

Magnetolectrical Characterization of Mixed Ba-Sr Ferrites

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Abstract

Results on structural, magnetic and electrical characterization of ferrimagnetic compounds of $Ba_xSr_{1-x}Fe_{12}O_{19}$ ($x = 0.0, 0.25, 0.50, 0.75$ and 1.0) prepared by the conventional ceramic method are reported. The composition dependence of saturation magnetization and coercivity shows a maximum values at $x=0.5$ and $x=0.25$, respectively. The conductivity independent of frequency, obtained from direct calculation of impedance plots, exhibits an acceptable Arrhenius behavior. Temperature dependence of the total *ac* conductivity shows, at high and low temperatures, the *dc* and *ac* components. It was observed an increase in conductivity as the Ba concentration increases. All associated activation energies and dielectric constant are also calculated.

Introduction

In recent years a renewed interest in M type ferrites with different substitutions has arisen due to possible uses in various novel devices. Ba and Sr hexaferrites find application as permanent magnets in motors and loudspeakers [1]. They are also applied in magnetic devices where dielectric media are necessary. Recently ultrafine particles of Ba ferrite have been considered as a promising medium for high-density perpendicular magnetic storage [2]. The properties of this kind of materials are well known; however, diverse magnetic and electrical properties arise when they are doped with other materials or when different techniques of preparation are used [3,4]. Studies on mixed Ba-Sr ferrites as single crystal [5] and as polycrystalline samples with admixtures of the group III oxides have been performed [6]. Although many studies have been performed on the magnetic properties of M-type ferrites, very few have been done on their electrical properties [7]. The most immediate interest in ferrites relies on its magnetic properties, but technological applications require a wider knowledge of general physical properties as well, especially when the materials are studied as function of composition or addition of different modifiers.

In this work results on *ac* and *dc* electrical properties, surface characterization and magnetic properties of mixed (Ba,Sr)-M type ferrites with different concentration of Ba and Sr are reported. Using the impedance spectroscopy technique, electrical conductivity of the samples was determined. This kind of measurements were made over a wide range of frequencies and temperatures. Magnetic characterization was performed in order to evaluate the coercivity (*iHc*), saturation (σ_s) and remanent (σ_r) magnetization, and orientation ratio (σ_r/σ_s).

Experimental procedure

The ceramic method was used in order to prepare mixed (Ba,Sr)-M type ferrites. Powders of $BaCO_3$, $SrCO_3$ and Fe_2O_3 with a purity higher than 99.99% were mixed stoichiometrically to obtain samples of general composition $Ba_xSr_{1-x}Fe_{12}O_{19}$, with $x=0.0, 0.25, 0.50, 0.75$ and 1.0 . All the constituent powders were mixed homogeneously by ball-milling in ethanol for two hours. The resulting powders were calcinated during 2:45 hours at 1273K and samples with cylindrical shape were compacted by applying a pressure of 3.5 Tons/cm². For the sintering process a temperature ramp of 300K/h and a dwell of 873K during one hour and a ramp of 300K/h up to 1473K for one hour was applied. The topographic surface images were obtained using a JEOL model JSM-T330A scanning electron microscope (SEM). X-ray powder diffraction patterns were recorded with a

Rigaku 2200 diffractometer. Magnetic characterization was carried out in spherical samples, at room temperature, using an Oxford vibrating sample magnetometer with $H_{\max} = 16$ kOe. Corrections due to the demagnetizing field were also done. Measurements of the electrical conductivity were recorded in the frequency range from 5 Hz to 13 MHz using an impedance analyzer HP4192A. An electric vertical furnace was used to carry out the frequency measurements in temperature range room temperature to about 500°C. The applied voltage was 1.0V, in all cases.

Results and discussion

X-ray diffractograms recorded for all the samples showed the same structure as that previously reported for the M type ferrite [8,9]. From SEM micrographs of samples with $x=0.25$, 0.50 and 0.75, it is observed that the average grain size for $x=0.25$ was larger than that for $x=0.75$ and $x=0.50$, but for the later case a more irregular grain shape was observed. Figure 1 shows the variation of the saturation magnetization and coercivity plotted as a function of the composition. The highest value of coercivity is obtained for $x=0.25$, whereas the highest saturation magnetization value is achieved for $x=0.50$. In the cases $x=0.0$ and $x=1.0$, low values of iHc are obtained. It is evident the beneficial role of the mixture Ba-Sr on the magnetic properties.

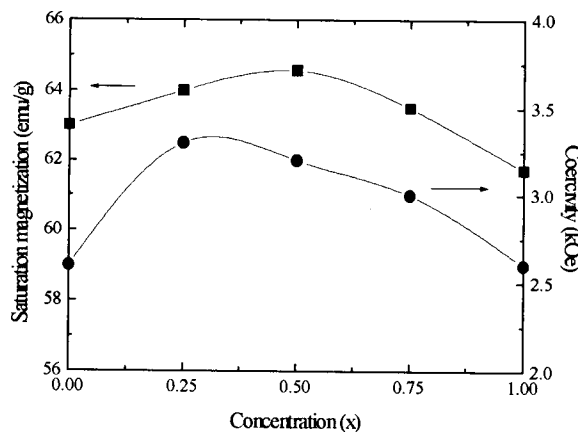


Fig. 1. Saturation magnetization and coercivity for mixed (Ba,Sr)-ferrites.

Electrical data were acquired in terms of the real (Z') and imaginary (Z'') components of the complex impedance. A simple equivalent circuit proposed to simulate the electrical behavior is constructed by two parallel RC loops connected in series corresponding, the first one (R_1C_1), to high frequency data and the second one (R_2C_2) to the low frequency region. Resistivity calculation was assisted by using the NLLS fitting routine [10] for each experimental temperature. Values of resistivity, calculated from the impedance curves, were used to plot Arrhenius curves of $\log \sigma$ against $1000/T$, as shown in figure 2. Conductivity data fit closely to an equation of the type $\sigma = \sigma_0 \exp[-E_a/kT]$, where σ_0 is the pre-exponential of conductivity, T is the absolute temperature, E_a is the activation energy and k the Boltzmann constant. The results associated with the region close to the origin will be referred to as the bulk properties σ_g . Capacitance values (C_1) on the high frequency regime are of the order of pF, which allows to assign that response as coming from the grains of the sample, whereas at low frequencies C_2 values are of the order of nF, an accepted [11] value for grain boundary phenomena, σ_{gb} . In figure 2 the total conductivity, σ_t , is also plotted.

The ac conductivity, $\sigma_i(\omega)$, is frequently reported in terms of the real part of admittance plotted as function of frequency; additional information can also be gained by plotting it against $1000/T$ at fixed frequencies. Using this fact we present ac results. Figure 3 shows the temperature dependence

of conductivity at selected fixed frequencies. In this figure each set of curves from (a) to (e) indicates decreasing content of Sr, in the understanding that the (a) set corresponds to $x=0$, (b) curve to $x=0.25$, and so on.

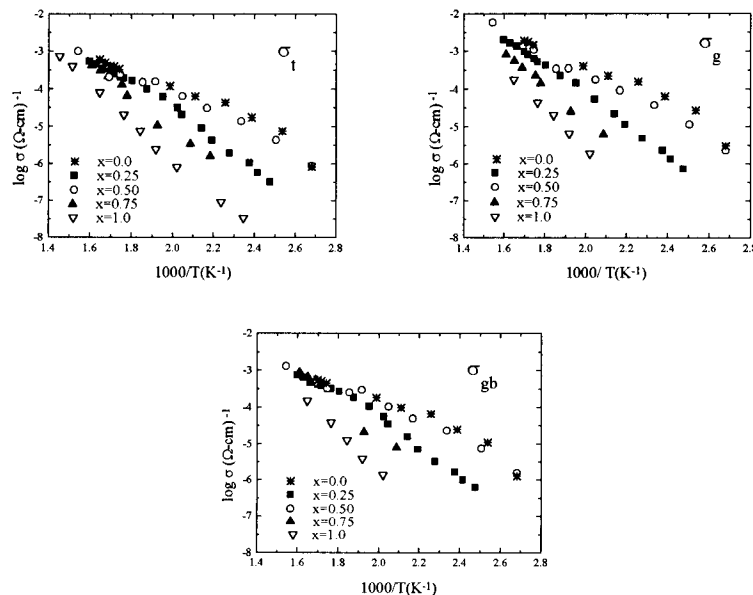


Fig. 2. Arrhenius curves of $\log \sigma$ versus $1000/T$ for σ_t , σ_g and σ_{gb} .

It is noticeable to observe an Arrhenius behavior in two temperature intervals with different activation energies. At high temperatures all conductivity curves converge to frequency independent values. Such conductive behavior corresponds to the σ_{dc} component. Table I shows activation energies, E_{dc} , associated with the dc conductivity. The region of temperatures above the point where the slope changes, must be associated with that phenomenology in which long range charge carriers dominate the conductive process, whereas at low temperatures the pure σ_{ac} component is manifested by separating the low frequency conductivity from that of the high frequency one. As it can be appreciated in Table II for all studied compounds, E_{ac} decreases gradually at increasing frequencies in the low temperature range, accompanied by an increase in the magnitude of the ac conductivity. The largest value of the dielectric constant, ϵ' , corresponds to $x=0.0$, decreasing as the barium content increases.

Conclusions

M-type ferrites of general composition $Ba_xSr_{1-x}Fe_{12}O_{19}$ were synthesized and their magnetic parameters, at room temperature, were found particularly interesting. The values of saturation magnetization and coercive force are the highest for $x=0.50$ and $x=0.25$, respectively. Concerning the electrical measurements, at temperatures above the critical temperature of all samples investigated, the conductivity becomes frequency independent. Such regime corresponds to the σ_{dc} component; however, at low temperatures the pure σ_{ac} component manifests. It was also observed that a variation of the ratio Ba/Sr disturbs the electrical conductivity mechanism, leading to a continuous increase in conductivity as the barium content increases. Finally, it was also possible to calculate the activation energies for the dc and bulk, grain and grain boundary conductivities, as well as the activation energies for the pure ac behavior of conductivity.

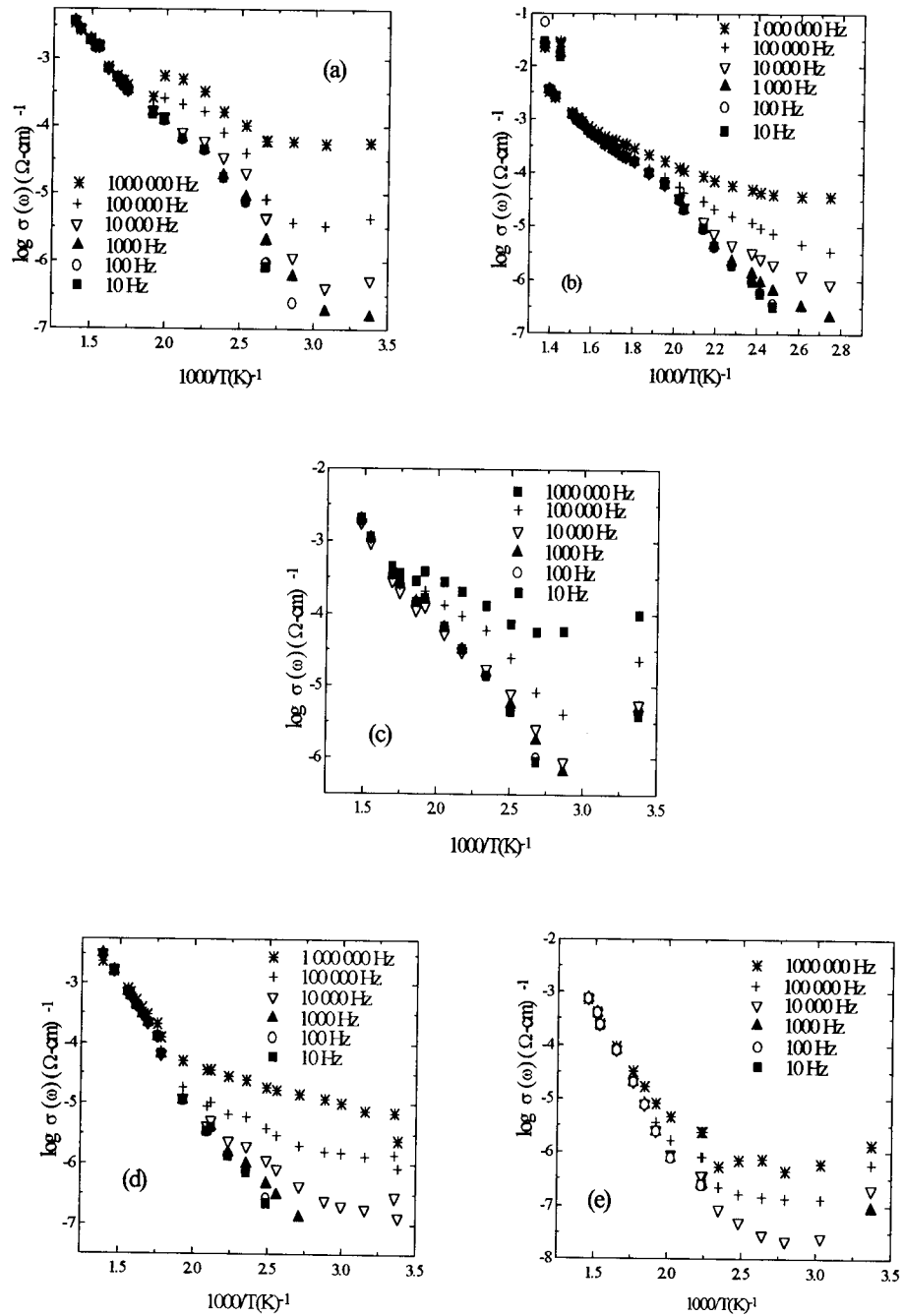


Fig. 3. Plots of $\log \sigma(\omega)$ versus $1000/T$ at fixed frequencies for (a) $x=0.0$, (b) $x=0.25$, (c) $x=0.50$, (d) $x=0.75$ and (e) $x=1.0$.

Table I. Activation energies for the *dc* (E_{dc}) and bulk conductivity (E_g).
All activation energies were calculated within an error of ± 0.003 eV.

x	E_{dc}	E_b	E_{gb}	E_t	Dielectric constant
0.0	0.60	0.42	0.38	0.39	1344
0.25	0.68	0.77	0.71	0.73	613
0.50	0.53	0.54	0.47	0.50	920
0.75	0.79	0.90	0.92	0.87	348
1.00	0.86	1.05	1.11	0.98	90

Table II. Activation energies for pure *ac* behavior.

Frequency (KHz)	E_{ac} x=0.0	E_{ac} x=0.25	E_{ac} x=0.50	E_{ac} x=0.75	E_{ac} x=1.0
10^{-2}	0.57	0.85	0.56	0.59	
10^{-1}	0.63	0.84	0.54	0.56	
1	0.53	0.56	0.49	0.47	
10	0.45	0.40	0.40	0.29	0.30
10^2	0.37	0.31	0.36	0.18	0.18
10^3	0.16	0.17	0.18	0.11	0.13

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References

- [1] Kojima, H. *Ferromagnetic materials*, Vol. 3, E. P. Wohlfarth ed., North Holland, Amsterdam, 1982.
- [2] Chantrell, R. W. and O'Grady, K., *J. Phys. D: Appl. Phys.* **25** (1992) 1.
- [3] K. Haneda, C. Miyakawa, and H. Kojima, *J. Am. Ceram. Soc.* **57** (1974) 354.
- [4] A. Chatterjee, D. Has, S. K. Pradhan and D. Chakravorty, *J. Magn. Magn. Mater* **127** (1993) 214.
- [5] L. Jahn and H. G. Müller, *phys. stat. sol.* **35** (1969) 723.
- [6] W. Wolski and J. Kowalewska, *Jap. J. Appl. Phys.* **9** (1970) 711.
- [7] Pal, M., Brahma, P., Chakravorty, D. and Agrawal, D. C., *J. Mag. Mag. Mater.* **147** (1995) 208.
- [8] V. Adelsköld, *Ark. Kemi. Mineral. Geol.* **12A** (1938) 1.
- [9] V. D. Townes, J. H. Fang and S. Perrota, *Z. Kristallogr.* **125** (1967) 1139.
- [10] B. A. Boukamp, *Equivalent Circuit*, University of Twente Dept. Chemical Technology, Netherlands.
- [11] A. K. Jonscher, *Dielectric Relaxation in Solids*, Chelsea Dielectric Press, London, (1983). J. R. Macdonald ed., *Impedance Spectroscopy*, John Wiley & Sons (1987). J. T. S. Irvine, D. C. Sinclair and A. R. West, *Adv. Mater.* **2** (1990) 132.