

## MAGNETIC AND ELECTRIC STUDIES OF V, Cd AND Gd IONS SUBSTITUTED Li-FERRITE

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### Abstract

All the investigated samples were prepared by using the conventional ceramic technique. The lattice parameter was increased for Cd and Gd ions substituted Li-ferrites and decreased for V ion substituted one. The porosity increased with the increasing of the ionic radii of the substituted ions for Li-ferrite. The initial permeability and the magnetization were increased (improved) for  $V^{5+}$  and  $Cd^{2+}$  ions substituted Li-ferrite and decreased for  $Gd^{3+}$ -substituted sample. The Curie temperature was decreased for all the substituted samples relative to the pure Li-ferrite. The dc electrical resistivity was improved for Gd substituted Li-ferrite and decreased for V and Cd substituted samples.

### 1. Introduction

Li-ferrite is a high resistive semi-conductor that has low eddy current loss and low cost. It has high Curie temperature, which is an important parameter for microwave devices. Also, it has a useful square hysteresis loop, which makes it preferable than other ferrites in many important applications in the electronic industry. Magnetic and electrical properties

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of Li-ferrite were investigated by many authors [6, 11, 12, 13]. These properties were modified for Li-ferrite through different substituted ions with many concentrations and different preparation conditions [3, 16, 17, 18]. It was reported that, the magnetization and the initial permeability of Li-ferrite of the chemical formula  $\text{Li}_{0.5+x}\text{Fe}_{2.5-2x}\text{Nb}_x\text{O}_4$  were improved up to  $x = 0.1$  [2]. But, the magnetization and the initial permeability were improved for Cu-Zn-ferrite substituted with Gd & Sm ions with  $x = 0.02$  [14]. Accordingly, the idea of this study is to investigate the magnetic and the electrical resistivity of Li-ferrite substituted with magnetic or non magnetic ions of different valance and different ionic radii, with  $x = 0.02$ .

## 2. Experimental Techniques

Li-ferrites of the chemical formula  $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$  was substituted with V, Cd, and Gd ions, which had different ionic radii. Cadmium and vanadium ions are non magnetic, but gadolinium ion is magnetic one. The chemical formulas that were used:  $\text{Li}_{0.5+x}\text{Fe}_{2.5-2x}\text{V}_x\text{O}_4$ ,  $\text{Li}_{0.5+3x}\text{Fe}_{2.5-2x}\text{Gd}_x\text{O}_4$ , and  $\text{Li}_{0.5+2x}\text{Fe}_{2.5-(4/3)x}\text{Cd}_x\text{O}_4$  for  $x = 0.0$  and  $0.02$ . The investigate ferrite samples were produced by a standard ceramic method (conventional technique). The oxides of each sample were weighted according to their molecular weights and then mixed together. For each sample, the resultant mixture was blended to a fine powder and then heated in a furnace (pre-sintered) at  $850^\circ\text{C}$  for 6h. The powders were grind until fine particle sizes were obtained and then pressed under a pressure of  $3 \times 10^8$  Pa into different shapes discs and toroids forms.

These samples were heated again (final sintering) at  $1050^\circ\text{C}$  for 6h and then slowly cooled to room temperature. X-ray diffractometer was used to obtain X-ray diffraction patterns, X"Pert Graphics & Identity with  $\text{CuK}\alpha$  radiation. The lattice parameter was calculated by using the following relation:

$$(\alpha^2)/(h^2 + k^2 + l^2) = \lambda^2 / 4 \sin^2 \theta,$$

where  $\lambda$  is CuK $\alpha$  radiation and  $\theta$  is the diffraction angle. By using the following equation:  $P = 100[1 - (d / d_x)]$ , the total porosity percentage was calculated for all the investigated samples. Here,  $d$  is the density of each sample and was measured according to Archimed's principle method and  $d_x$  is the theoretical X-ray density. For measuring the initial permeability,  $\mu_i$ , the toroidal sample was used as a transformer core based on Faraday's law of induction for each composition [1, 9]. The value of  $\mu_i$  was calculated by using the following equation:

$$V_s = K \mu_i,$$

where  $K$  is a constant value and depends on the number of turns of the primary and the secondary coils, dimension of the toroid, the current, and the frequency;  $V_s$  is the induced voltage in the secondary coil [10].

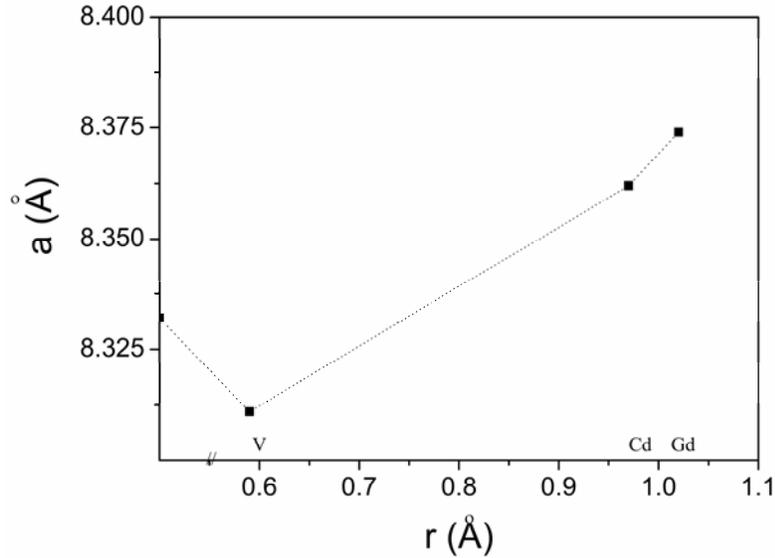
The IR spectra for pure Li-ferrite and Li-ferrite substituted with vanadium ions samples, were detected by using JASCO FT/IR-6100 spectrometer. The IR spectra were detected in the range from 200cm<sup>-1</sup> to 600cm<sup>-1</sup>.

For measuring the electrical resistivity for each sample, a thin contact layer was made on each face. The sample was inserted between two platinum electrodes.

### 3. Results and Discussion

The analysis of X-ray charts indicated that all the ferrite samples were formed from single cubic phase. The variation of the calculated lattice parameter with the ionic radii of the substituted ions for Li-ferrite was illustrated in Figure 1. The lattice parameter was increased for Cd and Gd substituted samples and decreased for V substituted one relative to the pure Li-ferrite. The increase of the lattice parameter attributed to

the increase of the ionic radii of substituted ions than that for  $\text{Fe}^{3+}$  ions ( $r_{\text{Cd}} = 0.97\text{\AA}$ ,  $r_{\text{Gd}} = 1.02\text{\AA}$ ,  $r_{\text{Li}} = 0.68\text{\AA}$ , and  $r_{\text{Fe}^{3+}} = 0.64\text{\AA}$ ) and the decrease of it attributed to the smaller ionic radius of  $\text{V}^{5+}$  and  $\text{Li}^{1+}$  ions than  $\text{Fe}^{3+}$  one ( $r_{\text{V}} = 0.59\text{\AA}$ ).



**Figure 1.** The lattice parameter against the ionic radii of the ions substituted Li-ferrite.

Far infrared spectroscopy analysis is used to investigate the cations distribution through the different sites for the pure Li-ferrite and Li-ferrite substituted with V ions. It is reported that, this analysis is an important tool to get information about the position of ions in the crystalline samples through the different vibration modes [9]. The different vibration modes for  $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$  and  $\text{Li}_{0.5+x}\text{Fe}_{2.5-2x}\text{V}_x\text{O}_4$  samples were listed in Table 1. From this table, it is cleared that,  $\nu_1$  was shifted to a higher frequency range for Li sample substituted with  $\text{V}^{5+}$  ions relative to the pure sample with,  $x = 0.0$ . This means that  $\text{V}^{5+}$  ions entered the tetrahedral sites. Meanwhile, the vibration mode  $\nu_2$  was

very small and shifted to a higher value relative to the pure sample. This result attributed to the displacement of a part from  $\text{Fe}^{3+}$  ions from tetrahedral sites to octahedral sites. The shift of the vibration mode values were related to the following relation:

$$\nu = \sqrt{(K/m)},$$

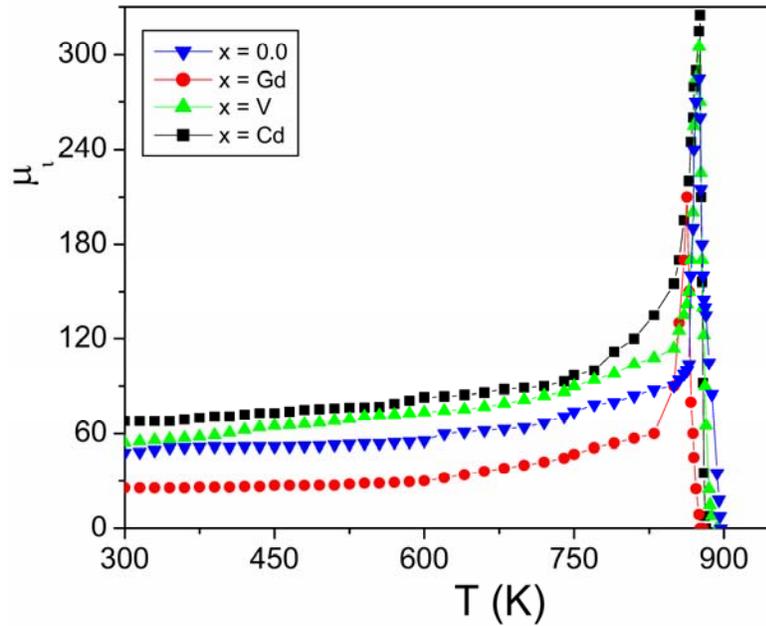
where  $K$  is the force constant and  $m$  is the mass of the ion [19]. For V substituted Li-ferrite, the lattice parameter was decreased, which led the force constant to increase. Furthermore, the mass of the  $\text{V}^{5+}$  ion is smaller than  $\text{Fe}^{3+}$  one ( $m_{\text{V}} = 50.942$ ,  $m_{\text{Fe}} = 55.847$ ). These two factors accounted on the shifting of the vibration modes to higher frequency values. It is reported that,  $\text{Gd}^{3+}$  ions entered B-sites, octahedral sites, and  $\text{Cd}^{2+}$  entered into A-sites, tetrahedral sites, according to their preference and electron configuration [7, 14, 20, 22].

**Table 1.** IR absorption bands for  $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$  and  $\text{Li}_{0.5+x}\text{Fe}_{2.5-2x}\text{V}_x\text{O}_4$  samples

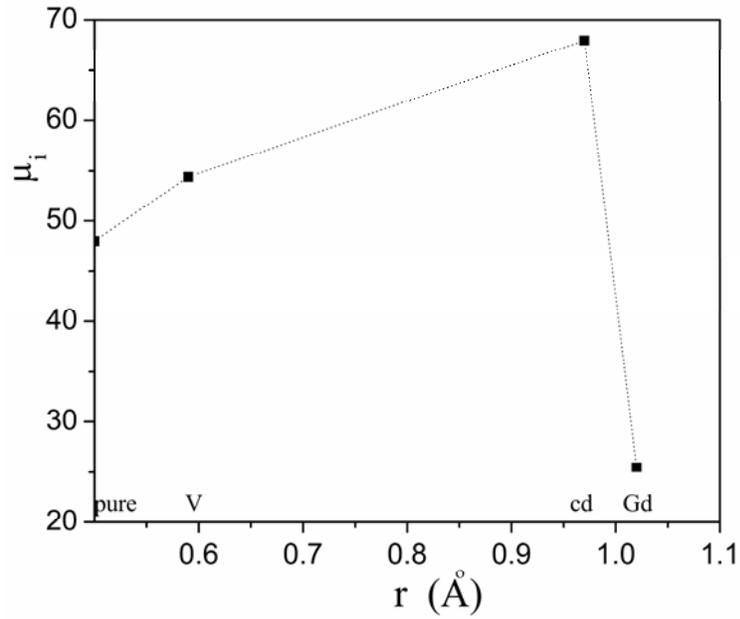
Sample	Tetra. sites				Octahedral sites			
	$\text{Fe}^{3+} - \text{O}$			$\text{Li}^{1+} - \text{O}$	$\text{Fe}^{3+} - \text{O}$		$\text{Fe}^{2+} - \text{O}$	
	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_5$	$\nu_6$	$\nu_7$	
$x = 0.0$	641	585	545	466	441	384	361	
$x = 0.02$	643	972	545	466	448	385	361	

Figure 2 shows the variation of the initial permeability,  $\mu_i$ , with temperature for all samples. The effect of substitution with  $\text{V}^{5+}$  and  $\text{Cd}^{2+}$  ions led to the increase of the initial permeability value relative to the pure sample, Li-ferrite. Meanwhile, the value of  $\mu_i$  decreased for Li-ferrite substituted with  $\text{Gd}^{3+}$  ions relative to the pure sample. At room temperature, the dependence of  $\mu_i$  on the ionic radii of the substitution ions was illustrated in Figure 3. This figure indicated the increase of the initial permeability with the increasing of the ionic radii of the

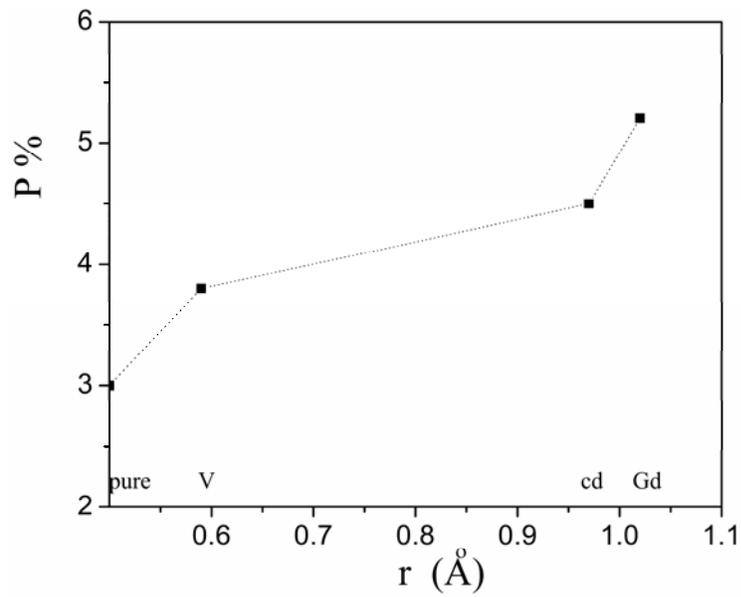
substituted ions until it reaches to  $\text{Cd}^{3+}$  ion, and then it decreases for the  $\text{Gd}^{3+}$  sample relative to the pure Li-ferrite. It is known that the initial permeability depends on the value of the saturation magnetization and the total number of pores [5]. It is reported that, the initial permeability increases with the decreasing of the percentage of pores and directly proportional to squaring the saturation magnetization [4]. But, the result of measuring the porosity, P%, showed that P% increased for all substituted samples relative to the pure sample, Figure 4. For all substituted samples P increased with the increasing of the ionic radii of the substituted ions. According to this contradiction, the porosity was not the main factor for increasing the initial permeability. Obviously, it was the main factor for decreasing the initial permeability for the Gd-substituted sample relative to the pure Li-ferrite.



**Figure 2.** The variation of the initial permeability with temperature for all samples.

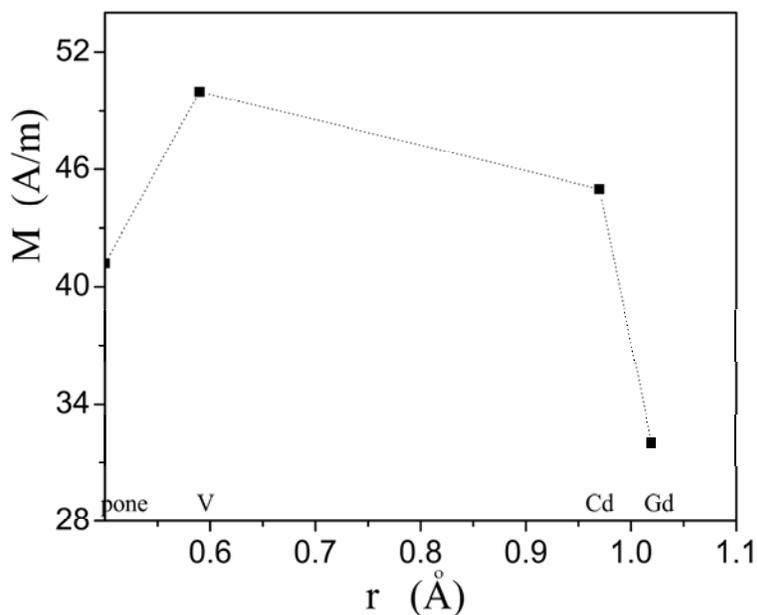


**Figure 3.** The dependence of the initial permeability on the ionic radii of the ions substituted Li-ferrite.



**Figure 4.** The variation of the porosity against the ionic radii of the substitute ions for Li-ferrite.

Meanwhile, the measurement of the magnetization against the applied magnetic field  $H$  (A/M) at room temperature was accounted on the increasing of the initial permeability for Cd and V substituted Li-ferrite relative to the pure sample. Figure 5 shows the dependence of the saturation magnetization on the ionic radii of the substituted ions for all substituted samples relative to pure Li-ferrite sample. One is clear that, the saturation magnetization was having the same behaviour against the variation of the ionic radii of the substituted ions, as the initial permeability for all substituted Li-ferrite samples except for Gd one, Figure 3. This means that the saturation magnetization increased for V and Cd substituted samples and decreased for Gd sample relative to the pure Li-ferrite. Then, the main factor for increasing the initial permeability with increasing the ionic radius of the substituted ions, was the increase of the magnetization for  $V^{5+}$  and  $Cd^{2+}$  substituted Li-ferrite. The decrease of the initial permeability for Gd substituted sample attributed to two factors, the decrease of the saturation magnetization and the increase of the porosity in it relative to the pure Li-ferrite sample.



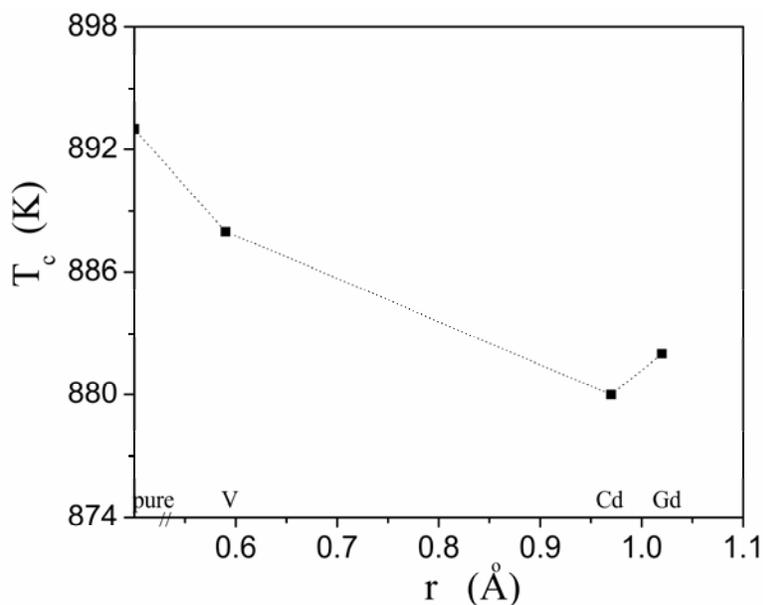
**Figure 5.** The dependence of the magnetization on the ionic radii of the ions substituted Li-ferrite.

The variation of the magnetization with increasing the ionic radius of the substituted ions, was discussed according to the cations distribution through A and B sites of the spinel Li-ferrite. It was reported that, for Li-ferrite of the chemical formula  $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ , all  $\text{Li}^{1+}$  ions occupied the octahedral sites [23]. In the case of the substituted samples, it is reported that Cd ions entered tetrahedral sites according to its electronic configuration, it is a non magnetic ion [7]. Li-ferrite substituted with vanadium ions was investigated by the infrared analysis. The result indicated that,  $\text{V}^{5+}$  ions occupied the tetrahedral sites, Table 1. Accordingly, some  $\text{Fe}^{3+}$  entered from tetrahedral sites into the octahedral one for the sample substituted with Cd and V ions. It is expected that vanadium ions occupied the tetrahedral sites because they have the same electronic configuration as  $\text{Cd}^{2+}$  ions. It is known that the net magnetic moment,  $m_{\text{total}}$ , for the spinel ferrites is the difference

between the net magnetic moment at the octahedral sites,  $m_o$ , and the tetrahedral one,  $m_t$ . Accordingly, the net magnetic moment increased more than that for the pure sample because the number of the magnetic moments is increased at the octahedral sites,  $m_{\text{total}} = m_o - m_t$ . This was account on the increasing of the magnetization for Cd and V substituted samples. The novel for this work is the increase of the magnetization and the initial permeability for Li-ferrite, when it was substituted with non magnetic ions, V or Cd with  $x = 0.02$ , relative to the pure Li-ferrite sample. This novel is important for the electronic industry. Meanwhile, for the Gd substituted sample, the Gd ions occupied the octahedral sites. As, the Gd ion has a magnetic moment greater than the  $\text{Fe}^{3+}$  one, the B-B magnetic interaction became comparable with the A-B super-exchange magnetic interaction. Thus, the collinear model in the case of the pure Li-ferrite sample changed into non collinear for Gd substituted sample at B-sites. In this case, the magnetization given by  $m_{\text{total}} = m_o \cos \theta_{YK} - m_t$ , where  $\theta_{YK}$  is Yafet-Kittel angel [21]. This result explained the decrease of the magnetization for Gd substituted Li-ferrite relative to the pure one.

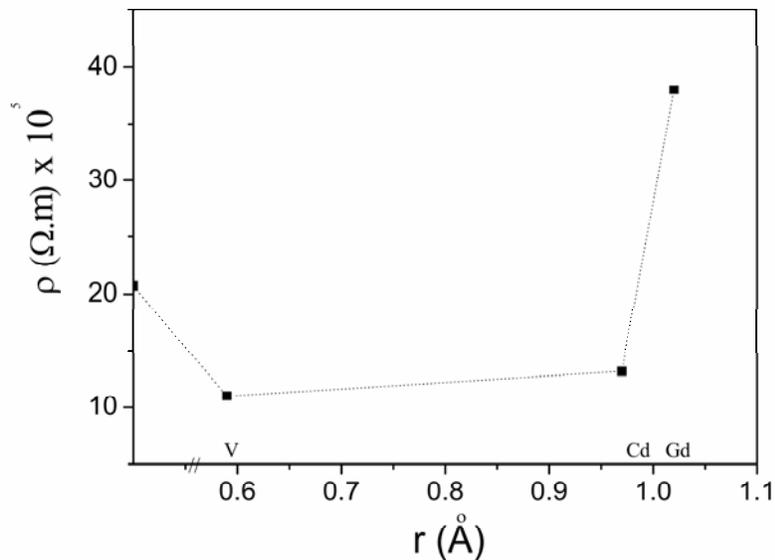
The values of Curie temperature for all investigated samples were determined by extrapolating the linear part of the initial permeability against the temperature after its highest value, and then its sudden drop. This highest value corresponds to zero anisotropy constant. Figure 6 shows the dependence of the determined Curie temperature values,  $T_c$ , on the ionic radii of all samples. It was noticed that  $T_c$  decreased for all substituted samples relative to the un-substituted one. But, the  $\text{V}^{5+}$  substituted sample had the greatest  $T_c$  value relative to Gd and Cd substituted samples. The decrease behaviour attributed to the decrease of  $\text{Fe}^{3+}$  ions at the tetrahedral sites for Cd and V substituted samples. Then, the relative concentration of the moments at A-and B-sites was decreased ( $N_A / N_B$ ). This led to the weakness of the A-B magnetic interaction and accordingly accounted on the decrease of the Curie temperature. For Gd sample,  $N_B$  was greater than that for other

substituted samples because Gd ions occupied B-sites. Then, there was no  $\text{Fe}^{3+}$  ions migrated from A-to B-sites as in other substituted samples. Accordingly, this led to the weakness of the A-B magnetic interaction. This accounted on the decrease of  $T_c$  value for Gd substituted sample relative to the Li-ferrite sample. Furthermore, the decreased Curie temperature value attributed to the increase of lattice parameter for Gd and Cd substituted samples relative to the pure sample. So, there was another decrease of A-B magnetic interaction. But, the decrease of lattice parameter for V substituted Li-ferrite must led A-B interaction to increase. Accordingly, the decrease of the Curie temperature for V substituted Li-ferrite, was dominant by the effect of  $N_A / N_B$  over the increase of lattice parameter. Accordingly, this accounted on the bigger value of Curie temperature of V substituted sample than that of other substituted ones, due to the effect of its small lattice parameter, which compensated some decrease of the Curie temperature.



**Figure 6.** The variation of the Curie against the ionic radii of the substitute ions for Li-ferrite.

The dependence of the dc electrical resistivity on the ionic radii of the substituted ions for Li-ferrite, at room temperature, is shown in Figure 7. The electrical resistivity,  $\rho$ , was increased for Gd substituted sample and decreased for the V and Cd samples relative to the pure Li-ferrite one. The increase of the electrical resistivity for Gd substituted Li-ferrite sample attributed to the increase of the total porosity, Figure 4. It is reported that, the increase of the inter or intra granular pores was directly proportional to the electrical resistivity [15]. The increase of the porosity hindered the hopping of the charge carriers, and this caused the resistivity to increase. Furthermore, the preference of the Gd ions to occupy B-sites hindered the hopping of the charge carriers between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . These two main factors accounted on the increase of the electrical resistivity for Gd substituted Li-ferrite sample. This result is a novel for Gd substituted Li-ferrite to be used for communication applications at high frequency range. In case of V and Cd substituted Li-ferrite samples,  $\text{V}^{5+}$  and  $\text{Cd}^{2+}$  ions preferred the A-sites leading some  $\text{Fe}^{3+}$  ions to migrate from A-sites to B-sites. This migration was accompanied by the increase of the formation of  $\text{Fe}^{2+}$  ions in B-sites [8]. Accordingly, the probability of hopping between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions was increased for these samples. This factor accounted on the decrease of the electrical resistivity for these samples. This means that, the production of  $\text{Fe}^{2+}$  ions dominants the increase of the porosity factor, Figure 4. Similar result was reported for calcium substituted Li-Zn ferrite [17].



**Figure 7.** The dependence of the electrical resistivity on the ionic radii of the ions substituted Li-ferrite.

#### 4. Conclusion

The substitution effect of Li-ferrite with  $V^{5+}$ ,  $Cd^{2+}$ , and  $Gd^{3+}$ , with  $x = 0.02$ , led to

- (1) The lattice parameter was increased for  $Gd^{3+}$  and  $Cd^{2+}$  substituted Li-ferrites, and was decreased for  $V^{5+}$  substituted sample.
- (2) The porosity was increased for all substituted samples relative to the pure Li-ferrite.
- (3) The magnetization was increased for  $V^{5+}$  and  $Cd^{2+}$  substituted Li-ferrites, and decreased for Gd substituted Li-ferrite sample. This result was explained according to the cations distribution among A and B-sites of the spinel ferrite.

(4) The initial permeability was increased for  $V^{5+}$  and  $Cd^{2+}$  substituted Li-ferrites due to the increase of the saturation magnetization, and decreased for Gd-substituted Li-ferrite due to the increase of the porosity.

(5) The dc electrical resistivity was increased for Gd substituted Li-ferrite sample due to the increase of the porosity, and decreased for other substituted samples due to the increase of the number of  $Fe^{2+}$  at B-sites.

The novel points for this work: The increase of the initial permeability and the magnetization for  $V^{5+}$  and  $Cd^{2+}$  substituted Li-ferrites, which are important parameters for electronic applications. Also, the increase of the electrical resistivity for Gd ions substituted Li-ferrites, which plays an important parameters for applications at high frequencies.

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