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Effects of rare-earth oxides on physical properties of Li–Zn ferrite

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Abstract

The influence of R_2O_3 substitution on the structure, magnetic and electrical properties of LiZn ferrite is examined. The results obtained reveal that by introducing a relatively small amount of R_2O_3 (R=Yb, Er, Dy, Tb, Gd and Sm) instead of Fe_2O_3, an important modification of both structure and properties can be obtained. R_2O_3 facilitates the formation of the secondary phases(orthoferrite, garnet) on the grain boundary which suppress the abnormal grain growth. The R ions tend to flatten the μ_i–T curves, shift the Curie point to lower temperature and increase the electrical resistivity. The effects of rare-earth ions were correlated with their ionic radius which changes from 0.86 Å in Yb to 1.0 Å in Sm.

Keywords: Ferrites; Substitutions; Rare-earths; Resistivity; Curie temperature; Saturation magnetization

1. Introduction

Lithium-based ferrite is a pertinent magnetic material for applications because of its better properties at high frequency (high resistivity, high Curie temperature, low dielectric losses) and lower densification temperature than NiZn ferrite. It is known that the preparation of the LiZn ferrite in dense polycrystalline form by conventional ceramic processing is difficult because the lithia evaporation implies a limitation of the sintering temperature. Previously [1] we investigated the effect of additives like CaO, Na_2O, Sb_2O_3, ZrO_2 on the densification of the LiZn ferrite composition. Continuing our studies on the LiZn ferrite, in this work the effects of minor substitutions of Fe by rare earth ions (Yb, Er, Dy, Tb, Gd, Sm) are reported. The aim of this investigation was to lower porosity and to increase resistivity without compromising the other desirable material properties. It is known that the rare earth oxides are good electrical insulators, their resistivities are greater than 10^6 Ω cm [2]. Also, the valences of the R-ions are of large importance for compound formation and can explain some properties. It was found [3,4] that Gd, Er and Lu are trivalent cations and the others are multiple-valence R ions. Ce and Tb are both 3^+ and 4^+, while Sm, Dy, Yb are 2+ and 3+.

2. Experimental

The chemical formula of the samples investigated was $Li_{0.3}Zn_{0.4}Fe_{1.96}R_{0.04}O_4$, where R=Yb, Er, Dy, Tb, Gd and Sm. The specimens were prepared by the solid-state reaction method using Li_2CO_3, ZnO, α-Fe_2O_3, Yb_2O_3, Er_2O_3, Dy_2O_3, Gd_2O_3, Sm_2O_3 and Tb_4O_7 as starting materials. The chemical constituents, of high purity (>99.9%) were mixed in a ball mill and the powder was pressed into toroidal and tablet shape. The compacts were sintered at 1150°C for 8 h. All samples were slowly cooled in the furnace. The bulk density was computed from the sample mass and dimension measurements. The d.c. resistivity was measured with a Wheatstone bridge. The Vickers microhardness was measured with a Vickers diamond indent at a 50 g load. The specific saturation magnetization was measured with a vibrating-sample magnetometer. The initial permeability was measured at a frequency of 1 kHz by a bridge method in a field of 5 mOe. The microstructure was evaluated using an optical microscope. The average grain size D_m was determined by a line-intercept method [5].

3. Results

In this paper we presented several relevant results. By X-ray analysis, it was evidenced that only pure LiZn ferrite is monophasic; the R-containing samples have besides the

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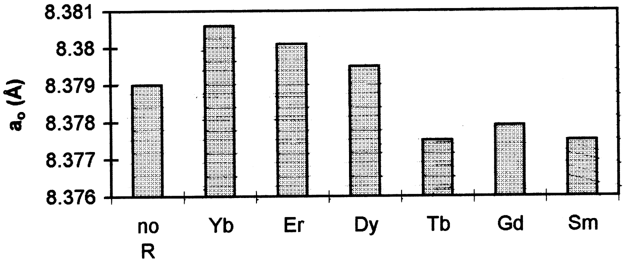

Fig. 1. Lattice parameter change vs. type of R ion.

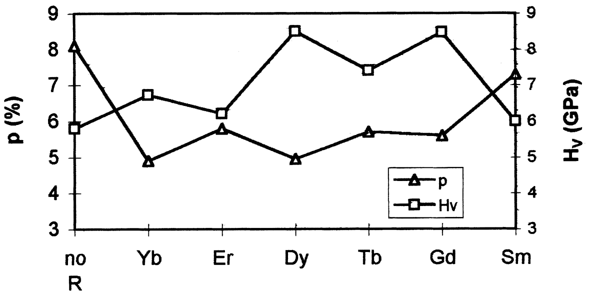

Fig. 3. The influence of R ions on the porosity and Vickers hardness.

spinel phase as major phase, secondary phases identified as garnet ($R_3Fe_5O_{12}$) or orthoferrite ($RFeO_3$), in a very small amount. The lattice parameters were calculated from X-ray measurements. In Fig. 1 the change in the lattice parameters a_0 of the LiZn ferrite by partial substitution of Fe with R ions is shown. R ions were arranged in order of increasing radius. The lattice constant changes non-monotonically with the type of R ion. The increase of a_0 for R ions with smaller radius (Yb, Er, Dy) can explain a partial incorporation of these ions in the spinel lattice. For R ions with larger radius (Tb, Gd, Sm) a plausible explanation for decrease in a_0 could be the compression of the spinel lattice induced by the secondary phases due to the differences in the thermal expansion coefficients. Generally, a high sintered density and uniform grain size are highly desirable for many ceramic products. The primary effect of secondary phase formation on the grain boundaries is to suppress the grain growth by limiting grain-boundary mobility [6]. From Fig. 2 one can observe an important decrease in the mean grain size of Dm by incorporation of R_2O_3. By preventing the exaggerated grain growth, the material porosity was improved. However, sintering at 1150°C did not result in a spectacular enhancement of densification for investigated samples. The influence of R_2O_3 on the porosity of LiZn ferrite is shown in Fig. 3. There is a lowering in the porosity from about 8% to about 5% by incorporation of R ions. This porosity lowering is caused by the presence of the secondary phases which limits grain growth by second phase ‘drag’ thereby eliminating the intragranular porosity. Of course, the decrease in the porosity is not so large because of the secondary phases which imply a higher temperature for densification. Generally, the whole technological process of preparation contributes to the porosity of samples. We followed only the effect of impurification of LiZn ferrite with rare-earth ions and all samples were prepared under identical conditions.

The Vickers microhardness H_V, measured at room temperature, is plotted in Fig. 3. A larger increase in H_V was obtained for Dy_2O_3 and Gd_2O_3 which suggests that the crystalline secondary phases formed on the grain boundary reinforce it. The small cations (Yb, Er) have a smaller effect on the H_V because they are partially soluble in the spinell lattice. Sm_2O_3 gave the smallest H_V value. Probably, during the sintering process SmO_2 could also appear which acts as a flux owing to its low melting point (642°C) and which can favour the growth of larger grains (Fig. 2) with inner pores.

The influence of R_2O_3 on the Curie temperature and resistivity is illustrated in Fig. 4. The R_2O_3 substitutions lower the T_c of LiZn ferrite with about 20°C due to a modification of the A–B exchange interaction strength when R ion substitutes Fe^{3+}. This is proof that in these compounds the Fe–Fe interaction dominates, the R–Fe interaction (3d–4f coupling) having a minor influence. It is evident from Fig. 4 that R_2O_3 causes a marked increase in the resistivity of LiZn ferrite. This effect is attributed to the afore-mentioned intergranular phases; the orthoferrite $RFeO_3$ contain Fe^{3+} ions only.

An interesting result was obtained concerning the temperature dependence of μ_i. All R ions tend to flatten the μ_i–T curves. In Fig. 5 the μ_i–T curves for some substi-

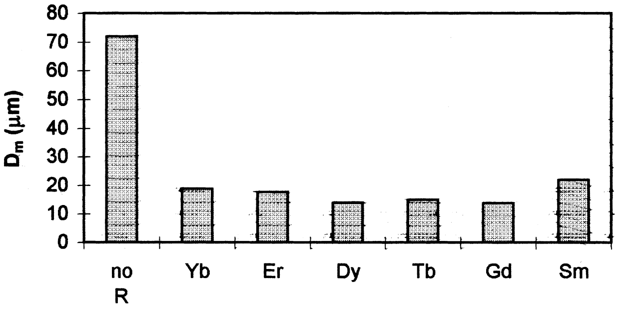

Fig. 2. Effect of R_2O_3 on the mean grain size of the LiZn ferrite.

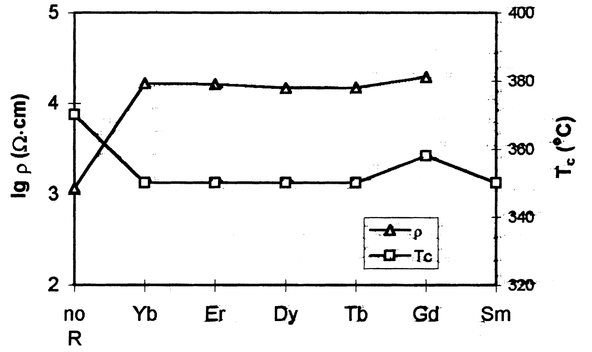

Fig. 4. The influence of R ions on the Curie temperature and resistivity.

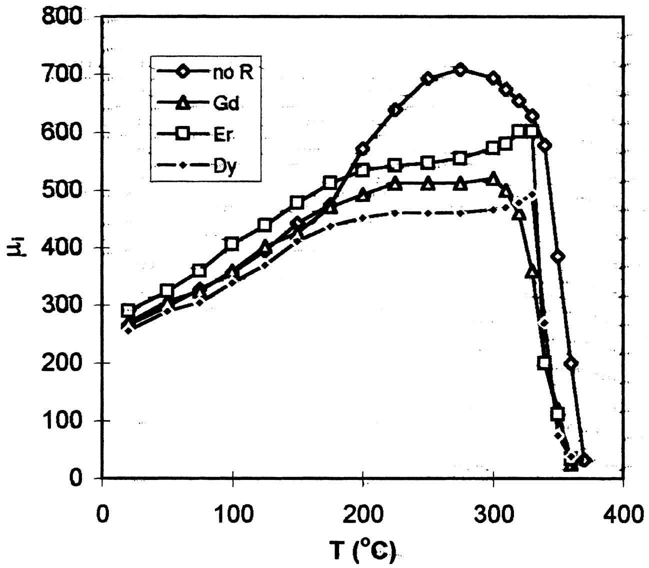

Fig. 5. Temperature dependence of the initial permeability for some samples.

tuted specimens and for pure LiZn ferrite are shown. The μ_i–T curve becomes flatter with increasing R radius. For R substituted ferrite one must take into account the R contribution to the magneto-crystalline anisotropy constant K_1 which is positive [7,8], whereas that of Fe^{3+} ions is negative. On the other hand the flattening of μ_i-T curve can be also attributed to the statistical composition difference which can determine a dispersion of the K_1 compensation temperature.

4. Conclusions

This study was an attempt to improve the quality of the classic LiZn ferrite by introducing a relatively small amount of R_2O_3 instead of Fe_2O_3.

The added R ion, because of its high radius, may form the secondary phases at the grain boundary that inhibit the grain growth and increase the resistivity. Also, R_2O_3 substitutions lower the porosity and improve the temperature dependence of μ_i.

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