distribution, but also on starting composition of substituted $Me'Fe_2O_4$ ferrite. A variety of Ni or $(LiFe)_{0.5}$ ferrites have emerged by substituting metal ions and the amount of ion replaced is dictated by the valence of the substituting ions and can be given by divalent ions Me^{2+}, as example. If $Me^{2+}=Zn^{2+}$, the substituted Ni ferrite is known $Ni_{1-y}Zn_yFe_2O_4$ or substituted $(LiFe)_{0.5}$ ferrite is $Li_{0.5-0.5y}Zn_yFe_{2.5-0.5y}O_4$. In addition, in the second substitution of NiZn ferrite, the additives are given by divalent $Me^{2+}=Cu^{2+}$ or Be^{2+} ions, which goes to B sites in $Ni_{1-y}Zn_yMe_xFe_2O_4$. In the case of second substitution of LiZn ferrite ion is given by tetravalent Ti^{4+}, which goes to B sites in $Li_{0.5-0.5y+0.5t}ZnyTi_tFe_{2.5-0.5y-1.5t}O_4$. This paper summarizes and compares the consequences of the above mentioned substitutions on changes of magnetic properties ferrites.

2. Experimental methods

The phase compositions of the substituted NiZn ferrites and Li ferrites synthesized by ceramic method and chemical way were analysed. The temperature dependences of the magnetic susceptibility χ (T) and the Curie temperature T_C were measured by the bridge method in an alternating magnetic field of 421 A/m at 920 Hz. The saturation magnetisation M_S was measured by means of vibration sample magnetometer. The results were compared with the results obtained by Mössbauer spectroscopy using the spectrometer with γ-ray source of ^{57}Co imbibed in a rhodium matrix measured by a convetional constant acceleration drive with a 512 channel analyser operating in the multiscaler mode and by PANanalytical X'PertPRO diffractometer using Co $K_\alpha$source. The average grain size was calculated by the Scherrer equation. Rietveld method as implemented in the DiffracPlus Topas program (Bruker AXS, version 4.2) was used for determining crystallographic parameters and estimation of weight fractions of as identified oxides. The complex permeability of synthesised samples was measured at room temperature in the frequency range was 1 MHz–1 GHz using an impedance analyser (HP4191A). The size and shape of the ferrite powder and grains of sintered samples have been examined by SEM.

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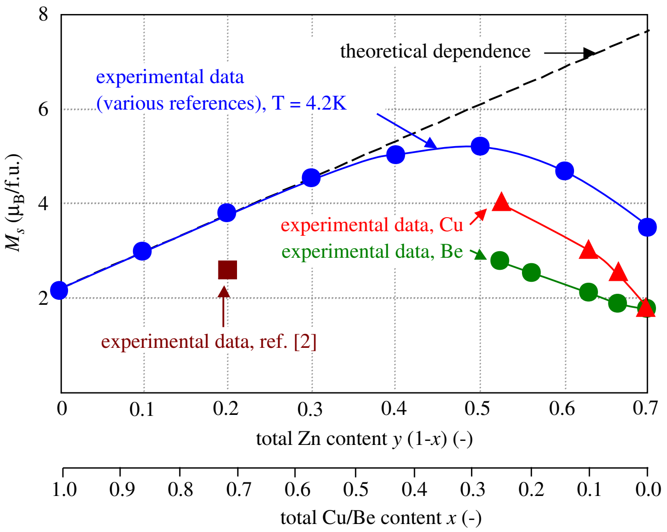

Fig. 1. Saturation magnetisation of substituted NiZn ferrites as a function of Zn, Cu/Be concentration.

3. Changes of NiZn ferrite properties caused by Cu/Be substitution

The measured data of presented substituted NiZn ferrites can be qualitatively compared to the well-known behaviour of the saturation magnetic moments of mixed $Ni_{1-y}Zn_y$ ferrites as a function of Zn concentration y with cation distribution $(Zn_yFe_{1-y})[Ni_{1-y}Fe_{1+y}]O_4$, which was measured at 4.2 K (Fig. 1) [3]. The cations in the parentheses occupy A (tetrahedral) sites and those in square brackets B (octahedral) sites. The saturation magnetisation M_S as a function of Zn content increases with increasing substitution (y), then it goes through the maximum for intermediate values of y, further decreases and finally vanishes for high Zn contents. As the Zn content increases, the magnetic moments in A sites decrease, while in B sites increase. If the magnetic moments of Fe^{3+} and Ni^{2+} are ~5 and ~2.2 μ_B, respectively, the saturation magnetisation can be expressed theoretically as $M_S=[y(10-2.2)+2.2]\ \mu_B$. This relationship (dashed line in Fig. 1) is not followed over the entire composition range. As the Zn content increases, AB super-exchange interactions become weak and BB interactions start to dominate. Instead of collinear anti-parallel alignment, a canted structure appears where the spins in B sites are no longer parallel. The Curie temperature T_C is primary determined by the AB interaction and therefore decrease with the number of AB interactions, i.e., with increasing y. The M_S, T_C and other properties of $Ni_{1-y}Zn_yFe_2O_4$ ferrite are dependent on Zn contents y. Therefore if in this system one wants to estimate the effects of substitution to improve its final properties, one must find suitable kind of substituent and the composition of starting the NiZn ferrite. For various y, the same substituents—Me_x^{2+} can have distinguishable effect in substituted system at the same x contents.

In the first example, change of ion distribution within the spinel structure, caused by partial substitution of divalent Ni^{2+} ions by $Me^{2+}=Cu^{2+}$ ions, was carried out in the $Ni_{0.8-x}Zn_{0.2}Cu_xFe_2O_4$ system described in [2], while the content of Zn remained unchanged, $y=0.2$. The placement of ions into the sites was governed by theoretical formula as follows

$$(Zn_{0.2}Fe_{0.8})[Ni_{0.8-x}Cu_xFe_{1.2}]O_4. \tag{1}$$

and the magnetic moment will be given by the expression

$$\overleftarrow{(5\times 0.8)}\overrightarrow{[2.2(0.8-x)+1x+5\times 1.2)]}\ \mu_B. \tag{2}$$

In this system the magnetic moment of B sites decreased, because Ni^{2+} ions with magnetic moment of ~2.2 μ_B were replaced by

Cu^{2+} ions with ~1 μ_B. Thus, the authors of [2] could observe the decrease of magnetic moment with the increasing Cu^{2+} content x at small concentrations. The main reason of that can be that Cu^{2+} ions prefer the B sites of the spinel structure, see Eq. (2). Then Cu^{2+} ions in B sites replace the respective part of Ni^{2+} ion, and the Fe^{3+} ions are not changed in both B and A sites. Thus the strength of AB super-exchange interaction among Fe^{3+} ions is invariable. Therefore the T_C for Cu^{2+} substituents remains practically unchanged in this case. If we could accept idea of the partial migration of Cu^{2+} ions into A sites [2], then Cu^{2+} ions in A sites shift the respective part of Fe^{3+} ions from A to B sites. Increase of Fe^{3+} ions concentration in B sites and simultaneously decrease of Fe^{3+} in A sites impose the decrease of AB interaction, from which the decrease of value of T_C results. But this was not found in experiment. This was one example of partial substitution of Ni only with Cu for region of $y<0.47$ in NiZn ferrite.

In the second step, for substitution in region of $y>0.47$ the other example of partial substitution in $Ni_{0.3}Zn_{0.7}$ starting ferrite was made. The effects of two different substituents of $Me^{2+}=Cu^{2+}$ or Be^{2+} on the microstructure and magnetic properties of $(Ni_{0.3}Zn_{0.7})_{1-x}Me_xFe_2O_4$ was investigated for $x=0\div 0.25$. The variation of saturation magnetisation M_S as a function of substituent contents x for $Me^{2+}=Cu^{2+}$ substitution measured at room temperature is also shown in Fig. 1. M_S was found to increase with increasing concentration of substituent x up to a certain value. Similar behaviour M_S vs. x was published in [6]. In presented experiment the substitution of Cu^{2+} ions the basic composition of $(Ni_{0.3}Zn_{0.7})_{1-x}Cu_x$ ferrite yields total magnetic moment according to the scheme:

$$(Zn_{0.7(1-x)}Fe_{0.3\ +0.7x})[Ni_{0.3(1-x)}Me_xFe_{1.7-0.7x}]O_4. \tag{3}$$

for $y=0.7$ the $Me^{2+}=Cu^{2+}$ substitution ($x>0$) results in decreasing of Ni^{2+} ions ($0.3x$) concentration in B sites by an adequate amount of Cu^{2+} ions. Further, there is a migration of some Fe^{3+} ions ($0.7x$) from B sites into A sites due to residual content of Cu^{2+} ions. These Fe^{3+} ions ($0.7x$) replace some Zn^{2+} ions ($0.7x$) in A sites, and the theoretical magnetic moment will be given by the expression

$$\overleftarrow{5(0.3+0.7x)}\overrightarrow{[2.2\cdot 0.3(1-x)+1x+5(1.7-0.7x)]}\ \mu_B. \tag{4}$$

where adequate Ni^{2+} ions with magnetic moment of ~2.2 μ_B were replaced by Cu^{2+} ions with ~1 μ_B in B sites. However, increasing the amount of Fe^{3+} ions in A sites are able to align more moments of B sites anti-parallel each other. It results in the increase of B sites effective saturation magnetisation due to decrease of canting between magnetisation vectors of B′ and B″ sub-lattices. Therefore the total saturation magnetisation increases with each substitution step up to critical x_c and then slightly decreases. By decreasing the amount of $0.7(1-x)$ of Zn^{2+} (except for Ni^{2+} ions) in the substitution $(Ni_{0.3}Zn_{0.7})_{1-x}Cu_x$ ferrite shown in Fig. 1 we have shifted Zn contents from $y=0.7$ to $y=0.7(1\_0.25)=0.525$. The behaviour of total magnetic moment can be verified by the measurement of the saturation magnetisation as a function of Zn contents, too. The well-known behaviour of the saturation magnetic moments of the $Ni_{1-y}Zn_y$ ferrites [3] (Fig. 1) clears up the fact that in this case the M_S has to increase with increasing Cu content, for region of Zn ions $y>0.47$. The strength of AB interaction and thus T_C are increased for $x=0.05$ up to 0.25 (see Fig.2). The main reason for the increasing of super-exchange interactions can be that Cu ions prefer B sites with consequent the increase of the amount of Fe^{3+} ions in A sites, as it follow from Eq. (4).

The M_S has been found to increase also with substituent concentration also for Be^{2+} ions. For $y=0.7$ the $Me^{2+}=Be^{2+}$ substitution ($x>0$) results in decreasing of Ni^{2+} ions ($0.3x$)