Influence of temperature on the dielectric behaviour of Co$^{2+}$ substituted Li-Ni-Mn ferrites

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Li-Ni-Mn ferrites substituted with Co$^{2+}$ having compositional formula Li$_{0.45-x/2}$Ni$_{0.1}$Mn$_{0.1}$Co$_x$Fe$_{2.35-x/2}$O$_4$ with $x$ ranging from 0 to 0.1 in steps of 0.02 were prepared by the conventional ceramic technique. The temperature dependence of the dielectric constant and loss tangent have been investigated. The dielectric constant increased with the increase of temperature, the increase being more pronounced at lower frequencies indicating the dominant role played by the interfacial polarization. Dielectric constant studied as a function of temperature showed peaks, which gets shifted to higher temperature as the frequency increased. The dielectric loss tangent was observed to increase with temperature. The results obtained are explained on the basis of Debye’s equation.

Keywords: Ferrites, XRD diffractogram, lattice constant, dielectric constant, loss tangents, polarization

Spinel ferrites are compounds of iron oxides and some transition metal oxides and they exhibit certain important electrical and magnetic properties, which make them extensively used in technological and industrial applications as magnetic storage and in microwave devices$^{1,2}$. Among them, Li-ferrites emerged as a good microwave device material due to their high Curie temperature, high squareness ratio, superior temperature stability of saturation magnetization, low intrinsic linewidth and low magnetic losses$^3$. Many factors such as processing conditions, type and amount of doped impurities affect the quality and hence the performance of these materials. The influence of some common additives like Zn, Ni, Co, Mn, Ti, Cu and Al on the various electrical and magnetic properties of Li-ferrites is known$^{3-5}$. Again deep understanding of the dielectric behaviour of these materials is important from the point of view of applications. The study of the effects of composition, frequency and temperature on the dielectric properties of ferrites offers much valuable information on the understanding of the mechanism of dielectric polarization$^5$. The present paper aims to study the influence of temperature on the dielectric properties of the Li$_{0.45-x/2}$Ni$_{0.1}$Mn$_{0.1}$Co$_x$Fe$_{2.35-x/2}$O$_4$ system.

Experimental Procedure

Li$_{0.45-x/2}$Ni$_{0.1}$Mn$_{0.1}$Co$_x$Fe$_{2.35-x/2}$O$_4$ ferrite compositions with $x$ ranging from 0 to 0.1 in steps of 0.02 were prepared by the double sintering ceramic technique. Appropriate proportion of AR grade chemicals, viz., Li$_2$CO$_3$, Mn$_2$O$_3$, CoCO$_3$, Fe$_2$O$_3$ and NiCO$_3$.2Ni(OH)$_2$.H$_2$O were taken and ball milled with distilled water for 5 h. The resulting mixtures were dried and calcined at 850°C for 6 h. A small amount of Bi$_2$O$_3$ (0.5 wt%) was added to the calcined powder in order to lower the sintering temperature and hence avoid volatilization of lithia and loss of oxygen, which occurs at high sintering temperature. The whole mixture was ball milled again for 5 h, dried, ground and sieved to fine powder and compacted into pellets using a small amount of PVA as binder and an applied pressure of 50 kN. The pelleted samples were finally sintered in air at 1050°C for 6 h and then furnace cooled.

X-ray diffractograms were recorded for the prepared samples and the formation of well-defined single-phase spinel structures for all the samples was confirmed. The lattice parameter was determined from the XRD data and density was measured using the Archimedes Principle. Curie temperature was measured by Soohoo’s method$^6$. Electrical contacts were made by Gold sputtering on the freshly polished flat surfaces of the pellets. The measurements of the dielectric constant and the corresponding loss tangents as a function of temperature were made on the pellets using a HP4284A LCR meter and a programmable temperature chamber interfaced to a PC.
Results and Discussion

XRD diffractogram of the samples confirmed the formation of single-phase spinel structure of the systems. Figure 1 shows a typical XRD pattern for the sample with \( x = 0.02 \). From the ‘d’ values provided by the X-ray diffraction data and the assigned \( hkl \) values corresponding to the peaks, the lattice constant, ‘\( a \)’ was calculated and given in Table 1. It is observed from the table that the value of ‘\( a \)’, increases with the increase of \( \text{Co}^{2+} \) concentration. This is explained on the basis of the ionic size of the constituent components. From the compositional formula it is observed that the amount of \( \text{Ni}^{2+} \) and \( \text{Mn}^{3+} \) are constant, however a \( \text{Co}^{2+} \) ion with ionic radii 0.82Å replaces a composite ion 0.5\( \text{Li}^{+} + 0.5\text{Fe}^{3+} \) with the average ionic radii of 0.705Å (ionic radii of \( \text{Fe}^{3+} \) and \( \text{Li}^{+} \) are 0.67Å and 0.74Å respectively\(^8\)). Therefore, with progressive \( \text{Co}^{2+} \) substitution an increase in the lattice constant is expected.

The compositional variation of the experimental density (\( d_{\text{exp}} \)) is given in Table 1 and it has been observed to increase with the increase of \( \text{Co}^{2+} \) substitution. X-ray density (\( d_{\text{x}} \)) also increased with substitution (Table 1). Since heavier \( \text{Co}^{2+} \) ions are substituting the lighter \( \text{Li}^{+} \) and \( \text{Fe}^{3+} \) ions, the result can be understood\(^8\). Table 1 also shows the compositional dependence of the Curie temperature for the system, which decreases with increase of \( \text{Co}^{2+} \) ion substitution. This is understood from the compositional formula where the progressive substitution of \( \text{Co}^{2+} \) ions leads to a replacement of \( \text{Fe}^{3+} \) ions, leading to a reduction in the \( \text{Fe}^{3+} \) ions content in the formula unit. Therefore, the number of the active \( \text{Fe}^{3+} - \text{O}^{2-} - \text{Fe}^{3+} \) linkages, which determines the Curie temperature\(^10\), decreases and hence the result.

The room temperature dc resistivity as a function of composition showed an increase with the increase of \( \text{Co}^{2+} \) ion concentration, \( x \geq 0.02 \) (Fig. 2). The behaviour is understood on the basis of the Verwey mechanism\(^11\) of cation distribution\(^9\) in (Fe)(Li\(_{0.45-x/2}\)Mn\(_{0.1}\)Ni\(_{0.1}\)Co\(_{x}\)Fe\(_{1.35-x/2}\)]O\(_4\)).

Substitution of \( \text{Co}^{2+} \) ions decreases the concentration of \( \text{Fe}^{3+} \) and \( \text{Li}^{+} \) ions and correspondingly the formation of \( \text{Fe}^{2+} \) ions, thus restricting the Verwey mechanism of electron hopping. This leads to the rise in the dc resistivity. The variation of room temperature dielectric constant as a function of cobalt concentration at 10 kHz showed a decrease trend with the increase of \( x \) (Fig. 2). This is understood by considering the space charge polarization and the cationic distribution\(^7\). Progressive substitution of \( \text{Co}^{2+} \) ions decreases the \( \text{Fe}^{3+} \) and \( \text{Li}^{+} \) ion concentration from the B sites. This also leads to reduced formation of \( \text{Fe}^{2+} \) ions during preparation. The electron hopping between \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) at the B-sites and hence the probability of producing space charge polarization is decreased implying a decrease in dielectric constant\(^8\).

The temperature variation of dielectric constant and dielectric loss tangents has been studied at 10 kHz and shown in Figs 3 and 4 respectively. An initial gradual increase in the value of dielectric constant has been observed for all the samples.

The dielectric constant in ferrites is attributed to the four types of polarization, viz., interfacial, dipolar, ionic and electronic polarization. At low frequencies, dipolar and interfacial polarization, which are strongly temperature dependent, play the dominant role. Interfacial polarization is known to increase with the increase of temperature while dipolar polarization decreases with the increase of temperature\(^12\). The charge carriers in ferrites are not completely free but strongly localized. The increase in temperature thermally activates the charge carriers and their drift mobility. This increases the electronic exchange.

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Table 1 — Structural and magnetic properties of the system

<table>
<thead>
<tr>
<th>( x )</th>
<th>( a ) (Å)</th>
<th>( d_{\text{exp}} ) (g/cc)</th>
<th>( d_{\text{x}} ) (g/cc)</th>
<th>( T_{\text{c}} ) (°C)</th>
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interaction thereby enhancing the dielectric constant. The present increase in the dielectric constant with increase in temperature may be indicative of the dominant role played by the interfacial polarization.

The dielectric constant except \( x = 0.00 \) is found to exhibit resonance peak; rising to a maximum value and then decreasing beyond a certain temperature. The observed temperature dependence can be explained with the help of Debye’s equation\(^{12,13} \) for dielectric constant and relaxation time, \( \tau \) given as

\[
\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \frac{\omega^2}{\tau^2}} \quad \text{and} \quad \tau = \tau_0 \exp\left(\frac{E_g}{kT}\right)
\]

where \( \varepsilon_s \) and \( \varepsilon_\infty \) are the low and high frequency dielectric constant respectively, \( \omega \) is the angular frequency of the applied field, \( E_g \) is the value of activation energy and \( k \) is the Boltzmann constant. At low temperature the value of relaxation time is high and hence dielectric constant is low. As the temperature is increased, thermal energy provided to the sample plays a role to decrease the relaxation time and hence there is an increase in dielectric constant. As temperature becomes higher, the value of \( \omega \tau \) becomes \( \ll 1 \). At a certain temperature, the dielectric constant reaches its maximum value equal to \( \varepsilon_s \). Beyond this temperature the dielectric constant is observed to decrease as the value of \( \varepsilon_\infty \) is expected to decrease with further increase in temperature\(^{12,14} \).

The variation of dielectric loss tangent (\( \tan\delta \)) as a function of temperature was studied for all the samples and the typical curves are depicted in Fig. 4. Similar to the behaviour of the dielectric constant, \( \tan\delta \) increased with the increase of temperature. This temperature variation curves could be understood on the basis of the Debye’s equation for loss\(^{13} \) given by the equation:

\[
\tan\delta = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{\varepsilon'_s + \varepsilon_\infty \omega^2 \tau^2}
\]

According to this equation, \( \tan\delta \) varies inversely to the relaxation time for a given frequency. As the relaxation time decreases with increase in temperature, \( \tan\delta \) is bound to increase. At still higher temperature, the rapid rise in the \( \tan\delta \) value has been attributed to the conduction losses, due to increased conduction at higher temperature\(^{12,14} \).

**Conclusions**

\( \text{Li}_{0.45-x/2}\text{Ni}_{0.1}\text{Mn}_{0.1}\text{Co}_x\text{Fe}_{2.35-x/2}\text{O}_4 \) with \( x \) ranging from 0 to 0.1 in steps of 0.02 were prepared by the ceramic
technique. The lattice constant and the density increased with increase of Co$^{2+}$ substitution. However, the Curie temperature decreased with Co$^{2+}$ concentration. The dc resistivity showed a rise with substitution but the dielectric constant decreased with progressive substitution. Dielectric constant increased with the increase of temperature indicative of the dominant role played by the interfacial polarization. The dielectric constant is found to exhibit resonance peak, and is explained with the help of Debye’s equation. Similar to $\varepsilon'$, tan$\delta$ increased with the increase of temperature which is understood on the basis of the Debye’s equation for loss.

References