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HAL Id: jpa-00255132
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Submitted on 1 Jan 1997

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Comparative Study of the Effects of Rare Earth Ions in a High Frequency Ni-Zn Ferrite

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Abstract: Some effects of the rare-earth ions on the properties of the polycrystalline stoichiometric ferrite with formula $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_{2}\text{O}_4$ are described. The results obtained reveal that by introducing a relatively small amount of $R_2\text{O}_3$ instead of $\text{Fe}_2\text{O}_3$, an important modification of both structure and properties can be obtained. $R_2\text{O}_3$ facilitates the formation of the crystalline secondary phases (orthoferrite, garnet) on the grain boundary which inhibit the ferrite grain growth. The $R$ ions tend to flatten the $\mu - T$ curve, shift the Curie point to lower temperature and increase the electrical resistivity. The variation of these properties with the $R$ species has been explained as an effect of the ionic radius size which varies from 0.86 for Yb to 1.07 for Ce.

Ni-Zn polycrystalline ferrites are low-cost materials that are attractive for microwave device applications, owing to their high resistivity, mechanical hardness, high Curie temperature and chemical stability. Indeed, they can be prepared easily by ceramic standard technology. It is well known that the intrinsic parameters of these ferrites depend on the composition, technological factors and additives or substitutions. By introduction of a relatively small amount of foreign ions, an important modification of both structure and magnetic properties can be obtained [1,2]. The aim of this work was to evaluate the influence of the various rare earth ions ($R = \text{Yb}, \text{Re}, \text{Dy}, \text{Tb}, \text{Gd}, \text{Sm}$ and $\text{Ce}$) on the ceramic parameters of a NiZn ferrite (grain growth, porosity) on the crystallographic (lattice constant) and magnetic properties (saturation, magnetization, initial permeability, Curie temperature). Rare earth ions substitute Fe ions and are considered as entering into B-sites of the spinel structure. Their contribution to the anisotropy constant $K_1$ is positive [3,4] while that of Fe$^+$ is negative.

The chemical formula of the samples investigated was $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_{2}\text{O}_4R_{2}\text{O}_3$ where $R = \text{Yb}, \text{Re}, \text{Dy}, \text{Tb}, \text{Gd}, \text{Sm}$ and $\text{Ce}$. The specimens were prepared by conventional ceramic method: ball milling of the pure oxides, pressing into toroidal and tablet form, presintering at $900\,^\circ\text{C}$ and finally sintering in air at $1300\,^\circ\text{C}$. More details are given in [5].

In this paper we present several relevant results. X-ray analysis shows that the $R_2\text{O}_3$ containing NiZn ferrites have besides the spinel phase as major phase, crystalline secondary phases, identified as garnet ($R_3\text{Fe}_5\text{O}_{12}$) or orthoferrite ($R\text{Fe}_3\text{O}_4$), in a very small amount. The results concerning X-ray analysis are given in Table 1. The secondary phases formed on the grain boundaries were resulted from the reactions: $3\text{R}_2\text{O}_3+5\text{Fe}_2\text{O}_3=2\text{R}_3\text{Fe}_5\text{O}_{12}$ and $5\text{Fe}_2\text{O}_3+5\text{R}_2\text{O}_3=10\text{RFe}_3\text{O}_4$ and involved two processes: diffusion of $\text{Fe}_2\text{O}_3$ out of ferrite grains to the grain boundaries and its reaction with $R_2\text{O}_3$. It should be emphasized, however, that the process of dissolution of $\text{R}_2\text{O}_3$ in the spinel lattice may also occur, leading to a slight modification of the lattice constant as results from Table 1. The $R$ ions with smaller radius give a slight increase of $a$ while those with larger radius determine a decrease of it.

The primary effect of secondary phases on the grain boundaries was to suppress the grain size development during the sintering. This effect depends on the $R$ radius size. From Fig. 1 one can observe the decrease in the mean grain size $D_m$ with increasing ionic radius. The samples are ordered after increasing $R$ ion radius. Although a decrease of the grains was obtained, the samples are generally porous (Fig. 1). The highest porosity was obtained for $\text{Sm}_2\text{O}_3$ substitution and can be explained by the appearance of $\text{Sm}_2\text{O}_3$ which acts as a flux owing to its low melting point ($642\,^\circ\text{C}$). Thus $\text{Sm}_2\text{O}_3$ facilitates the growth of larger grains with inner pores. One supposes that the presence of secondary phases requires higher ferritization temperatures to enhance the densification. Generally, the high porosity of samples is caused by the whole technological process of samples preparing. We followed only the effect of impurification of Ni-Zn ferrite with the rare earth ions (the maximum rate of impurification - 0.02), the samples being prepared in the same conditions.

Table 1: Lattice constant and secondary phases of studied samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a$(Å)</th>
<th>other phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ni}<em>{0.7}\text{Zn}</em>{0.3}\text{Fe}_{2}\text{O}_4$</td>
<td>8.3687</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Ni}<em>{0.7}\text{Zn}</em>{0.3}\text{Fe}_{2}\text{O}_4\text{Yb}_2\text{O}_3$</td>
<td>8.3701</td>
<td>trace of YbFeO$_3$</td>
</tr>
<tr>
<td>$\text{Ni}<em>{0.7}\text{Zn}</em>{0.3}\text{Fe}_{2}\text{O}_4\text{Er}_2\text{O}_3$</td>
<td>8.3698</td>
<td>trace of ErFeO$_3$</td>
</tr>
<tr>
<td>$\text{Ni}<em>{0.7}\text{Zn}</em>{0.3}\text{Fe}_{2}\text{O}_4\text{Dy}_2\text{O}_3$</td>
<td>8.3674</td>
<td>DyFeO$_3$, trace of Dy$_2$Fe$_2$O$_7$</td>
</tr>
<tr>
<td>$\text{Ni}<em>{0.7}\text{Zn}</em>{0.3}\text{Fe}_{2}\text{O}_4\text{ Tb}_2\text{O}_3$</td>
<td>8.3680</td>
<td>Tb$_2$Fe$<em>5$O$</em>{12}$, trace of TbFe$_3$O$_4$</td>
</tr>
<tr>
<td>$\text{Ni}<em>{0.7}\text{Zn}</em>{0.3}\text{Fe}_{2}\text{O}_4\text{Gd}_2\text{O}_3$</td>
<td>8.3660</td>
<td>GdFeO$_3$, Gd$_2$Fe$_2$O$_7$</td>
</tr>
<tr>
<td>$\text{Ni}<em>{0.7}\text{Zn}</em>{0.3}\text{Fe}_{2}\text{O}_4\text{Sm}_2\text{O}_3$</td>
<td>8.3703</td>
<td>trace of SmFeO$_3$</td>
</tr>
<tr>
<td>$\text{Ni}<em>{0.7}\text{Zn}</em>{0.3}\text{Fe}_{2}\text{O}_4\text{Ce}_2\text{O}_3$</td>
<td>8.3683</td>
<td>Ce$_2$O$_3$</td>
</tr>
</tbody>
</table>

The primary effect of secondary phases on the grain boundaries was to suppress the grain size development during the sintering. This effect depends on the $R$ radius size. From Fig. 1 one can observe the decrease in the mean grain size $D_m$ with increasing ionic radius. The samples are ordered after increasing $R$ ion radius. Although a decrease of the grains was obtained, the samples are generally porous (Fig. 1). The highest porosity was obtained for $\text{Sm}_2\text{O}_3$ substitution and can be explained by the appearance of $\text{Sm}_2\text{O}_3$ which acts as a flux owing to its low melting point ($642\,^\circ\text{C}$). Thus $\text{Sm}_2\text{O}_3$ facilitates the growth of larger grains with inner pores. One supposes that the presence of secondary phases requires higher ferritization temperatures to enhance the densification. Generally, the high porosity of samples is caused by the whole technological process of samples preparing. We followed only the effect of impurification of Ni-Zn ferrite with the rare earth ions (the maximum rate of impurification - 0.02), the samples being prepared in the same conditions.
Figure 1: Average grain size and porosity as function of rare earth type

Figure 2: Temperature dependence of the initial permeability of the rare earth ion species

An interesting result was obtained concerning the temperature dependence of $\mu_r$. Fig. 2 shows the $\mu_r$-T curves. One should note that all R ions, except for Ce, tend to flatten the $\mu_r$-T curves and this is explained by the positive contribution of R-ions to the $K_J$ constant. From Fig. 2 one sees also that the value of $\mu_r$ decreases for R ions with small radius, but increases with increasing their radius. The R ions with small radius enter into the spinel structure and owing to their electronic configuration, distort the lattice, generating an internal stress that will hinder the domain wall displacement. For Ce substitution, $\mu_r$ increases continuously with increasing temperature up to the Curie point. The peculiarity of Ce ions can be associated with the hybridization of 4f states with 3d band [6]. Also, $R_2O_3$ decreases $T_c$ of NiZn ferrite with $5\cdot 10^3 \celsius$, irrespective of R ion type, owing to a decrease in the Fe-Fe interaction number.

$R_2O_3$ acts beneficially on the electrical resistivity $\rho$. In Fig. 3 is demonstrated that, except for Ce, all R ions led to rise in the $\rho$. This influence is consistent with the concept of the insulating secondary phases on the grain boundaries ($RFeO_3$ contains Fe$^{3+}$ ions only). The highest $\rho$ was obtained for Gd substitution. The small value of $\rho$ for Ce is attributed to its valency fluctuation, between Ce$^{3+}$ and Ce$^{4+}$. Regarding the saturation specific magnetization $\sigma_s$, this almost independent on R ion type at room temperature. In Fig. 3 are plotted $\sigma_s$ measured at 77 K and 293 K as functions of the species of R ions. $\sigma_{293K}$ is some extent variable: it is 92 emu g$^{-1}$ for Yb, Dy and Tb and rises to 102-103 emu g$^{-1}$ for Er and Gd. The larger value of $\sigma_{293K}$ for Er and Gd ions may be due to a ferromagnetic ordering of the R ion moments at low temperatures or to a change in distribution of the Fe$^{3+}$ ions on the two sublattice in the spinel structure. Further investigations are necessary.

In conclusion, the rare-earth ions (Yb, Re, Dy, Tb, Gd, Sm and Ce) substituting the Fe ions in Ni$_{0.7}$Zn$_{0.3}$Fe$_{2}O_4$ ferrite modify the intrinsic properties of the ferrite. The following explanations have been proposed to justify their effects: i) the R ions enter only partially into the spinel lattice, the rest form secondary phases, on the grain boundaries; ii) the R ions have a positive contribution to the $K_J$ constant; and iii) the magnetic ions distribution differs from that of NiZn ferrite without R. Among the rare earth ions investigated, we appreciated that Gd ion with large radius and stable valence 3+ realises the best compromise between the properties of the high frequency NiZn ferrite.

References