JOURNAL OF MATERIALS SCIENCE 25 (1990) 5142–5146

Electrical conduction and dielectric behaviour of the oxidic spinel $Li_{0.5+0.5x}Cr_{0.3}Ti_xFe_{2.2-1.5x}O_4$

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The electrical conductivity of polycrystalline lithium–chromium ferrites substituted successively with Ti^{4+} was studied as a function of composition and temperature. The resistivity increased with composition and all the samples exhibited a change in slope in the resistivity–temperature curve. Two different regions with a large variation in activation energies were found. The dielectric constant and loss factor for different compositions were measured in the frequency range of 10 kHz to 10 MHz. The dielectric permittivity showed a dispersion with frequency for all the samples. Peaks were observed for the samples with $0.4 \leqslant x \leqslant 0.8$. The possible mechanisms involved are discussed.

1. Introduction

Ferrite spinels have attracted wide attention because of their remarkably high electrical resistivity and low losses. They form very good dielectric materials and have therefore found many technological applications over a wide range of frequencies. It has been observed that electrical properties are controlled by the oxidation states and location of the cations at the tetrahedral (A) and octahedral (B) sites in the lattice. The firing temperature and atmosphere, appropriate type and amount of substituents and the method of preparation of the compound are mainly responsible for the changing properties of the ferrite [1–3]. The desired quality of ferrite for a specific application can be obtained by understanding the mechanisms involved and carefully changing the above factors. It has been shown [4, 5] that the addition of substituents like Zn^{2+}, Ti^{4+}, Cr^{3+}, etc., in lithium ferrite markedly influence the microstructural, electrical and magnetic properties. In a work reported earlier [4], the cation distribution of Ti^{4+} substituted Li–Cr ferrite was established from Mössbauer and magnetic studies. In the present paper, a systematic investigation of the d.c. resistivity as a function of composition and temperature and, dielectric permittivity and loss factor as a function of substitution and frequency of the Li–Cr ferrite, are reported.

2. Materials and methods

The samples of lithium–chromium ferrite substituted with varying amounts of titanium were prepared by a standard double sintering ceramic technique using analytical reagent grade Fe_2O_3, Cr_2O_3, TiO_2 and Li_2CO_3. 0.5 wt % Bi_2O_3 was added to the mixture to minimize losses of lithia and oxygen during the sintering process and to enhance densification and grain growth at the lower sintering temperatures. The mixture was presintered at 800° C for 5 h in air and the final sintering temperature was 1025° C for 4 h in air. The rate of annealing was $80° C h^{-1}$. The details of the preparation were reported elsewhere [4]. The compositional formula of the series was $Li_{0.5+0.5x}Cr_yTi_x$-$Fe_{2.5-y-1.5x}O_4$, where y was kept constant at 0.3 and x was varied from 0.0 to 1.0 in steps of 0.2. Samples with $x = 0.9$ were also prepared and studied. The single-phase spinel structure for all the samples was confirmed by X-ray diffraction analysis. The variation of lattice constant, a, with composition is shown in Fig. 1a. The experimental densities of the samples were found to be 96% to 98% of the X-ray densities. The Curie temperature, T_C, was found to decrease with increase in Ti^{4+} concentration as shown in Fig. 1b.

The electrical resistivity measurements were carried out on pellets of 13 mm diameter and a uniform thickness of 3 mm, using a two-probe d.c. method. Air-dried silver epoxy was used on freshly ground surface for electrical contacts. The measurements were made from room temperature to 425 K, using a Keithley 614 digital electrometer. The temperature was measured using a chromel–alumel thermocouple.

For dielectric behaviour, the same specimens were used and measurements were taken using a Hewlett Packard 4275A Multifrequency LCR meter in the frequency range 10 kHz to 10 MHz at room temperature. The capacitance was directly measured and the dielectric constant was calculated using the relation $\varepsilon' = Cd/\varepsilon_0 A$, where C is the capacitance measured, d the thickness of the pellet, A the area of cross-section and ε_0 the permittivity of free space.

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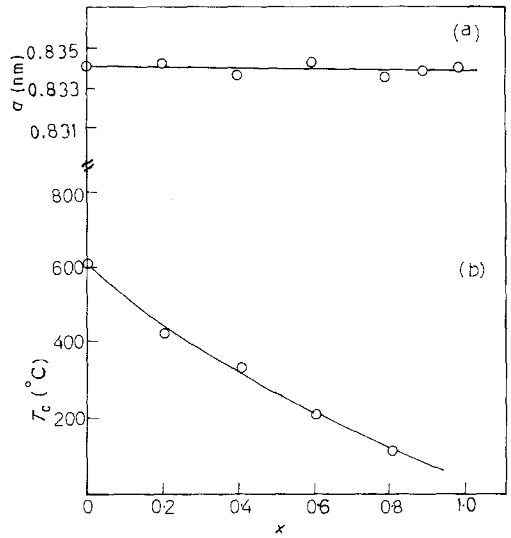


Figure 1 Variation of (a) lattice constant, a, and (b) Curie temperature, T_c, with composition.

3. Results and discussion

3.1. Resistivity studies with composition and temperature

The observed variation of room temperature d.c. resistivity (ρ) with the titanium concentration is shown in Fig. 2. The resistivity was found to increase with increasing titanium content. There is a sharp rise in resistivity for $x = 0.4$ to 0.8 samples, but a sharp decline in the slope is observed beyond $x = 0.8$. The temperature dependence of resistivity in the range room temperature to 425 K is shown in Figs 3a and b. A marked change in the slope is observed in all the samples studied. This was first anticipated to be due to the Curie temperature, but the measured Curie temperatures for all the samples were found to be higher (Fig. 1b) than the temperatures at which the observed changes in slope occur. This indicates that the conduction in these ferrites is not due to the presence of stable oxidation states of the cations, but that a more complex conduction mechanism is involved. Similar observations have been reported by various workers [6–11].

It is known that the resistivity–temperature behaviour obeys the relation

$$\rho = \rho_0 \exp (E_\rho/kT) \qquad (1)$$

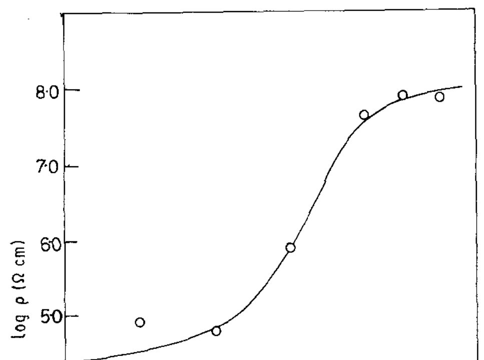


Figure 2 Room temperature resistivity, log ρ, as a function of titanium concentration.

which indicates the semiconducting nature of the ferrites. Here ρ is the resistivity at an absolute temperature T, k is the Boltzmann constant and E_ρ is the activation energy.

Ferrites form a cubic close-packed oxygen lattice with the metal ions situated at the tetrahedral (A) and octahedral (B) sites. The electrical conduction in these ferrites can be explained in terms of the Verwey mechanism [12] which consists of electron exchange between the ions of the same element present in more than one valence state distributed randomly over crystallographically equivalent lattice sites. The cation distribution for the present series, as established in an earlier publication from Mössbauer and magnetic investigations [4] is given as

$$\mathrm{Li}_{0.5x}\mathrm{Fe}_{1-0.5x}[\mathrm{Li}_{0.5}\mathrm{Ti}_x\mathrm{Cr}_{0.3}\mathrm{Fe}_{1.2-x}]\mathrm{O}_4 \text{ for } 0 \leqslant x \leqslant 1.0.$$

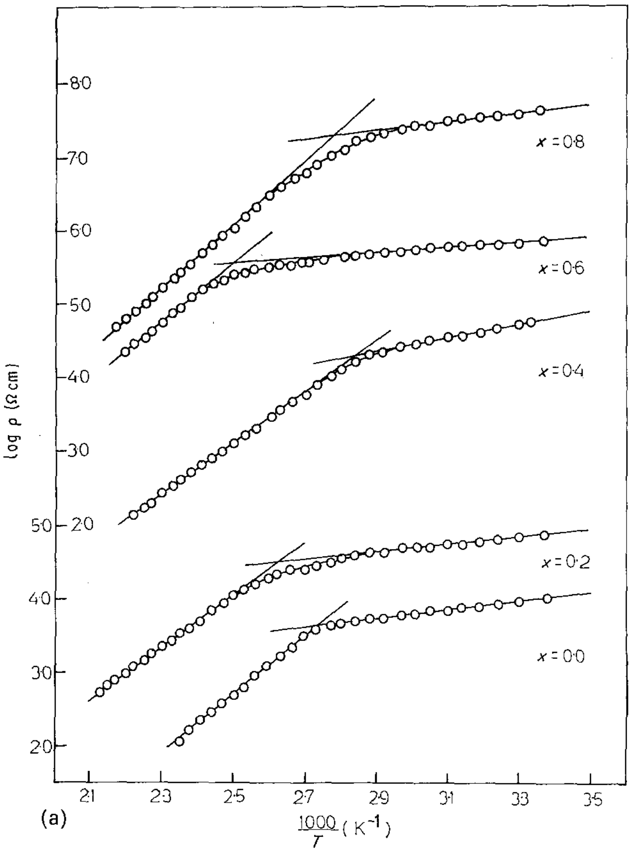
The Cr^{3+} ions are known to have very strong preference for six-fold coordination. The diamagnetic Li^+ and Ti^{4+} ions also have the tendency to occupy the B site, but above a concentration of 0.5, Li^+ ions start drifting to the A site [4]. The conduction in these ferrites is due to the electronic exchange between Fe^{2+} and Fe^{3+} ions on the octahedral sites [2, 5]. The appearance of Fe^{2+} ions may be due to the partial evaporation of Li^+ ions at the ferrite surface during the sintering process at high temperatures. Also a slight oxygen deficiency is suspected because Fe_2O_3 is able to lose oxygen when heated at elevated temperatures [13]. This oxygen non-stoichiometry will also give rise to some Fe^{2+} ions so as to maintain the electrical neutrality.

The expected hopping mechanism is $Fe^{2+} + Fe^{3+} \rightleftharpoons Fe^{3+} + Fe^{2+}$. Because Fe^{2+} ions preferentially occupy the B site, A–A hopping, therefore, does not take place. Moreover, as the B–B distance is smaller than the A–B distance, the electron hopping between B–B ions becomes the main mode of conduction.

Fig. 2 shows that the resistivity increases with Ti^{4+} content. It is seen that with the progressive substitution of Ti^{4+} ions, the iron ion content in the lattice decreases. This relatively decreases the formation of Fe^{2+} ions, hence the increase in resistivity with increasing x. Also the tetravalent Ti^{4+} ions are known to form stable electrical bonds with Fe^{2+} ions [14] thereby localizing the charge carriers. This localization of Fe^{2+} ions hinders the Verwey mechanism of electron exchange between the Fe^{2+} and Fe^{3+} ions at the B sites, resulting in an increase in the bulk resistivity.

The variation of resistivity with the inverse of temperature shows a change in slope for all the samples (Fig. 3). It is therefore not possible to assign only one value of activation energy. In the present case, the curves are divided into two regions; region I or the low-temperature region, and region II or the high-temperature region. The values of activation energies thus obtained from these two regions are plotted against x in Fig. 4. For the low-temperature region the activation energy lies between 0.07 and 0.24 eV and for the high-temperature region it is between 0.67 and 1.03 eV.

Lithium ferrite contains lithium ions and reducible iron ions and therefore it is expected that the present samples may exhibit both electronic and ionic



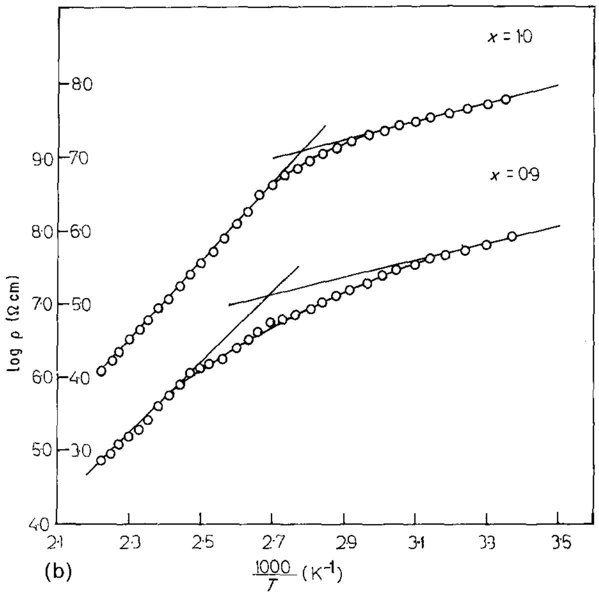


Figure 3 Variation of resistivity, log ρ, with inverse of temperature $1/T$ for samples with (a) $x \leq 0.8$, (b) $x = 0.9$ and 1.0. (a) The outer scale of log ρ is for the samples $x = 0$ and 0.2 while the inner scale is for sample $x = 0.4, 0.6$ and 0.8. (b) The outer scale of log ρ is for sample $x = 0.9$ and the inner scale is for sample $x = 1.0$.

conductivities [7, 15, 16]. The predominance of one mode over the other in the two regions may be responsible for the different values of activation energies.

3.2. Dielectric behaviour

The variation of room-temperature dielectric permittivity (ε') and loss tangent ($\tan \delta$) as a function of frequency in the range 10 kHz to 10 MHz are illustrated in Figs 5a to c. The dielectric permittivity shows a dispersion with frequency for all the samples. In the low-frequency region the value of ε' is very high and its value decreases with increase in Ti^{4+} concentration. In the high-frequency region, the value of ε' decreases to a very small value and it becomes nearly independent of frequency.

The plot of loss factor, $\tan \delta$, as a function of frequency shows that as the Ti^{4+} concentration increases, a peak appears in the reported frequency range. For $x = 0.4$, the peak is clearly visible at higher frequencies, and as x is increased this peak shifts towards the lower frequency side and finally for $x = 1.0$, the peak is not observable. Similar observations for dielectric permittivity and loss factor have been reported for a number of ferrites [17, 18].

The observed variation of dielectric permittivity with composition and frequency can be interpreted on the basis of space charge polarization. According to Maxwell [19] and Wagner's [20] two-layer model, the space charge polarization arises due to the inhomogeneous dielectric structure of the material. It is composed of large well-conducting grains separated by the thin poorly conducting intermediate grain boundaries. The dielectric permittivity is governed by the number of space-charge carriers and the resistivity of the sample.

The compositional dependence of the dielectric constant has been interpreted by various workers [21, 22] by assuming the mechanism of dielectric polarization to be similar to that of conduction. The electron exchange interaction $Fe^{2+} \rightleftharpoons Fe^{3+}$ results in a local displacement of the electrons in the direction of an electric field which determines the polarization of the ferrite. We propose a similar explanation for the present ferrite series. As mentioned earlier, the Fe^{2+} ions formed during processing preferentially occupy the

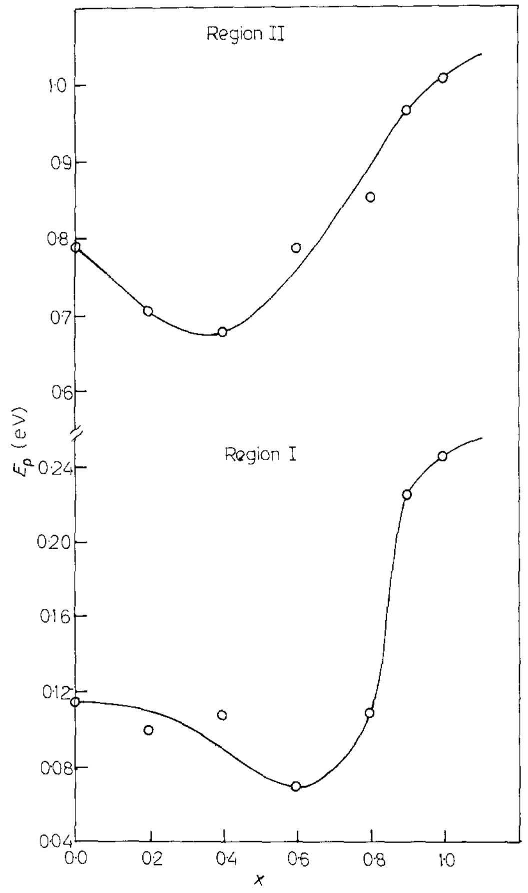
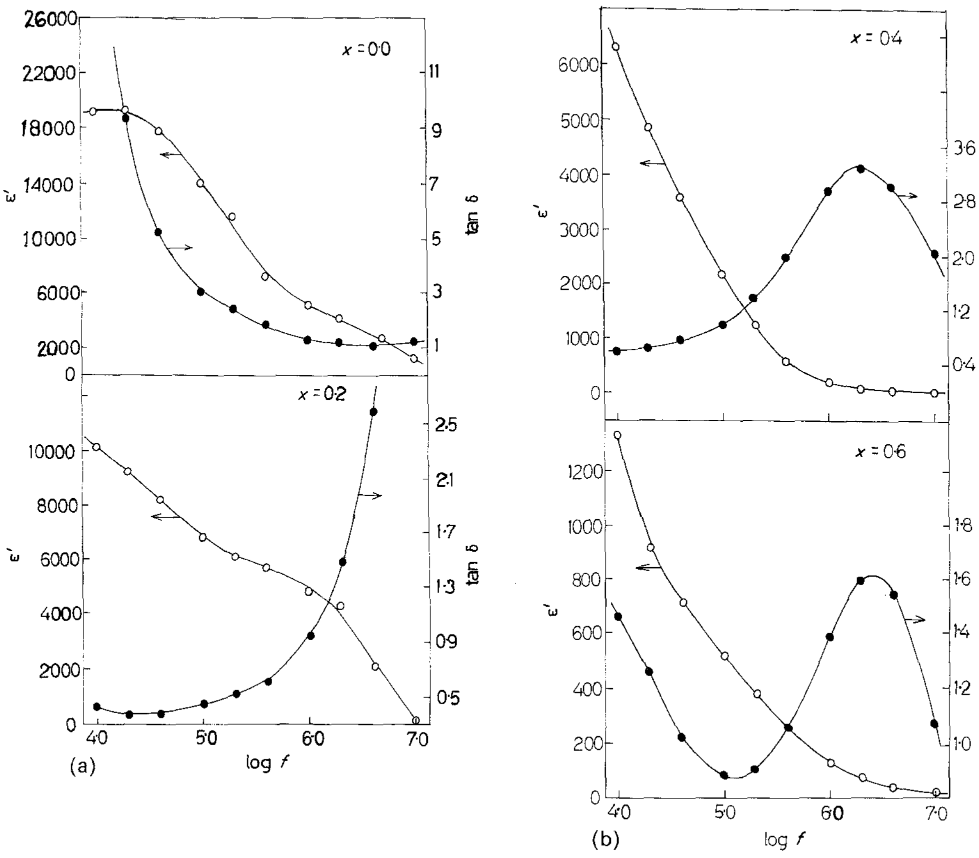


Figure 4 Activation energy, E_p, as a function of composition.



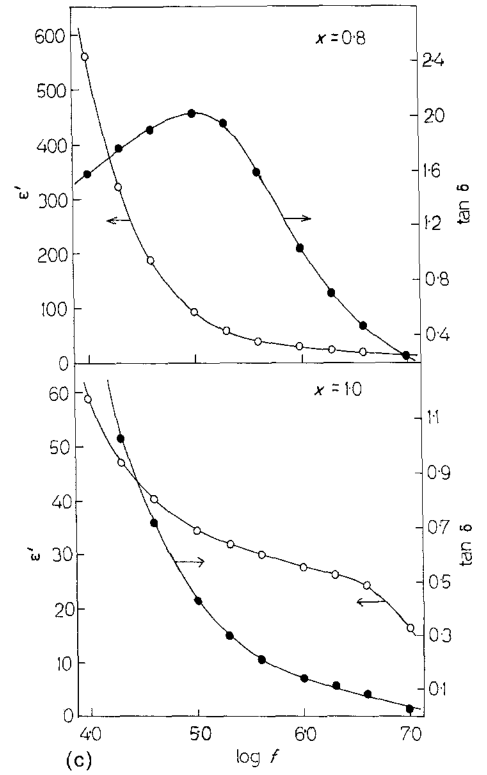


Figure 5 Variation of (○) dielectric constant, ε', and (●) loss factor, tan δ as a function of frequency for the samples (a) $x = 0.0$ and 0.2, (b) $x = 0.4$ and 0.6, (c) $x = 0.8$ and 1.0.

octahedral site. As the concentration of titanium ions increases, the iron ion content at the B site decreases, thereby decreasing the number of Fe^{2+} charge carriers. Also the localization of Fe^{2+} ions due to the formation of a stable electrical bond hinders the $Fe^{2+} \rightleftharpoons Fe^{3+}$ exchange interaction. This results in a decrease in dielectric polarization and hence a decrease in the dielectric permittivity with substitution level x. For the sample with $x = 0.0$, the iron ion concentration is maximum and the trapping of Fe^{2+} ions by Ti^{4+} ions is also zero. Therefore the observed high value of permittivity is expected.

The dielectric constant–frequency curves show dispersion due to the Maxwell–Wagner interfacial polarization. This is also in agreement with the Koops phenomenological theory [23]. The variation in dielectric relaxation intensity, which is defined as the difference between the low- and high-frequency values of dielectric permittivity with titanium concentration, is therefore primarily governed by the change in the value of the dielectric permittivity at low frequencies. This has been observed to decrease with increasing x. This is evinced by the high resistivity values for higher substitution level which impedes the build up of space charge polarization. Therefore, the dielectric relaxation intensity decreases with x as expected.

Acknowledgements

The authors thank the Ferrite Division, Solid State Physics Laboratory, New Delhi, for their help in the preparation of samples and useful discussions. One of the authors (D.K.) thanks the Council for Scientific and Industrial Research (CSIR) New Delhi, for financial assistance.

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Received 28 March
and accepted 24 April 1990