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Improvement of the Magnetic and Electrical Properties of Cu-Zn Ferrites

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Polycrystalline Cu-Zn ferrites substituted with different rare-earth ions (R = La, Nd, Sm, and Gd) are investigated. The initial permeability and homogeneity increased for samples with R = Nd, Sm, and Gd relative to the unsubstituted one (US). On the other hand, the magnetization and energy loss are decreased for all substituted samples. The electrical resistivity increased only for samples with R = La and Nd relative to US.

Keywords Cu-Zn ferrites, electric resistivity, grain size, magnetic properties

1. Introduction

Ferrites are very important materials in technology. They are used in radio and television, microwave and satellite communication, digital recording, and as permanent magnets. The advantage of ferrites is that they have higher efficiency and lower costs and are easier to manufacture than other metals. Sattar et al. studied the electrical and magnetic properties of single phase $Cu_{0.5}Zn_{0.5}Fe_{2-x}R_xO_4$, where x = 0.0 and 0.1 and R = La, Nd, Sm, Gd, and Dy.[1,2] They found that an Sm substituted sample showed the highest initial permeability. Later, Sattar and the present author aimed to study the magnetic and electrical resistivity properties of $Cu_{0.5}Zn_{0.5}Fe_{2-x}Sm_xO_4$ where x ranges from 0.0-0.1 but at another presintering time. It was reported that the sample with x = 0.02 has the highest initial permeability and Curie temperature.[3] Furthermore, the electrical resistivity increased with increasing Sm content. These results are very important for technology. Therefore, this study aimed to improve the magnetic and electrical properties of Cu-Zn ferrites substituted with different rare-earth ions taking the same percentage, x = 0.02, and the same preparation condition as that reported in Ref. 2.

2. Experimental Techniques

Compositions with the chemical formula $Cu_{0.5}Zn_{0.5}Fe_{2-x}R_xO_4$ where x = 0.0 and 0.02 and (R = La, Nd, Sm, and Dy) were prepared by the ceramic technique. High purity oxides, 99.9%, of CuO, ZnO, Fe_2O_3, and R_2O_3 were mixed together according to their molecular weights. The mixture of each sample was ground to a fine powder and then presintered at 900 °C for 30 h. The presintered powders were ground again and pressed under a pressure of 4×10^3 Kp/cm^2 into toroids and discs. They were finally sintered at 1000 °C for 6 h in two cycles and then slowly cooled to room temperature. X-ray diffraction patterns were performed using a diffractometer type PW3710 with CuK_α radiation. The porosity percentage P was calculated according to the relation

$$P = 100(1 - d/d_x)\%$$

where d is the density of each sample in g/cm^3, as measured in toluene using Archimedes' principle, and d_x is the theoretical x-ray density as calculated using the formula: $d_x = 8M/Na^3$, where M is the molecular weight; N, Avogadro's number; and a (Å), the average lattice parameter of each sample. The microstructure of the investigated system was studied using the scanning electron microscope (SEM), type JEOL JEM 1200 EXII (Ain Shams University, Cairo, Egypt). The sample was etched in a boiling HCL for 5 min, then a thin layer of gold was deposited on the sample surface. The average grain size was determined by drawing random lines on the obtained photographs and counting the number of grain boundaries. The grain size G.S. (μm) was then calculated by dividing the length of the straight line over the number of grain boundaries. Measurement of the magnetization (Am^{-1}) was based on Faraday's law of electromagnetic induction. The initial permeability μ_i was measured as a function of temperature at a constant frequency f = 10 KHz and its value was calculated using Poltinnikov's formula.[4] The core loss E is calculated using the hysteresis loop. For electrical resistivity measurements, the polished surfaces of each sample were rubbed with In-Ga as a contact material. Each disc was placed between two platinum electrodes of a cell and the resistivity measured at room temperature. The percentage error in the resistivity measurement was about 2%.

3. Results and Discussion

X-ray diffraction patterns indicated that all samples are formed in a single cubic phase. The average lattice parameter a (Å) is calculated for all samples and is listed in Table 1. One recognizes that on substitution the lattice parameter remained more or less constant except the sample with R = Gd. The calculated porosity is given also in Table 1. Notice that the porosity slightly increased on substitution relative to the unsubstituted one (US). Table 1 shows the calculated grain size

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for all samples. Obviously, the average grain size increased for all substituted samples relative to US except the sample with R = La.

Figure 1 shows the variation of the initial permeability μ_i with temperature for all samples. Typically, μ_i changes slowly with temperature and then drops to zero at Curie temperature T_c. Relative to US, the magnitude of μ_i for samples with R = Gd, Sm, and Nd is higher while that of the sample with R = La is lower. The magnitude of the initial permeability changes in the following order: μ_i (Gd) > μ_i (Sm) > μ_i (Nd) > μ_i (US) > μ_i (La). The change in μ_i is in the same sequences as the grain size (Table 1; i.e., samples with larger grain size have higher initial permeability, which is the expected behavior and is in agreement with that previously reported.[5,6] In the system $Cu_{0.5}Zn_{0.5}Fe_{1.9}R_{0.1}O_4$ where R = La, Nd, Sm, Gd, and Dy, μ_i increased only for the sample with R = Sm by ≈ 60% relative to US.[2] In this work, on decreasing the percentage of rare earth from 0.1-0.02, μ_i increased by ≈ 78% and 80% at about 310 K for the samples with R = Sm and Gd, respectively, relative to US.

The values of the Curie temperature T_c for all samples, as determined from μ_i (T) curves, are listed in Table 1. T_c is nearly constant and is about 455.5 ± 3.5 K for all samples. This value is in agreement with that previously reported,[3] T_c = 454 K ± 2 K. The constancy of T_c may be due to the small percentage of rare-earth ions and confirms the fact that R-R interactions are very weak.

The sharpness of the decrease of μ_i with temperature at T_c gives an indication about the homogeneity of the samples (i.e., a sharper decrease of μ_i with temperature means a more homogeneous sample).[7] Figure 2 represents the variation of homogeneity $\Delta\mu_i/\Delta T$ as a function of the ionic radius of the rare-earth ion (SARGENT-WELCH). It is perceivable that relative to US the homogeneity increased for samples with R = Nd, Sm, and Gd and decreased for the sample with R = La. The changes of homogeneity have the same order as that of the grain size, which is the expected behavior, with the exception that the samples with R = Sm and Gd are interchanged (Table 1). This interchange may be due to the formation of SmO_2 at the grain boundaries during the sample preparation.[3] Accordingly, the percentage of Sm ions inside the grains is less than that for the other rare-earth ions. Thus it may be concluded that the decrease of the content of rare-earth ions below x = 0.02 leads to an increase of the homogeneity. This conclusion is in agreement with our previous work on $Cu_{0.5}Zn_{0.5}Fe_{2-x}Sm_xO_4$ where x changes from 0.0-0.1. It was found that the homogeneity increased with decreasing x.[3] Concerning the La-substituted sample it was assumed that the La ions reside at the grain boundaries and cause a pressure on the grain.[2,6,8] This will inhibit the grain growth and explains the decrease of grain size and occurrence of more pores leading to a reduced homogeneity compared with US. Figure 3 shows that the diffraction pattern intensity of (311) reflections has the same order as that of the sample homogeneity. The increase in intensity indicates a strong crystalline structure corresponding to an increased homogeneity of the samples. The effect of a decrease of the rare-earth ions concentration below x = 0.02 on the magnetic and electrical properties will be considered in a forthcoming paper.

Table 1 The Average Lattice Parameter a, Porosity (P), Grain Size (G.S.), Curie Temperature (T_c) and Ionic Radius of the Substituted Ion r

Sample	a, Å	P, %	G.S., μm	T_c, K	r, Å
US	8.4103	10.78	1.895	453	…
La	8.4189	12.33	1.450	452	1.15
Nd	8.4138	11.33	2.210	454	1.08
Sm	8.4019	9.945	3.460	459	1.04
Gd	8.3800	10.895	6.210	458	1.02

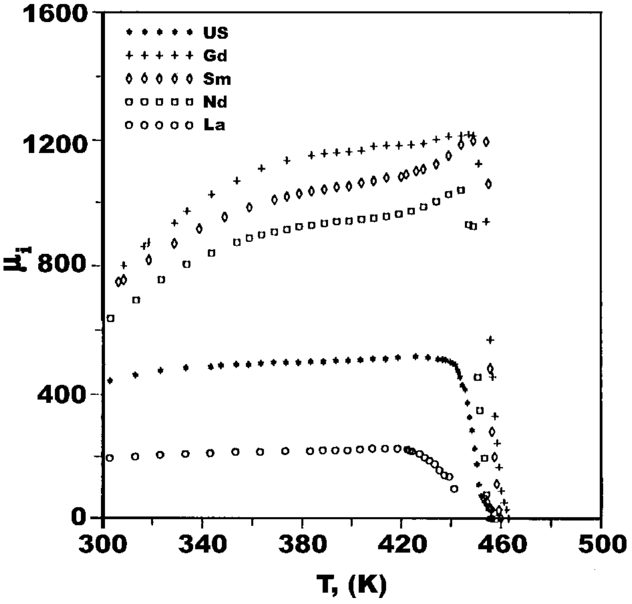

Fig. 1 Temperature dependence of the initial permeability

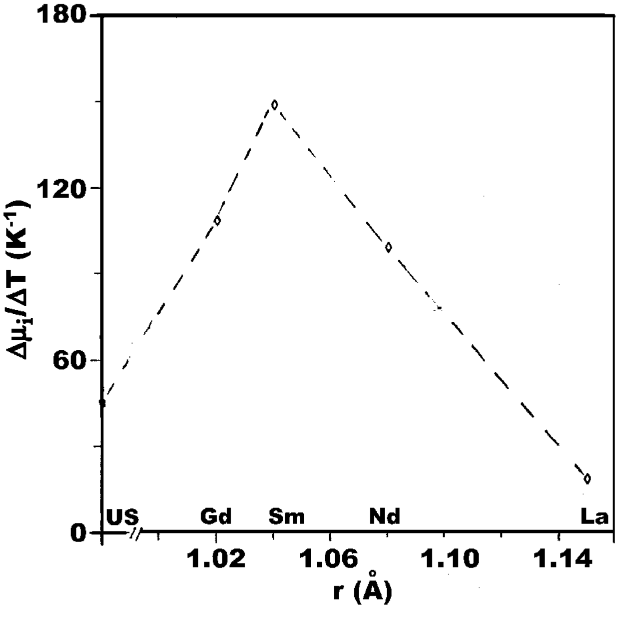

Fig. 2 The dependence of homogeneity $\Delta\mu/\Delta T$ on the ionic radius of rare earth ions r (Å)

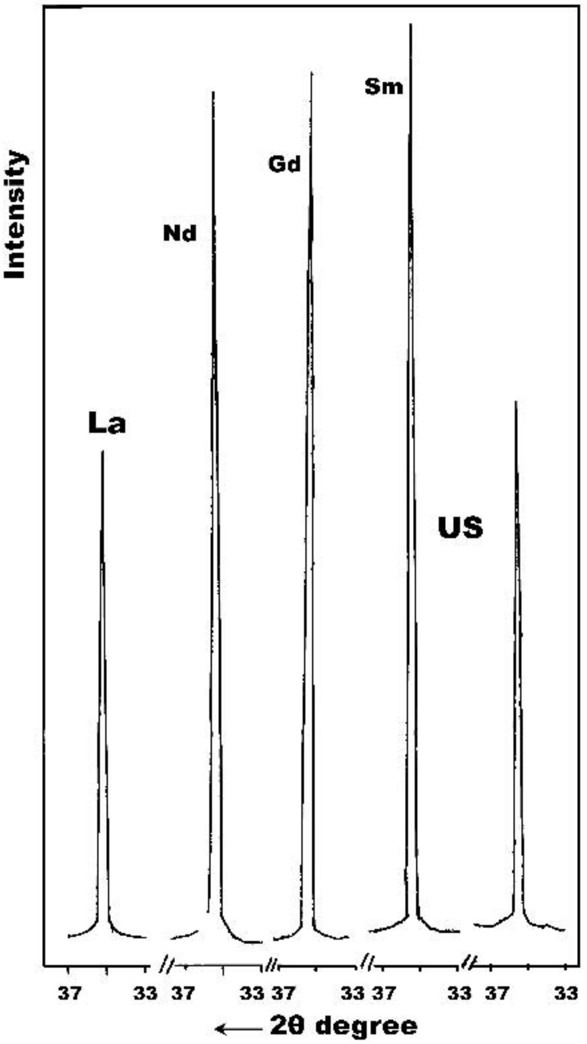

Fig. 3 The diffraction pattern intensity of the (311) peak for all samples

Figure 4 shows the change of magnetization and energy loss with the ionic radius, at a constant applied magnetic field, H = 1200 A/m. Clearly, the magnetization decreased on substitution in the same order as the energy loss. This means that the energy loss is proportional to the magnetization, which is the expected behavior and agrees with that previously reported.[9] The magnetization takes the following order M (US) > M (Sm) > M (Gd) > M (Nd) > M (La). Magnetization decreased with increasing the ionic radius of the substitution ions with the exception that the sample with R = Sm and R = Gd are interchanged. This may be due to the presence of SmO_2 as mentioned above. The decrease of magnetization can be understood according to the assumption that the rare-earth ions, except the La ion, enter the grains, and that R-R interactions are negligible, furthering the decrease of the Fe concentration relative to US. The lowest magnetization for the La sample is due to the presence of more pores inside the grains relative to the other samples, as discussed above.

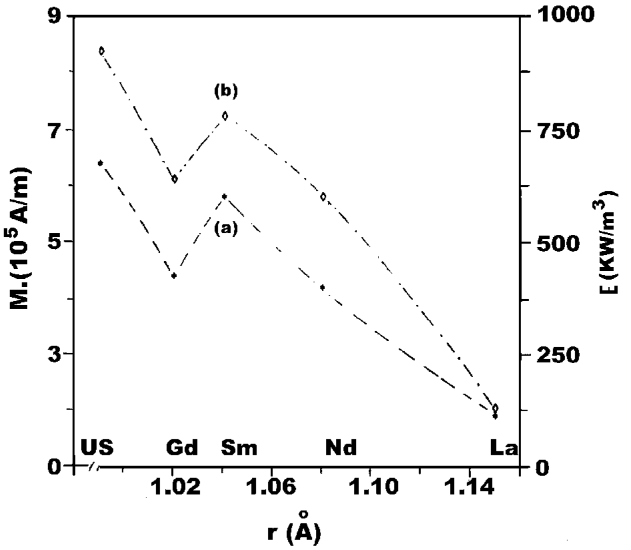

Fig. 4 The dependence of **(a)** magnetization M (A/m) and **(b)** energy loss E (KW/m^3) on the ionic radius of rare-earth ions at constant magnetic field H = 1200 A/m

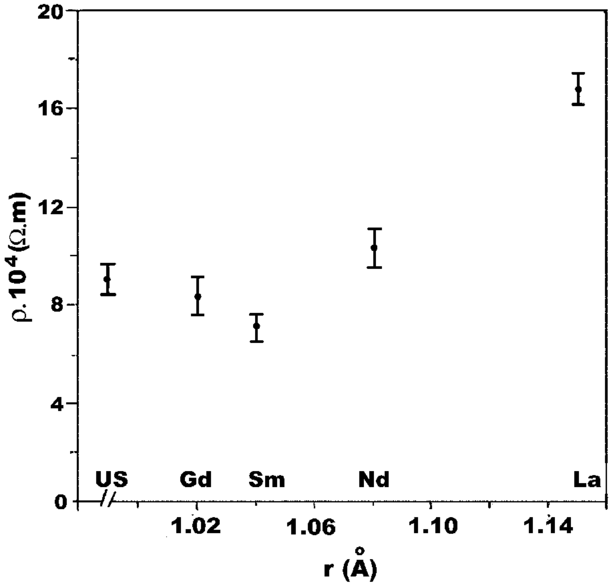

Fig. 5 The dependence of the electrical resistivity ρ on the ionic radius of rare-earth ions at room temperature

Figure 5 represents the variation of the electrical resistivity ρ with the ionic radius of the rare-earth ion at room temperature. Relative to US, ρ increased for samples with R = Nd and La and decreased for samples with R = Gd and Sm. It is known that the conduction mechanism in ferrite is mainly due to hopping of charge carriers between Fe^{2+} and Fe^{3+} ions on B-sites.[10] Accordingly, the presence of rare-earth ions inside the grains inhibits the motion of electrons between Fe^{2+} and Fe^{3+} ions, which leads to an increase of the electrical resistivity for all substituted samples except the La sample. Although Sm and Gd ions enter the grains, ρ decreased relative to US. The decrease of ρ for the Gd-substituted sample may be attributed to the decrease of the lattice parameter (Table 1). For the sample with R = Sm, the presence of SmO_2, which is formed during the preparation of the sample, favors the formation of vacancies at the iron sites to maintain electron neutrality.[3,10] This leads to an initiation of thermal dissociation of oxygen[11] and causes the number of electrons to increase and hence the electrical resistivity to decrease. In addition, the increase of grain size relative to US leads to a decrease of the grain boundary and hence a decrease of the electrical resistivity. The increase of the electrical resistivity for the La sample can be attributed to the decrease of grain size relative to US and an increase of the grain boundary thickness due to the presence of La ions at these boundaries. These layers act as insulators. These two factors, in addition to the small increase in porosity, lead to an increase of ρ in the La sample.

4. Conclusion

The initial permeability at 310 K for Sm and Gd substituted samples, with $x = 0.02$, increased (improved) by about 80% and the energy loss decreased for all substituted samples relative to US. Furthermore, resistivity decreased for samples with R = Sm and Gd and increased for other substituted samples relative to US. The grain size increased relative to US for all substituted samples except that with R = La. The Curie temperature was nearly constant and independent of the type of the substituted rare-earth ion.

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