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Effect of mechanical pressure and sintering temperature on the electrical properties of the rare earth ferrite $Li_{0.6}Co_{0.1}Dy_xFe_{2.3-x}O_4$; $0.0 \leq x \leq 0.2$

S. T. BISHAY
Physics Department, Faculty of Girls, Ain Shams University, Asma Fahmi Street, Heliopolis, Cairo, Egypt
E-mail: dr_samiha@hotmail.com

Polycrystalline samples of mixed ferrite $Li_{0.6}Co_{0.1}Dy_xFe_{2.3-x}O_4$; $0.0 \leq x \leq 0.2$ were prepared by the standard ceramic technique. X-ray diffraction analysis was carried out to assure the formation of the samples. The resistance was measured at different temperatures (300–800 K) as a function of frequency (200 kHz–5 MHz) for the investigated samples prepared at different sintering temperatures ($1100^{\circ}C \leq T_s \leq 1250^{\circ}C$). It is found that this type of rare earth ferrite gives a distinguishable behavior at $T_s = 1200^{\circ}C$ where the resistance of the samples at room temperature reduced to ≈90% of their values of the others sintering temperatures. The data showed also that the resistance of these samples sintered at 1100°C is changed at 100 kHz from 12 MΩ without applying pressure to 19 kΩ with 0.8 MPa. This change occurs in a reversible manner (i.e., after removing the mechanical pressure effect the resistance of the samples well return to their initial values again immediately). Thus this type of rare earth ferrite could be more applicable in several advanced electronic devices and can be used as a sensor for the mechanical pressure.

1. Introduction

Ferrites are technologically important materials. They are widely used as transformer cores, inductors, and data storage and microwave devices. These applications demand materials with high electrical resistivity, high permeability and low losses at higher frequencies. The first use of ferrite materials in a power application was to provide the time dependent magnetic deflection of the electron beam in the television receivers, where the two-ferrite components used were the deflection yoke and the fly back transformer. These technologically useful properties can be achieved by careful control of composition and microstructure [1, 2]. A measurement of dc conductivity of a ferrite gives little insight into the actual conductivity of the bulk material. However, the nature of in homogeneity observed in the case of ferrites could be inferred well with the help of knowledge of the variation of dielectric constant with frequency and composition [3–7]. Li-Co polycrystalline ferrites are low-cost materials, mechanically hardness with high Curie temperature and chemically stable. Indeed, they can be prepared easily by standard ceramic technique. In this case, the technological problem consists, mainly, in the practical possibility of avoiding discontinuous growth of the grains, assuring at the same time a high density in the final material [8]. In rare earth ferrite it is known that the rare earth atoms play an important role in the conduction mechanism in the 4f-3d intermetallic compounds [9–11]. It is known that the magnetic behavior of the ferromagnetic oxides is largely governed by the Fe-Fe interaction (the spin coupling of the 3d electrons). By introducing R ions into the spinel lattice, the R-Fe interactions may start to have an appreciable effect (3d-4f coupling), which can lead to small change in the magnetization and Curie temperature. However, the R-R interactions are very weak since their results form the indirect mechanism 4f-5d-5d-4f [12, 13].

In this connection, the effect of substitution rare earth ions on LiCo-ferrite was considered previously [14], where some physical properties of LiCoR-ferrite (R is Ytterbium) were investigated and it was reported that the resistivity of those type of rare earth ferrite decreases with increasing temperature. Furthermore, the resistivity improvement of LiCoYb-ferrite by gamma radiation was studied [15] where a drastic improvement on the conductivity of $Li_{0.6}Co_{0.1}Yb_{0.1}Fe_{2.2}O_4$ was noted. Also, the thermal studies of the electrical conductivity of LiCoYb-ferrite have exhibited the possibility of using this type of rare earth ferrite as charge storage batteries [16].

Along the same direction, the present paper, is concerned with investigating the dependence of the resistance of LiCoR-ferrite (R is Dysprosium) on temperature and frequency at different sintering temperature

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and mechanical stress. The elastic properties of ferrites are important because of their applications in industry as well as in basic research. In industry, the elastic data are very much useful to determine the strength of the materials under various strained conditions while in basic research, the data are useful in obtaining an insight into the structure of the inter-atomic and inter-ionic forces in solids especially of the long-range type forces. A study of the elastic behavior of a ferrite also would enable one to compute the thermodynamic parameters of importance such as Debye characteristic temperature [17, 18]. It has been observed that although a number of studies such as thermal, magnetic, and electric properties of rare earth ferrites have been carried out; no effort has been made to investigate their elastic behavior [19, 20].

2. Experimental

The samples were prepared by standard ceramic technique [14–16]. The nominal chemical formula of the investigated samples is $Li_{0.5+z}R_xCo_zFe_{2.5-2z-x}O_4$; $z = 0.1$, $0.0 \leq x \leq 0.2$ (with x varying in steps 0.025), where R is Dy. The starting materials oxides CoO, Fe_2O_3 and Dy_2O_3 in analar grad form (BDH) were used with LiOH (which was changed to Li oxide before the preparation). The whole mixture was transferred to an electrical shaker for 2 h in order to assure good mixing, to improve the homogeneity a magnetic stirrer was used. The mixing was performed in an agate ball mill for 2 h in the presence of ethyl alcohol. The powder were pressed into pellet form and calcined in air at 850°C for 5 h. The ball mill used again to obtain fine powder. Wet milled again, and pressed into tablet form of diameter 1 cm and thickness about 1.5 mm using a pressure of 15 MPa. Finally the pellets were classified into four groups and sintered at 1100, 1150, 1200, and 1250°C for 10 h and allowed to cool to room temperature with the same rate as that of heating (2°C/min). The pre and final sintering was done using a UAF 16/5 (UK) furnace. The two surfaces of each sample were polished to assure the uniform thickness and to decrease the surface porosity. They were coated by silver paste in order to achieve good conduction. Two terminals method was used to measure the ac resistance for the investigated samples at different temperatures (300–800 K). A stainless-steel cell with negligible resistance was utilized for such purpose. The bridge used for these measurement as a function of frequency (200 kHz–5 MHz) is RLC bridge model HIOKI 3531(Japan). The temperature of the samples was measured using a Digi-Sense thermometer with K-type thermocouple. The junction of the thermocouple was in contact with the sample to prevent any temperature gradient. The accuracy of the temperature measurement was better than ±1°C. Using a pressure gauge as shown in Fig. 1several definite pressures affected the prepared pellet and the ac resistance was measured as a function of the frequency at room temperature.

3. Results and discussion

A study of the elastic behavior of ferrites is very important and essential mainly to understand the nature of inter-atomic and inter-ionic forces in them. Moreover, ceramic materials in general and ferrites in particular are very strong and cannot be deformed under normal conditions. However, since these are not structural materials they cannot be used straight because their strength-to-weight ratio is not outstanding resulting in them often being brittle [17, 18]. Stress, in turn, produces magnetization changes due to magnetostriction and piezomagnetic effects and sudden shocks can also cause domain-wall motion and migration [19]. Therefore, care should be taken to avoid mechanical stressing both in fabrication and service; otherwise permeability may be drastically degraded. In view of these factors, a study of the pressure effect is very much useful and essential.

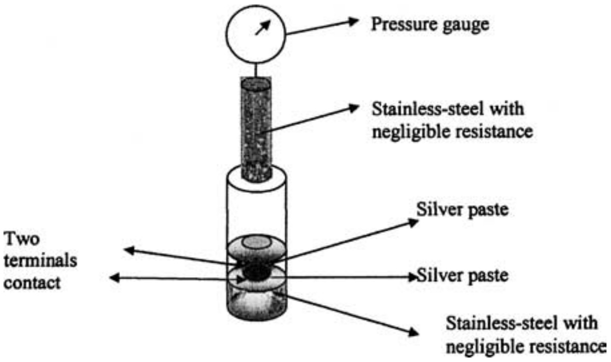

Figure 1 Schematic representation for the cell used to measure the resistance of the sample when a mechanical pressure is applied.

Fig. 2illustrates the dependence of the resistance on the applied mechanical pressure as a function of frequency for 4 groups of $Li_{0.6}Co_{0.1}Dy_xFe_{2.3-x}O_4$; $x = 0.075$ (as a typical Dy-concentration) sintered at 1100, 1150, 1200, and 1250°C. It is noted that the resistance of this type of rare earth ferrite decreases with increasing sintering temperature, mechanical pressure and the applied field frequency. Moreover, for all frequencies the resistance decreases with increasing the mechanical pressure and the registered observation has emphasized that these decreases occur with reversible manner (i.e., with removing the applied pressure the resistance of the samples return to their values again immediately). This may be due to under high pressure there is a chance for the 4f deep electrons of the dysprosium atoms to share in the conductivity process. From another point of view, the dysprosium ions with ionic radius (0.99 Å) which is larger than that of iron (0.57 Å) will diffuse to the grain boundaries and form an isolating ultra-thin layer around grain [8]. Under high mechanical pressure some of these dysprosium ions have a chance to enter the lattice causing an increase in the conductivity. Also, under pressure some elastic deformation in the lattice parameters takes place; decreasing the resistivety i.e., this type of rare earth ferrite can replace the piezoelectric crystals in the applications. The change in ΔR of the resistance of $Li_{0.6}Co_{0.1}Dy_{0.075}Fe_{2.225}O_4$ is reported in Table Ifor different frequencies (from 100 Hz to 5 MHz) for different sintering temperature ($1100°C \leq T_s \leq 1250°C$); (where ΔR = the resistance of the sample at pressure (0.11 MPa)—their corresponding values at 1.13 MPa).

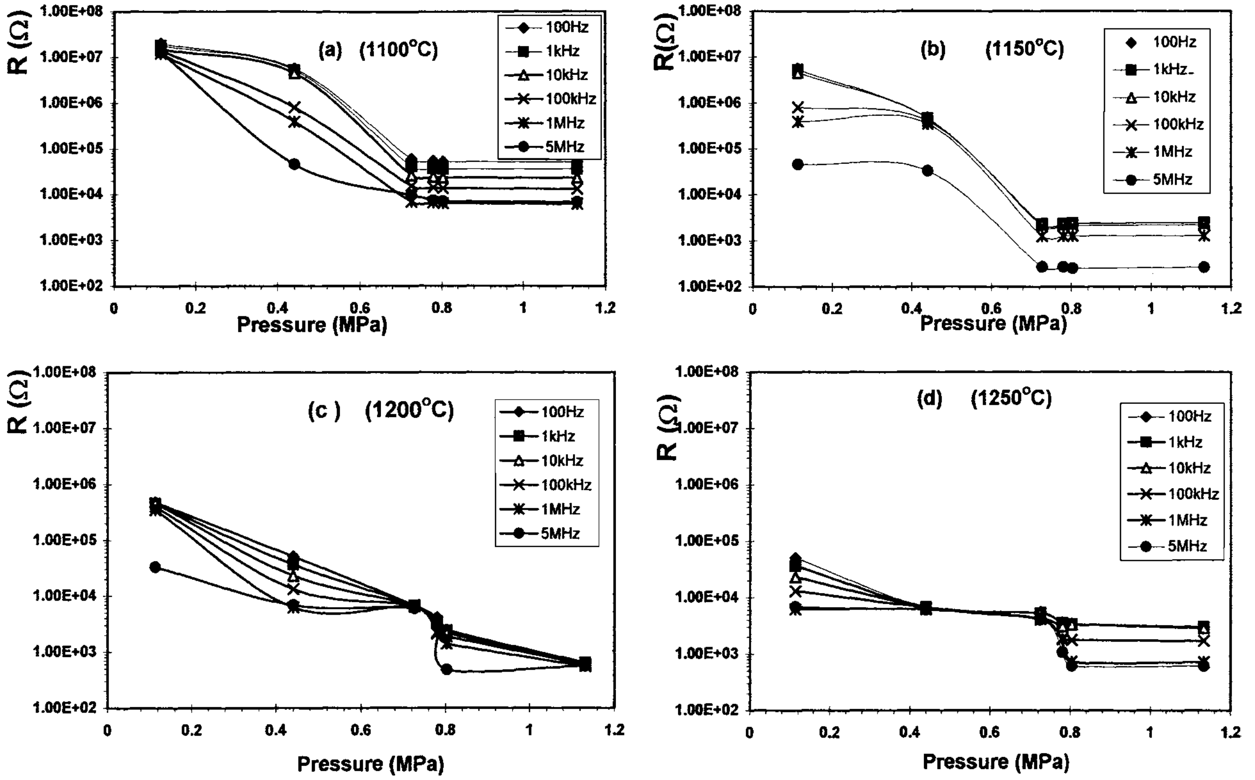

Figure 2 The dependence of the resistance on the mechanical pressure as a function of frequency for $Li_{0.6}Co_{0.1}Dy_xFe_{2.3-x}O_4$; $x = 0.075$ sintered at: (a) 1100°C, (b) 1150°C, (c) 1200°C, and (d) 1250°C.

The reported data in Table I indicate that the effect of pressure on the reduction of resistance becomes of less significance when the sintering temperature T_s increases. This is expected because the increase of T_s causes the samples to be solidified and accordingly they can resist the effect of mechanical pressure. Also, ΔR decreases with increasing the frequencies, since for high frequencies the dipoles cannot follow up the variation of frequency i.e., the conductivity decreases and the resistance increases. Consequently, the effect of pressure on reducing the resistance of the samples decreases.

Sintering is defined as the process of obtaining a dense, though body by heating a compact powder for a certain time at a temperature high enough to significantly promote diffusion, but clearly lower than the melting point of the main component. It is an extremely complex process with many interaction variables [22]. Fig. 3a–dshows the resistance temperature dependence (300–800 K) as a function of frequency (200 kHz–5 MHz) for four groups of $Li_{0.6}Co_{0.1}Dy_xFe_{2.3-x}O_4$; $x = 0.075$ sintered at $T_s = 1100$, 1150, 1200, and 1250°C. From the figure it is noted that, the resistance "R" decreases with increasing both temperature T (K) and frequency "f" up to an inflection point after which "R" decreases with increasing temperature but in direct proportional relation with "f". The inflection temperature point is $\simeq$610 K for the samples sintered at 1100, 1150 and 1250°C while for the samples sintered at 1200°C, the inflected temperature appears at 550 K. The decreases of the resistance with temperature can be interpreted as follows: in solid state sintering, the material is in solid phase during the whole process. Reaction sintering refers to chemical reaction and densification of a mixture in a single thermal treatment. In this process, the reduction in free energy due to the chemical reaction is an additional driving force. It has also economic advantages in terms of time fuel costs, since fewer stages are involved. Reaction sintering can lead to a preferential orientation of grains [23], which can have an important effect on the properties. In the first sintering (1100°C), neighboring particles form a neck by surface diffusion and presumably also at high temperature by an evaporation condensation mechanism. Grain boundaries begin to form at the interface between the particles with different crystallographic orientation. Pores appear as void between at least three contacting particles, shrinkage occurs. The result is the highest resistance values at room temperature. During (1150°C) most the densification occurs. The mobility of the atoms or ions is greatly enhanced by the presence of lattice defects. Grain growth begins during 1200°C accordingly the pore decreases. At 1250°C, grain growth is considerably enhanced and remaining pores may become isolated. When the grain growth is very high pores may be left behind by rapidly moving grain boundaries

TABLE I The change of resistance $\Delta R = R_{(0.1\text{MPa})} - R_{(1.13\text{MPa})}$ for $Li_{0.6}Co_{0.1}Dy_xFe_{2.3-x}O_4$; $x = 0.075$ as a function of sintering temperature (T_s) at different frequencies

	$\Delta R(\Omega)$					
T_s (°C)	100 Hz	1 kHz	10 kHz	100 kHz	1 MHz	5 MHz
1100	19949.5	17963.8	14976.9	13986.8	11993.8	1993.2
1150	5659.8	5288.5	4544.2	803.4	392.1	45.7
1200	479.4	459.4	454.4	399.4	349.4	32.4
1250	47.8	33.2	20.2	11.5	5.5	6.2

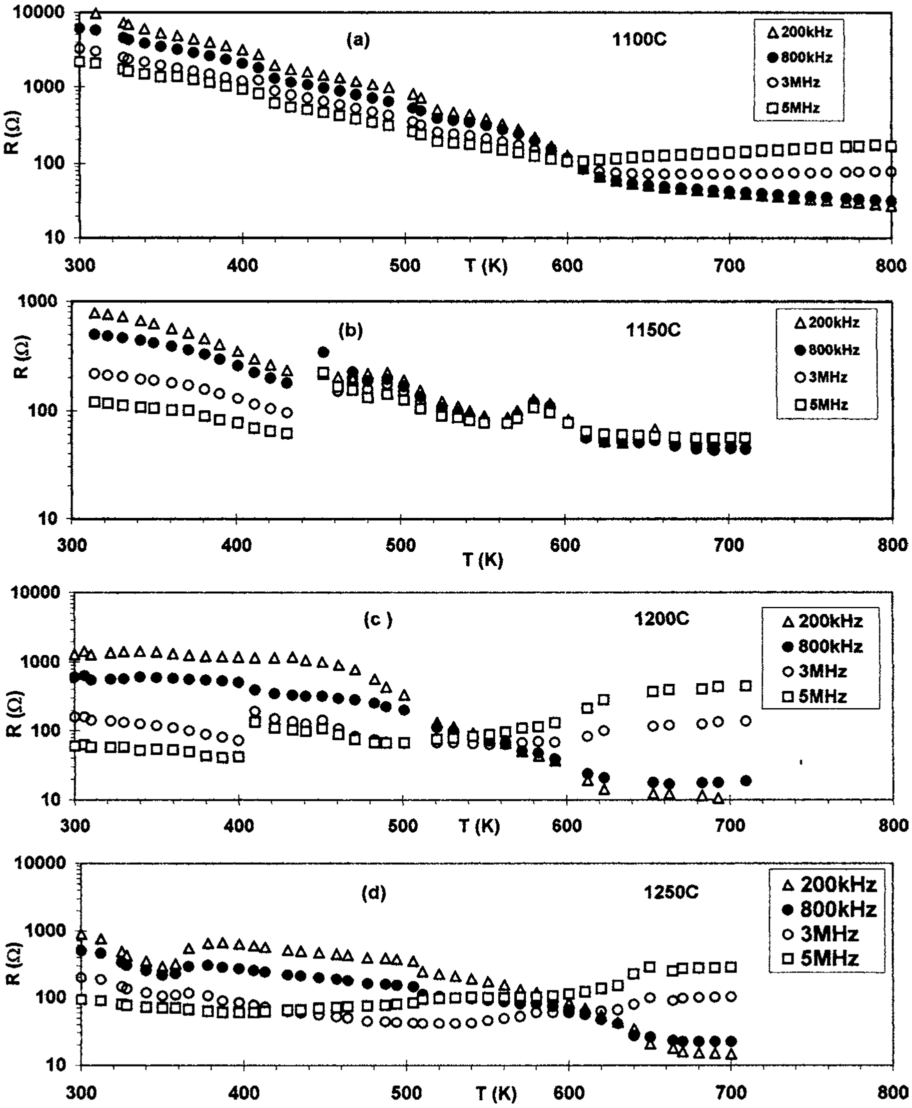

Figure 3 The dependence of the resistance on temperature as a function of frequency for $Li_{0.6}Co_{0.1}Dy_xFe_{2.3-x}O_4$; $x = 0.075$ sintering at: (a) 1100°C, (b) 1150°C, (c) 1200°C, and (d) 1250°C.

resulting in pores that are trapped inside the grains. This intergranular porosity is practically impossible to be eliminated, leading to poor magnetic and mechanical properties. When the sintering temperature is very high, a grain boundary can break away from impurities and produces exaggerated grain growth. High sintering temperature can lead to the partial volatilization of some cations. On the other hand the appear of an inflection point may be due to the reason that before the inflection point the reduction in the free energy occurs i.e., heat content decreases and the system becomes exothermic, accompanied by a decreases in the resistance with increasing the frequency. After the inflection point, the system changes its state to become endothermic where the heat content increases causing increasing in the lattice vibration, which cannot follow up the field variation therefore the resistance increases with increasing the frequency.

4. Conclusion

It is found that the suitable sintering temperature for this type of rare earth ferrite (lithium cobalt dysprosium ferrite) is 1200°C, where its resistance at room temperature reduces to about 90% of its value of the other sintering temperature. On the other hand the experimental work enhances the ability of these samples to change their resistance values immediately with the applied mechanical pressure (changes from ≈12 MΩ to ≈19 kΩ). Therefore the sample under investigation could be more applicable in several advanced electronic devices by subjecting them to mechanical pressure and can be used as a sensor for the mechanical pressure.

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