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Effect of substitution with potassium and chromium oxides on the magnetic and electrical properties of Li-ferrite

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ABSTRACT

Li-ferrite samples substituted with potassium and chromium oxides were prepared by using ceramic method. The chemical formula $K_yLi_{0.5-y}Cr_xFe_{2.5-x}O_4$ ($x = 1.15, 1.2, \ldots$ and 1.35; $y = 0.0$ and 0.05) was used. The Curie and compensation temperatures, T_c and T_o are decreased respectively with the increasing of the Cr content for all samples with potassium and without potassium. For Li–Cr ferrite, the values of T_o dose not change with potassium substitution ions relative to that sample without potassium at each Cr content. However, the Curie temperature, T_c and ac resistivity were increased (improved) with the potassium substitution relative to the samples without potassium at each Cr content. Furthermore, the magnetization was improved with the increasing of Cr content for, Li-ferrite at a temperature greater than the compensation temperature.

1. Introduction

Li-ferrites considered as high resistive semiconductor, that has low eddy current loss and their costs are very low. Lithium ferrites have important applications more than other spinel structure because they have high saturation magnetization, square hysteresis loop and high Curie temperature [1,2]. Accordingly, Li-ferrites are preferred to be used for microwave devices and memory core industry.

Furthermore, the modification of these properties has been investigated by various authors through the substitution of Li-ferrite, prepared by ceramic method (conventional method) with different ions of different concentration [3–6]. Fu reported that, the preparation of Li-ferrites by non-conventional method (microwave induced combustion) have lead to decrease the saturation magnetization and the Curie temperature with increasing chromium content, Cr [7]. In our work we aimed to study the effect of Cr and potassium ions, K^{1+}, substitute Li-ferrite, prepared by solid state reaction (ceramic method), on the magnetization, Curie temperature and ac resistivity. We aimed to focus the study at temperature greater than the compensation temperature, T_o. For $T > T_o$ one expect the increase of the net magnetization with increasing Cr content because the net magnetic moments, $m = m_A - m_B$, will increase. This is very useful for different applications especially for hardware of the computers and microwaves. This is because the increase of the magnetization for temperature greater than the room temperature is special behavior for Li-ferrites. Furthermore, we aimed to study the effect of Cr and K ions on the resistivity of Li-ferrites. This can be investigated through the ac electrical resistivity measurements. The real part of ac electrical conductivity σ_{ac} consists of: $\sigma_{ac} = \sigma_{dc}(T) + \sigma(\omega, T)$; the first term is temperature dependent and obeys Arrhenius relation. The second term is frequency and temperature dependent [8–10].

2. Experimental techniques

2.1. Preparation of the samples

Polycrystalline samples with the chemical formula $K_yLi_{0.5-y}Cr_xFe_{2.5-x}O_4$ ($y = 0.0$ and 0.05; $x = 1.15, 1.20, \ldots, 1.35$) were prepared using the standard ceramic method. Oxides of each sample, iron oxide (Fe_2O_3), chromium oxide (Cr_2O_3), lithium carbonate (Li_2CO_3) and potassium oxide (K_2O) were mixed together according to their molecular weight ratios to obtain homogeneous mixture, purity of oxides (99.99%). The mixture was milled using electrical ball mill type (Retsch RM100). The powder of each sample was presintered at 800 °C for 8 h then ground again and pressed under a pressure of 5 ton/cm^2 into toroidal and disc shapes. They were finally sintered at 1150 °C for 6 h, slowly cooled to room temperature and then polished.

2.2. Characterization

X-ray diffraction analysis was carried out for all samples using diffractometer type (X'Pert Graphics) with CuK_α. All samples have a single cubic phase. The use of potassium with more concentration than 0.05 leads to the formation of more than one phase. The lattice parameter, a (Å) was calculated using the d-spacing equation. The porosity percentage P (%) was calculated using the relation: $P = (1 - d_b/d_x)$ 100%; where d_x (g/cm^3) is theoretical X-ray density and is given by $d_x = (8\,M/N_A a^3)$, where

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M is the molecular weight and N_A is the Avogadro's number. The bulk density d_x was calculated using Archimedes' principle.

IR spectra were recorded for the samples $K_yLi_{0.5-y}Cr_{1.35}Fe_{1.15}O_4$ with $y = 0$ and 0.05 only. The spectra were detected using JASCO FT/IR-6100 spectrometer in the range from 200 cm^{-1} to 600 cm^{-1}. Based on Faraday's law of induction the magnetization, M (A/m) was measured from 173 K to 623 K.

The dc electrical conductivity, σ_{dc} (Ω m) was measured in the temperature range from 223 K to 663 K by two-electrode method with In–Hg used as a contact material. The current passing in the sample does not exceed 10 mA to avoid the Joule heating effect. The real part of the ac conductivity, σ_{ac}, of the samples was measured by using ac two-probe method. The frequency ranges from 100 Hz to 5 MHz and the temperature ranges from 193 K to 623 K. The measurement performed using Hioki 3532-50 hitester LCR meter bridge.

3. Results and discussion

3.1. Physical properties

X-ray diffraction patterns for all samples confirmed the formation of a single spinel structure. It was found that the calculated average lattice parameter, $\bar{a}$ (Å) for the samples without potassium (K^{1+}), $y = 0$ decreases slightly with increasing chromium content, $x = Cr$, and it dose not change for the samples with potassium, $y = 0.05$. The slight decrease of $\bar{a}$ with increasing Cr content is attributed to the difference of ionic radii of Fe^{3+} ion ($r = 0.67$ Å) and Cr^{3+} ion ($r = 0.64$ Å). Similar behavior has been observed for Cr–Ni–Sn and Cr–Mg ferrites [11,12]. The constancy of the lattice parameter with potassium ion substitution may be attributed to the small variation in Cr content which leads to a small decrease in $\bar{a}$) the large ionic radius of K^{1+} ions which expects to increase it. These two factors compensate each other and account on the constancy of $\bar{a}$.

Fig. 1 shows that, the X-ray density, d_x (g/cm^3) is almost constant for the two systems, $y = 0.0$ and 0.05 with increasing Cr content. But, it is indicated that the value of d_x for the system with potassium is greater than that for system without potassium at each value of Cr content. This can be attributed to the greater value of molecular weight, M, of potassium (39.1029 g) than Li (6.939 g), d_x is directly proportion with M.

Fig. 2 illustrates the dependence of porosity percentage, P (%), on Chromium concentration, x, for all samples. It is clear that P increases with increasing Cr ions for the samples with $y = 0.0$ and 0.05. However, the value of P for the samples with $y = 0.05$ are greater than that for y = 0.0 at each certain x. The increase of P with increasing Cr ions content could be explained as follows: It was reported that the presence of Cr in ferrites has two effects [13]:

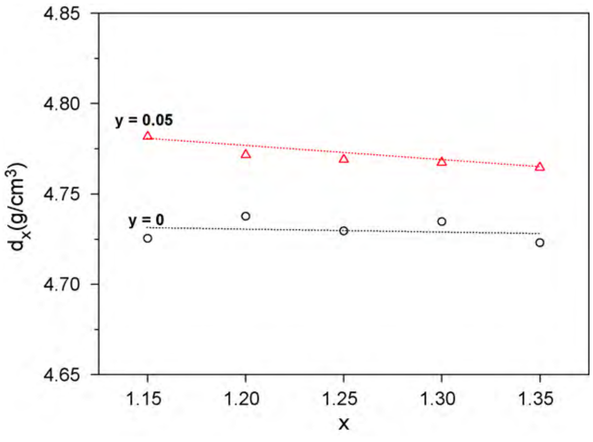

Fig. 1. Composition dependence of the X-ray density for the two systems, $y = 0$ and 0.05.

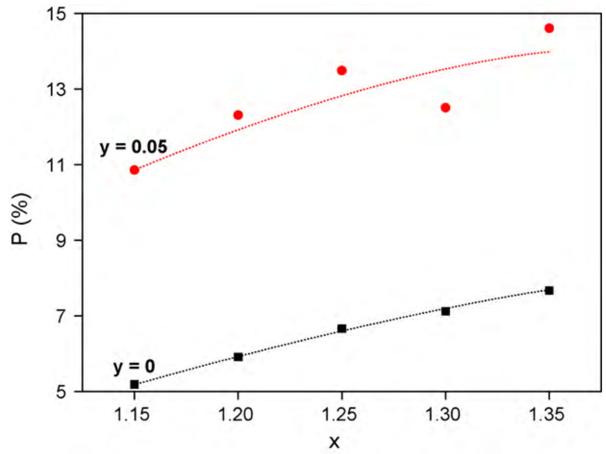

Fig. 2. Composition dependence of porosity for samples with $y = 0$ and 0.05.

(1) Formation of non uniform grains which leads the inter-granular pores to increase.
(2) Decrease of the grain size which causes the intragranular pores to increase. Accordingly, the increase of P with increasing Cr content is due to the increase of inter- and intragranular pores. The large ionic radius of K^{1+} ions may cause the grains to be more none uniform in addition to the effect of Cr ions. This account on the large value of porosity for the samples with $y = 0.05$ than that for the samples with $y = 0.0$ at each certain x.

From another point of view, Table 1 shows the difference between X-ray density and bulk density, d_b, for the two systems with $y = 0.0$ and 0.05. According to the equation of porosity, $P = (d_x - d_b)/(d_x)$, P is directly proportion with $(d_x - d_b)$. Table 1 indicated that $(d_x - d_b)$ is increased with increasing Cr content. This is account on the increase of porosity with increasing Cr content. Furthermore, one notice that $(d_x - d_b)$ for samples with $y = 0.05$ is greater than that for samples with $y = 0.0$ at each Cr content. This explains why the porosity value at each Cr content increases for samples with potassium relative to that without potassium.

It is known that, the Far-infrared spectroscopy is a good tool to get information about the cations distribution through the different vibrational modes [14]. Table 2 represents the IR spectral band positions for the samples with $y = 0.0$ and 0.05 of the composition $K_yLi_{0.5-y}Cr_{1.35}Fe_{1.15}O_4$. The first three spectral bands (frequencies, υ) are due to the tetrahedral and octahedral complexes [14]. The fourth band is due to the lattice vibration. The splitting of bands is attributed to the different modes of vibrations.

It is clear that υ_1 is shifted to a lower value for the sample containing potassium, K^{1+}, $y = 0.05$ than the sample without potassium while υ_2 is almost constant. This indicates that K^{1+} ions occupy the tetrahedral sites only and the very small decrease in υ_2 can be attributing to the movement of some Fe^{3+} ions from tetrahedral sites to octahedral one.

Table 1
The differences between X-ray and bulk density for the two systems, $y = 0$ and 0.05.

x	$d_x - d_b$ (g/cm^3)	
	$y = 0$	$y = 0.05$
1.15	0.24490	0.51925
1.20	0.28014	0.58744
1.25	0.31502	0.64332
1.30	0.33725	0.59625
1.35	0.36197	0.69616

Table 2
Wave numbers of IR bands in cm^{-1} for $K_yLi_{0.5-y}Cr_{1.35}Fe_{1.15}O_4$, $y = 0.0$ and 0.05.

Sample	Tetra. bands A-site		Oct. bands B-site						Lattice vibration		
	Fe^{3+}–O		Li^{1+}–O		Fe^{3+}–O		Fe^{2+}–O				
	υ_1			υ_2			υ_3			υ_4	
$y = 0.0$	565	515	455	422	397	355	326	303	280	249	226
$y = 0.05$	555	507	451	422	395	353	326	301	280	249	226

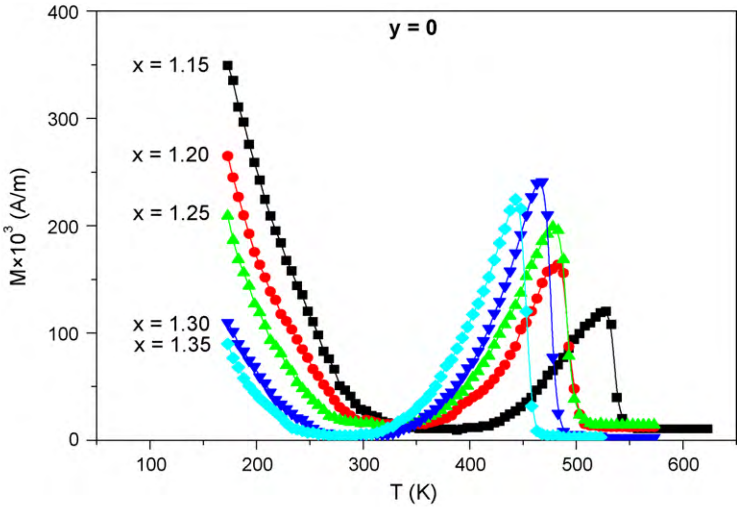

Fig. 3. Magnetization variation with temperature for samples with $y = 0$.

3.2. Magnetic properties

Fig. 3 shows the variation of magnetization, M (A/m), with temperature, T (K), for the samples with $y = 0$. For all samples, M falls gradually to a minimum value close to zero at certain temperatures depending on the value of chromium content, x. These first minima correspond to the compensation temperatures, T_o (K) of each sample [15,16]. At T_o the net magnetization M_B at octahedral sites (B-sites), equals the net magnetization M_A at tetrahedral sites (A-sites), but with different direction of magnetization. This behavior is very interesting because it is not the general dependence of magnetization on temperature for ferrites [17]. Then the magnetization grows to a maximum value where it drops sharply to nearly zero. It is clear that, the magnetization peak intensity is increased after the compensation temperature and this peak shifted to lower temperature with increasing Cr content. The Curie temperature, T_c (K), is determined for all samples by extrapolating the linear part of the curve, after the maximum, to the temperature axis. Similar behavior is observed for the samples with $y = 0.05$. Fig. 4 shows the variation of T_c with Cr content, x, for the samples with $y = 0.0$ and 0.05. Obviously, T_c decreases with increasing Cr concentration for all samples. Furthermore, it has greater value for the samples with $y = 0.05$ than the other samples with $y = 0.0$ at each Cr content.

To account on the decrease of T_c with increasing Cr content it is known that T_c depends on the magnetic interaction between the magnetic moment at A-sites and B-sites. This magnetic interaction (super-exchange interaction, A–B interaction) depends on the magnitude of the magnetic moments at A and B-sites. The substitution of Fe^{3+} ions with magnetic moment (5 μ_B) by Cr^{3+} ions with magnetic moment (3 μ_B) reduces the A–B magnetic interaction which leads to decrease the value of A–B interactions. This explains the decrease of T_c with increasing Cr content, x. The increase of T_c for samples with potassium ions, K^{1+}, $y = 0.05$, can attributed to the displacement of some Fe^{3+} ions from A to B-sites as a result of entering K^{1+} to A-sites. Then, the number of magnetic moments at B-site will increase and consequently the B–B double exchange interaction will increase. This account on the larger value of T_c for the samples with $y = 0.05$ than that for the samples with $y = 0.0$. Accordingly, potassium ions, K^{1+} improve the values of T_c for Li-ferrite at each Cr contents relative to the samples without K^{1+}, which is very useful for the applications.

Fig. 5 shows the variation of the compensation temperature, T_o (K), with Cr content, x, for the samples with $y = 0.0$ and 0.05. It is observed that T_o decreases with increasing Cr content for both system. Obviously, the values of T_o dose not change with potassium substitution ions relative to that sample without potassium at each Cr content. The decrease of $T_{o,}$ with increasing Cr content may be attributed to the strong preference of Cr^{3+} ions for B-sites. The substitution for Fe^{3+} ions by Cr^{3+} ions decreases the B-sub-lattice magnetic moment, m_B, and hence the B–B magnetic interaction

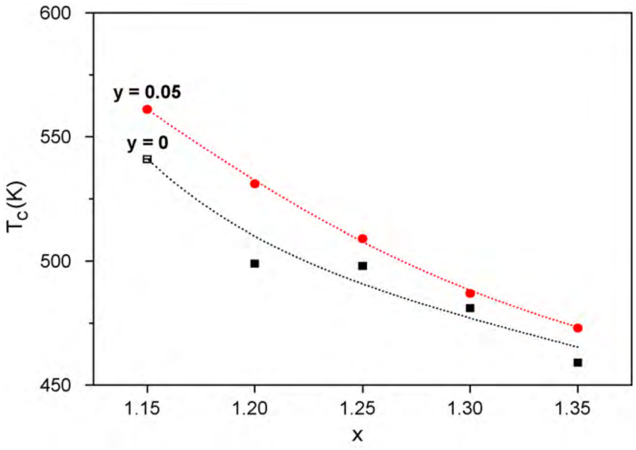

Fig. 4. Composition dependence of Curie temperature for systems with $y = 0$ and 0.05.

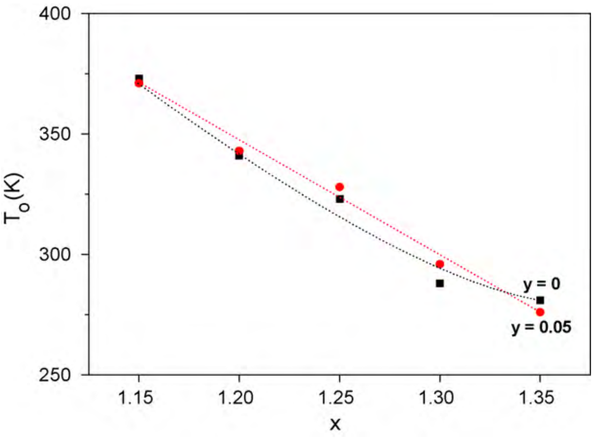

Fig. 5. Composition dependence of compensation temperature for the systems, $y = 0$ and 0.5.

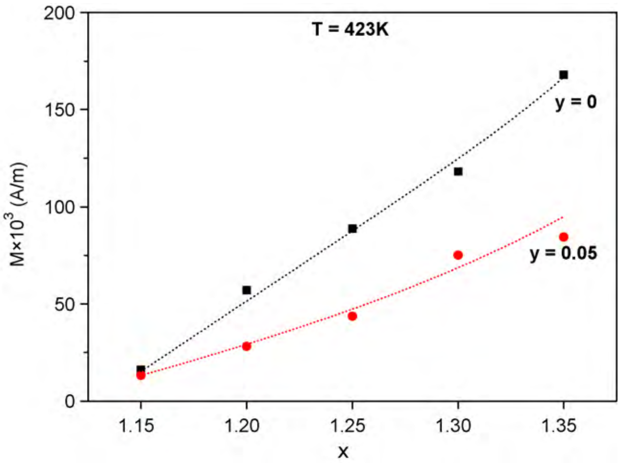

Fig. 6. Composition dependence of the magnetization after the compensation, for the samples with $y = 0$ and 0.05.

will decrease while m_A and A–A intra-site magnetic interaction are independent on the Cr content. The decreasing rate of net magnetization of the above two factors at B-site may increase and this shifts the temperature at which the magnetization of B-site, M_B, compensates the magnetization of A-site, M_A, to a lower value with increasing chromium content. This result accounts on the decreasing of the compensation temperature with increasing Cr content.

For the samples with potassium, the presence of K^{1+} with larger ionic radius (1.33 Å) than the ionic radius of Fe^{3+} ions ($r = 0.67$ Å) at A-site may causes a compression on the ions at this site. This may lead to a slight increase of the A–A double exchange interaction. Accordingly, the magnetization is slightly increased due to increasing number of Fe^{3+} ions at B-sites and due to a slight increase in A–A magnetic interaction at A-sites. The increment at both sides may compensate each other for all samples containing potassium. This explain why the value of the compensation temperature dose not changed for the sample containing potassium relative to the sample without potassium at each Cr content, x.

After the compensation, T_o, the net magnetization M is given by $M = M_A - M_B$, the increase of magnetization with temperature can attributed to a more increase of intra-site double exchange interaction at A-site, A–A interaction and a more decrease of B–B interaction at B-site. Consequently, the peak intensity of the magnetization after compensation can attributed to the saturated A–A interaction and the minimum B–B interaction (Fig. 3). The increase of this maximum with increasing Cr content can attribute to both decreasing of B–B interaction and decreasing magnetic moment at B-sites without affecting that at A-sites. Also, the shifting in this peak to lower temperature with increasing Cr content is due to the increasing rate of decreasing B–B magnetic interaction. Then the magnetization at A-site become saturated at lower temperature with increasing Cr content.

Fig. 6 shows the composition dependence of the magnetization, M (A/m), for the samples with $y = 0.0$ and 0.05 at constant temperature, $T = 423$ K, after T_o for both samples with $y = 0.0$ and 0.05. The very interesting results for applications is the increasing of magnetization with Cr content for the samples with $y = 0.0$ than that for the samples with $y = 0.05$ at any certain Cr content. The decrease of magnetization for sample with potassium relative to that without potassium can attribute to the increase of number of magnetic moment at B-site.

Table 3 listed the composition dependence of the ac resistivity, ρ (Ω m), at three constant frequencies, 100 Hz, 1 kHz and 100 kHz for the two systems $K_yLi_{0.5-y}Cr_xFe_{2.5-x}O_4$ ($y = 0$ and 0.05) and at constant temperature after the compensation temperature, T_o. The table reveal that the resistivity at any frequency increases for the sample with $y = 0.0$. But, for the samples with $y = 0.05$ the resistivity increase with increasing Cr content for the samples with $x \leq 1.25$ and then slightly decreases for $x > 1.25$. One also noticed that at certain Cr content, x, the value of ρ decreases with increasing the value of the constant frequency, 100 Hz, 1 kHz and 100 kHz, respectively. Furthermore, one found that the value of ρ for the samples with $y = 0.05$ is greater than that for the samples with $y = 0$ at each certain x for $x \leq 1.25$.

The increase of ρ for all samples with $y = 0.0$ and for the samples with $y = 0.05$ and $x \leq 1.25$ can be explained as follows:

It is reported that Fe^{2+} ions are formed during the sintering process at very high temperature [8]. These Fe^{2+} ions have strong preference for B-sites. According to the hopping model, the conduction in ferrites is accomplished through the jumping of electron between cations in different valence states. These cations are mainly Fe^{3+} and Fe^{2+}. The hopping between Fe^{2+} ions on B-sites and Fe^{3+} ions on A-sites is excluded due to the large separation distance. The substitution of Fe^{3+} ions on B-sites by Cr^{3+}, as mentioned before in the magnetic results, do not participate in the hopping process and leads to the following conclusion:

(1) Decrease the available number of Fe^{3+} ions and hence the converted fraction of Fe^{2+} will decrease.
(2) Block up the hopping of electrons between Fe^{2+} and Fe^{3+} ions.
(3) The increase of inter- and intragranular porosity with increasing Cr content leads to increase the resistivity values (Fig. 2).

These effects account on the slight increase in the resistivity with increasing Cr concentration, x. A similar behavior has been reported for $Sn_{0.05}Ni_{1.05}Cr_xFe_{1.9-x}O_4$, $Mn_{0.1}Mg_{0.9}Cr_xFe_{2-x}O_4$ and $Zn_{0.4}Ni_{0.6}Cr_xFe_{2-x}O_4$ [18–20]. The slight decrease in ρ for $x > 1.25$

Table 3
The composition dependence of ac resistivity at $T = 423\,K > T_o$ for $K_yLi_{0.5-y}Cr_{1.35}Fe_{1.15}O_4$, $y = 0.0$ and 0.05 at constant frequency.

f	100 Hz		1 kHz		100 kHz	
ρ	10^3 (Ω m)		10^3 (Ω m)		10^2 (Ω m)	
Cr content	y		y		y	
	0.0	0.05	0.0	0.05	0.0	0.05
1.15	07.55	16.5 0	3.80	6.40	2.00	5.10
1.20	0 8.12	22.07	4.12	6.91	2.40	6.20
1.25	10.02	28.32	5.10	10.11	3.82	10.20
1.30	17.11	21.09	7.20	8.80	6.52	7.01
1.35	31.21	20.80	8.00	8.61	6.67	6.94

for the samples with $y = 0.05$ can be attributed to the formation of Cr^{2+} ions. The anisotropy of these ions is very small [21], which leads to decrease the resistivity. Also, the electrons will be hopping between Cr^{3+} and Cr^{2+} ions at B-sites. These two factors account on the slight decrease in ρ for the samples with $x > 1.25$.

For all the samples with $y = 0.0$ and the samples with $y = 0.05$, $x \leq 1.25$, the decrease in ρ with increasing frequency at each certain x can be attributed to the increase in hopping of charge carriers between Fe^{2+} and Fe^{3+} ions. But for the samples with $y = 0.05$ and $x > 1.25$ the decrease of ρ can be attributed to the increase in hopping of the charge carriers between Cr^{3+} and Cr^{2+} ions in addition to Fe^{2+} and Fe^{3+} ions.

The increase of the ac resistivity for the samples containing potassium, $y = 0.05$ than that for the sample without potassium, $y = 0.0$ at each $x \leq 1.3$ can be attribute to the increase of porosity value (Fig. 2). This means that the replacement of Li^{1+} ions with K^{1+} ions improve the ac resistivity for $T > T_o$ and for $x \leq 1.25$.

4. Conclusions

From this work, the novel for the application is the improving (increasing) of T_c with K^{1+} substitution (non-magnetic ion) for Li–Cr ferrite at each Cr contents. Furthermore, the increase (improvement) of the magnetization with increasing Cr content for Li-ferrite for $T > T_o$. This increase is above the room temperature which is very useful for the different applications especially microwave devices and the memory component of the computers sets. For Li–Cr ferrites, T_c and T_o decreased with increasing Cr content. For temperature greater than the compensation temperature and at different frequencies, the resistivity is increased for Li-ferrite substituted with chromium oxides and a more increase is found for Li–Cr ferrite substituted with potassium at each Cr content value. This is very useful for application especially at high frequency. The hopping conduction mechanism was increased with increasing the frequency.

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