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A study of some properties for substituted Li –ferrite using Positron annihilation lifetime

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ABSTRACT

Positron annihilation lifetime spectroscopy (PALS) at room temperature is used to investigate polycrystalline substituted Li-ferrite samples. The dry standard ceramic technique is used to prepare all investigated samples. The variation of positron annihilation parameters I_1 %, I_2 %, τ_1, and τ_2 are demonstrated with porosity and the initial permeability against the ionic radii of substituted ions for Li ferrite samples. The correlation between I_2, τ_2 with r (Å), has opposite behavior with the ionic radii of the substituted ions. Whereas the correlation between I_1 and τ_1; has nearly the same behavior with the ionic radii of the substituted ions except for V and Gd samples. There is mostly a direct correlation between the electrical resistivity and I_2 values except for Sm sample with increasing the ionic radii of substituted ions. The initial permeability is increased with the ionic radii of the substituted ions. Li-ferrite with substitution 2 % grow slower than that substituted with 1 % under the same preparation condition. There is a correlation between the lifetime of the positrons and the hopping of the electrons at the octahedral sites (B-sites).

Keywords: Li-ferrite, porosity, electrical resistivity, PAL.

1. INTRODUCTION

The positron annihilation lifetime spectroscopy (PALS) has been proved to be useful in providing information about electron density, defect and phase transition of condensed matters, including high-T_C superconductors, semiconductors, alloys and

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ceramics [Hautojarvi 1995]. Due to the well-known sensitivity of positrons towards local electron density changes, PALS is especially suited for the study of open volume defects and microstructural features in solids. From the decomposition of the lifetime spectra, different positron annihilation states can be obtained and correlated with structural open volume defects in metals, semiconductors [Somoza 2001], and alloys [Misheva 2000], as well as ceramics [Guo 1995, Fradin 2001, Guo 1995, Sanjukta 2004]. A positron implanted in this type of materials can have different lifetimes depends on the electron density at the annihilation site. In the bulk of the material, the positron will have free annihilation with an electron. While in the presence of defects, like vacancies, vacancy-clusters and voids (or microvoids), the electron density experienced by positron is reduced leading to increase in its lifetime. Thus, information about the size, type and relative concentration of various defects can be given by positron lifetime spectroscopy.

Ferrites have been used as inductor cores at high frequencies range because they have high resistivity compared with metallic cores. Also, one of the important properties of magnetic materials is the initial permeability. In general, these two properties depend on the compositions and on the microstructure of ferrites, as well [Samy 2010, El-sayed 2004, Sattar 2007]. In this work we concentrated on the distribution of pores at different sites of substituted Li –ferrite samples, and its effect on the electrical resistivity as an electrical parameter, and the initial permeability as a magnetic one. By using positron annihilation spectroscopy (PAS), it is possible to obtain meaningful characteristic for the distribution of pore defects for polycrystalline substituted Li ferrite samples. These defects play a dominant role in physical properties of ferrites. So, we analyze the annihilation parameters for positrons that trapped at grain boundaries and pores (nanoscal defects) and investigate the effect of substitution with ions of different radii and different concentrations (1 % and 2 %) on these parameters. These ions are reported to be distributed at A-sites (tetrahedral sites) for V, Cd and Nb ions, and at B-sites (octahedral sites) for Gd and Sm ions of spinel ferrites [El-sayed 2004, Samy 2011, Smit 1959, Mazen 1992, Standely 1972, Kolekar 1994].

2. EXPERIMENTAL TECHNIQUES

Positron lifetime measurements were carried out at room temperature using a 11 μCi ^{22}Na source sealed between two kapton foils (thickness less than 1 mg/cm^2) with a small active diameter of l-2 mm in sandwich geometry with the pellets and a standard fast-fast coincidence lifetime spectrometer. Two identical plastic scintillator detectors fitted with Hamamatsu photomultiplier tubes [H3378-50] NO. BA0828 with a prompt resolution of about 250 ps (full width at half-maximum, FWHM) was used in the present study. With a channel constant of 6.5 ps, lifetime spectra were recorded for each sample with about 5 X 10^6 counts accumulated under the peak. After source correction was determined using a properly defect free Silicon sample, the lifetime spectra were analyzed in two components trapping model using the computer program LT [Kansy 1996]. The fitted lifetime τ_1 and τ_2 are of the order of a few hundred ps. The respective intensities I_1 and I_2 (with $I_1 = I - I_2$) indicate the relative number of positrons that annihilate with different annihilation processes. On the basis of the two-state trapping model [Hautojarvi 1979], the shorter-lifetime component τ_1 and its intensity I_1 belonged to positrons annihilating in the matrix and dislocation loops , τ_2 and I_2 characterizing the annihilation of positrons trapped in vacancy clusters and three-dimensional monovacancies defects.

Li-ferrite of the chemical formula $Li_{0.5}Fe_{2.5}O_4$ was substituted by V, Nb, Cd, Gd and Sm ions instead of iron which have different ionic radii. Cadmium, Niobium and vanadium ions are non magnetic, but Gadolinium and Samarium ions are magnetic ones. The chemical formulas that were used: $Li_{0.5+x}Fe_{2.5-2x}M_xO_4$, $Li_{0.5+3x}Fe_{2.5-2x}R_xO_4$ and $Li_{0.5+2x}Fe_{2.5-(4/3)x}Cd_xO_4$ [x = 0.01 & 0.02; M = V or Nb and R = Gd or Sm]. The polycrystalline samples were prepared by a dry standard ceramic method. The oxides of each sample were weighted according to their molecular weights and then mixed and blended together to a fine powder. The powders are heated (pre-sintered) and grind until fine particle sizes were obtained, then pressed into discs form and heated again (final sintering), and then slowly cooled to room temperature. More details are reported in ref. [Samy 2011]. The X-ray analysis indicated the formation of one single spinel phase for all samples, diffractometer type X"Pert Graphics & Identiy with CuK_α radiation was used. The theoretical x-ray density d_x is calculated. The percentage of the total porosity was calculated using the following equation $P = 100[1-(d/d_x)]$. The density of the sample d is calculated according to Archimed's principle method. For ceramic samples, the total porosity is equal to the sum of intergranular pores and intragranular ones [Kigery 1996]. More details for measurements of the initial permeability and the electrical resistivity are reported in ref. [Samy 2011].

3. RESULTS AND DISCUSSION

3. 1 Substitution with 2 % concentration for Li ferrite

Fig.1 shows the variation of the relative intensity I_2, and the lifetime τ_2 with the ionic radii of the substituted ions for Li-ferrite samples. It is noticed that I_2 mostly increases with the ionic radii of the substitution ions, and then decreases for Sm Li-ferrite sample. This defect is the sum of nanoscal grain boundaries thickness and intergranular pores. This means the increase of the grain boundaries defect and intergranular pores concentration with the increasing of the ionic radii of substituted ions. The slight increase in I_2 for V sample relative to Nb ones could attribute to the smaller ionic radius of V^{5+} than that for $Fe^{3+}$and Nb^{5+}, r (V^{5+}) = 0.59 Å, r(Fe^{3+}) = 0.63 Å and r (Nb^{5+}) = 0.69 Å. This result might indicate that the grain size for V sample is smaller than that for Nb sample. Dng et al. [Dong 1991] reported that when the grain size is decreased the thickness of the grain boundaries is increased. Meanwhile, an opposite (reverse) behavior appears for τ_2 values. This behavior of τ_2 indicates that small ionic radii of substituted ions (same concentration) permit the positron to reside at defect sites with longer lifetime.

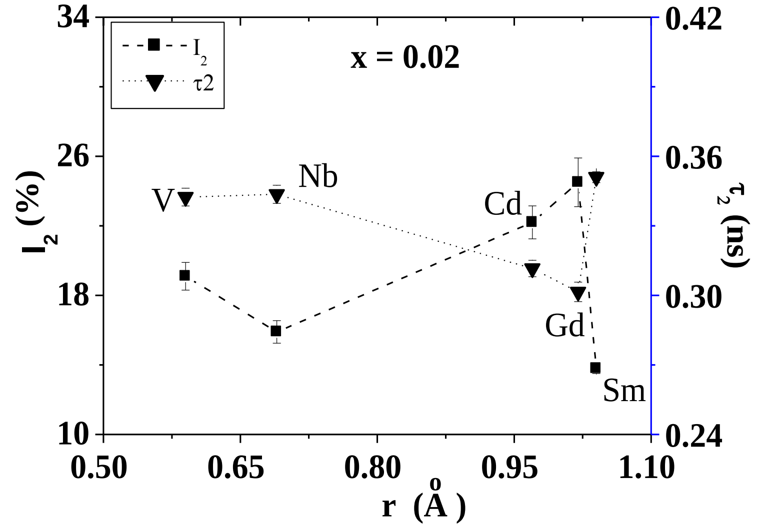

Fig. 1 The variation of relative intensity I_2 and the lifetime τ_2 with the ionic radii of the ions substituted Li-ferrite.

The exception for Sm-sample might be due to the formation of SmO_2 during the preparation condition. The dissociation of SmO_2 leads to the formation of vacancies inside the grains [Samy 2003], this causes the concentration of Sm Ions to be less than 0.02 [Samy 2006, Samy 2010].

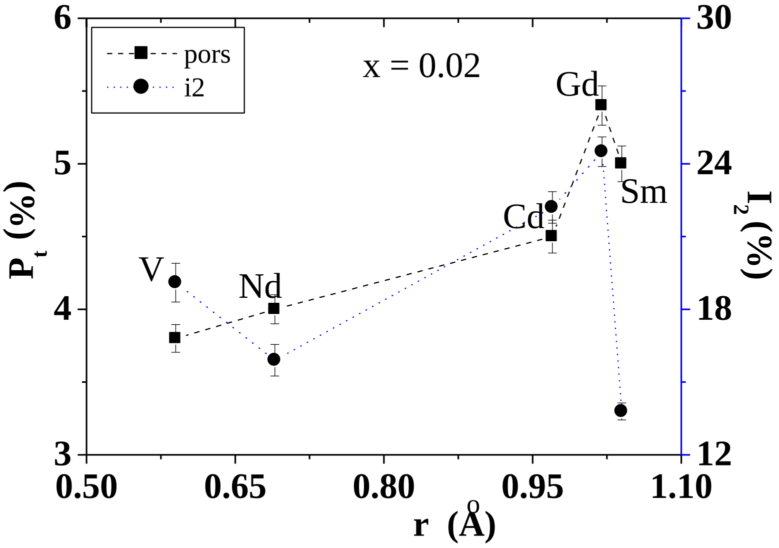

Fig.2. Variation of the total porosity and I_2 % as a function of the ionic radii of the substituted ion.

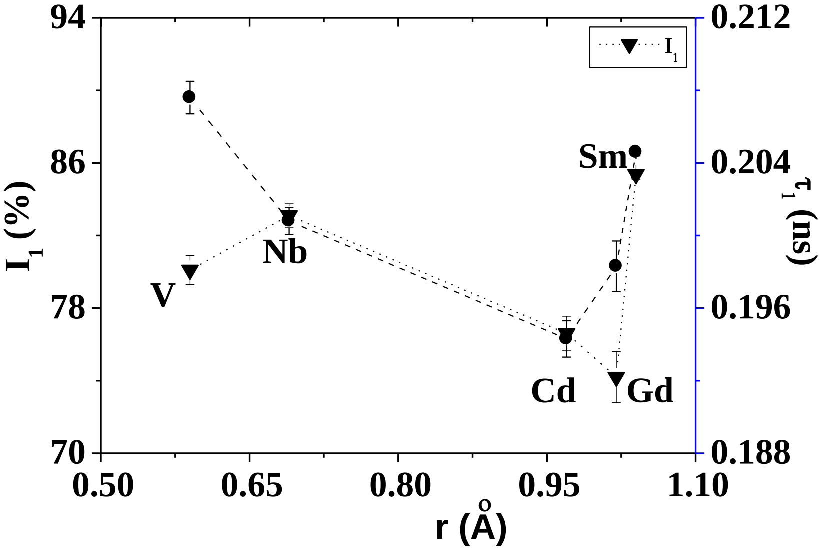

Fig.3. Dependence of the relative intensity I_1 and lifetime τ_1 with the ionic radii of the substituted ions.

Similar result was reported for substituted Cu-Zn ferrite [Samy 2010]. This accounts on the decrease of I_2 for Sm sample relative to the Gd one. According to this conclusion, I_1 value for Sm sample might be affected by the formation of these defects inside the grains. It means the increase of I_1 which is conformed Fig. 3. To account on this point, one might take into consideration the experimental variation of total porosity P_t and I_2 with the ionic radii of the substituted ions Fig. 2. From the experimental results, there is a correlation between the total percentage of porosity P_t and the relative intensity I_2 % as a function of the ionic radii of the substituted ions (magnetic or non magnetic ions). There is an increase of porosity with the increase of the ionic radii, but decreases for Sm sample due to the decrease in the concentration of Sm ions inside the bulk sample. This could be one factor for the decrease of I_2 for Sm sample Fig. 1, and consequently the decrease of intergranular pores Fig. 2. Since, I_1 mostly decreases with increasing the ionic radii of the substituted ions except for Sm sample Fig. 3. Then one can consider that I_1 mostly results from the intragranular pores and dominants the crystallographic defects inside the bulk sample. Meanwhile, as the concentration of I_1 decreases the lifetime τ_1 of positron to reside at intragranular pores is decreased Fig. 3. This behavior mainly attributes to the increase in the hopping of the electrons with decreasing the intragranular pores in case of ferrites. This decreases the lifetime of the positron inside the grains. Furthermore, Gd and Sm ions have large ionic radii and prefer to reside at octahedral sites, B-sites for Gd and Sm samples [Kolekar 1994, Rezlescu 1994]. This leads to decrease the hopping of the electrons at B-sites of the ferrite samples which causes to increase τ_1. This permits the positron to reside at defects inside the bulk with longer lifetime for these samples relative to the other samples. Accordingly, there is a correlation between the lifetime of the positrons and the hopping of the electrons for substituted Li-ferrite.

Another correlation appears between the electrical resistivity and the relative intensity I_2 as a function of the ionic radii of the substitution ions Fig. 4. The electrical resistivity ρ and I_2 % mostly increase with increasing the ionic radii of the substituted ions except for Sm sample. This means, as the defects of grain boundaries thickness and intergranular pores increase, there is an increase in the resistivity. Furthermore, the total porosity takes the same behavior as I_2 Fig. 2. One might consider that the intergranular pores increase with the increase of the ionic radii of the substituted ions and dominant the grain boundaries thickness. For Sm sample, I_2 decreases relative to its value in Gd sample which accounts on the decrease of ρ. This means that there is an increase of the intragranulare pores for Sm sample and is conformed experimentally, Fig. 3. For V sample, although I_2 is slightly greater than that for Nb sample, ρ is smaller for V sample than that for Nb one. Accordingly, the effect of intragranular pores is dominant the effect of grain boundaries thickness and accounts on the smallest value of ρ for V sample than that for Nb one.

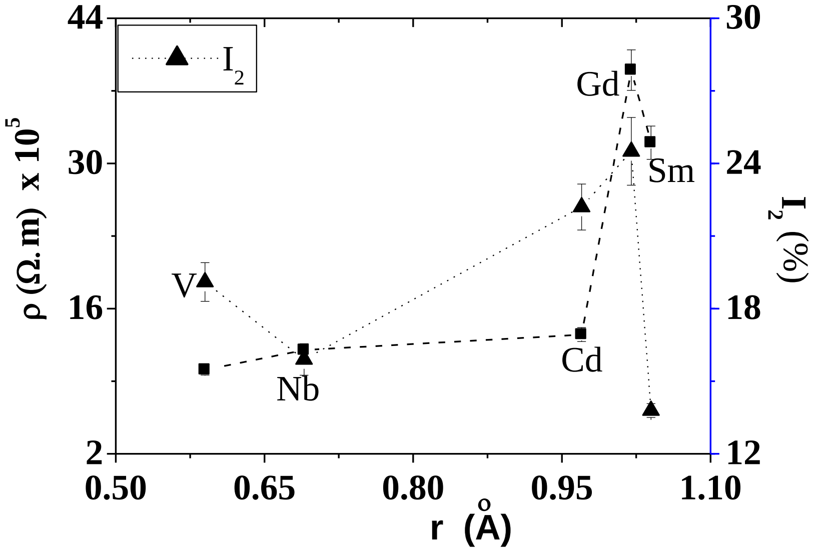

Fig. 4 Variation of the electrical resistivity ρ and I_2 % against the ionic radii of the substitute ions for Li-ferrite.

Fig.4 indicates that Gd-sample has the highest I_2 or intergranular pores. This conform the reported improvement of the electrical resistivity for Gd – sample [Samy 2011]. But, in this work the conclusion is concentrated on the intergranular pores content. Accordingly, positron annihilation parameters help to concentrate the discussion of the electrical resistivity on intergranular pores as a dominant parameter for the increase of the electrical resistivity. The increase of the electrical resistivity has important application at high frequencies ranges.

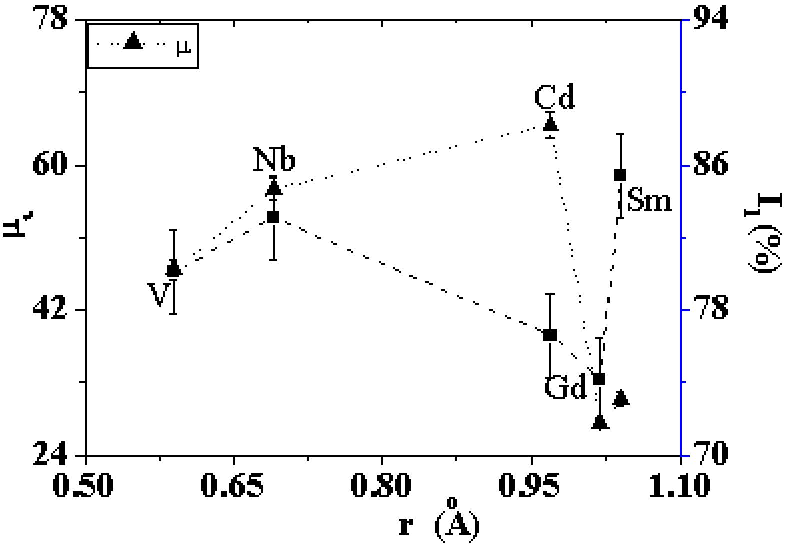

Fig. 5 The dependence of the initial permeability μ_i and I_1 on the ionic radii of the ions substituted Li-ferrite

Fig. 5 shows the dependence of the initial permeability μ_i at room temperature and I_1 on the ionic radii of the substituted ions. The increase in μ_i attributes to the decrease of intragranular pores which is associated to I_1 inside the bulk, Fig. 5 except for Gd-Li sample and Sm –Li one. To account on the decrease of μ_i for Gd-Li sample, we must take into consideration the distribution of intragranular pores inside bulk ferrite. It is known that the initial permeability results from reversible motion of domain walls under the effect of very small applied magnetic field, and the rotation of spins inside the domains (negligible) [Jain 1976]. So, as μ_i for Gd-sample is very small although it has small intragranular pores concentration compared to the other samples. One might consider these pores are concentrated at the walls of the domains. This makes the motion of domain walls harder inside the grains and accounts on the very small initial permeability value for Gd sample relative to the other samples. From another point of view, it is reported that the saturation magnetization M_s decreases with increasing the ionic radii of the substituted ions for Li-ferrite [Samy 2011]. The decrease of μ_i could be explained according to Globous relation, $\mu_i \alpha (M_s)^2$ [Jain 1976], accordingly the decrease of the initial permeability μ_i is mostly dominated by the decrease of the saturation magnetization value for Gd-Li sample which overcomes the decrease of the intragranular porosity. But, the decrease in the initial permeability for Sm-Li-sample attribute to the increase of vacancies as mentioned before. This accounts on the increase in its intensity value I_1 Fig. 5 and consequently explain the decrease of μ_i for Sm-Li sample. Meanwhile, the increase of μ_i for all other samples indicates that the dominant factor is the decrease of intragranular pores which overcome the magnetization effect inside domains of the crystalline sample. So, there is a correlation between the initial permeability and the relative intensity I_1, in other words intragranular pores. It is reported that the initial permeability decreases with increasing the total pores P_t for most of poublished papers [El-sayed 2004, Sattar 2007, Samy 2011]. An important point obtained by positron annihilation analysis for ferrites is the dependence of the initial permeability on the intragranular pores rather than the considering of the total pores, although it is a qualitative consideration. This novel point is very important to studying the properties of ferrites to know qualitively the distribution of pores inside and outside the grains and the distribution of intragranular pores inside domains and at the walls of them.

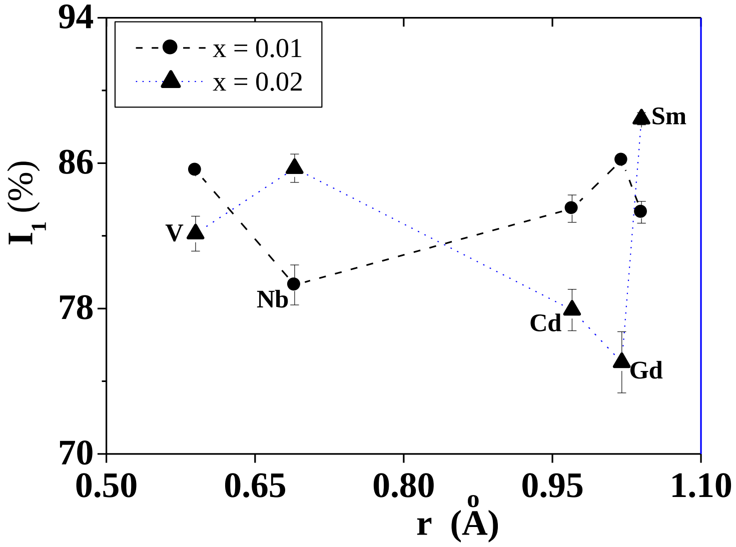

Fig. 6. Dependence of the relative intensity I_1 with the ionic radii for x = 1 % and 2 %

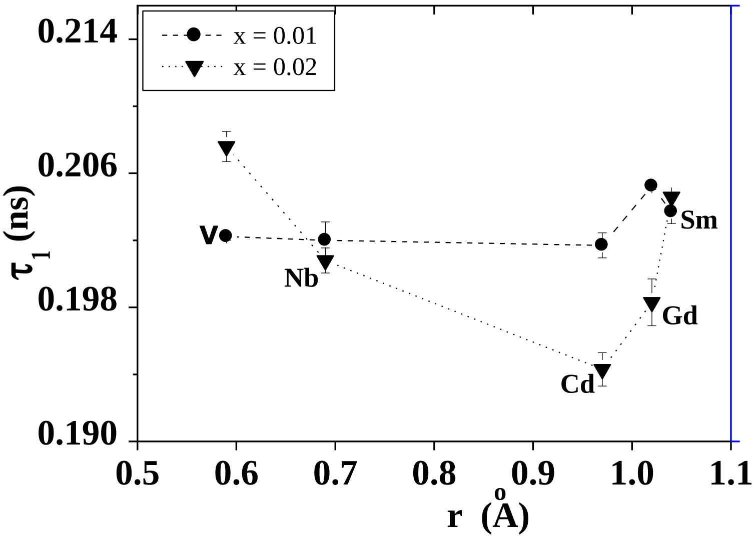

Fig. 7. Variation of lifetime τ_1 with the ionic radii for x = 1 % and 2 %

3.2 Substitution with 1% for Li ferrite

The dependence of the relative intensity I_1 with the ionic radii for Li ferrite samples with substitution 1 % is in opposite behavior relative to these samples with 2 % substitutions Fig. 6. So, for samples with substitution 1 %, the intragranular defects increase with the ionic radii which cause the un-homogeneity for these samples. This behavior can not be explained according to the cations distribution between A- sites and B-sites of the crystalline structure of spinel ferrite. This reverse behavior relative to that obtained for 2 % samples may attribute to the growth of the samples. Samples with substitution 2 % grow slower than the samples which are substituted with 1 % under the same preparation condition. Another factor for the un-homogeneity for 1 % substituted samples the formation of Fe^{2+} ions. It is reported that Fe^{2+} ions are formed during the preparation condition of ferrites [Samy 2010]. The concentration of these ions could be greater for samples substituted with 1 % than that substituted with 2 %. Although, I_1 and τ_1 have nearly the same behavior but reversed for both substitution x = 1 % and 2 %, they still have the same consideration, Fig. 6 and Fig. 7. The lifetime of positron increases with increasing the concentration of intragranular defects inside the samples due to the decrease of the hopping of the electrons.

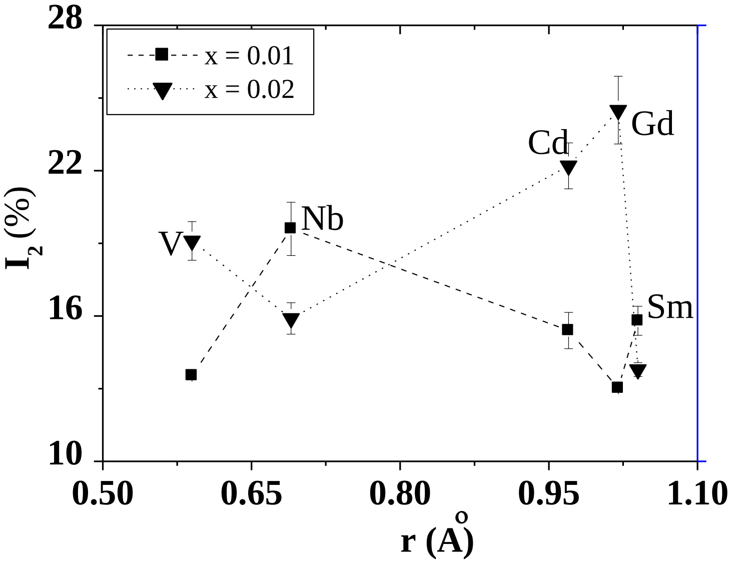

Fig. 8. Variation of the relative intensity I_2 with the ionic radii for x = 1 % and 2%

Furthermore, the slow growth of the samples substituted with 2 % relative to that with 1%, conform the reverse behavior of I_2 values, Fig. 8. Also, the lifetime of the positrons at grain boundaries “τ_2” is reversed for substituted samples with 1 % relative to that with 2 % concentration Fig. 9. So, τ_2 and I_2 still have the physical meaning, with decreasing defects concentration at grain boundaries the positrons reside with longer lifetime Fig. 8 and Fig. 9.

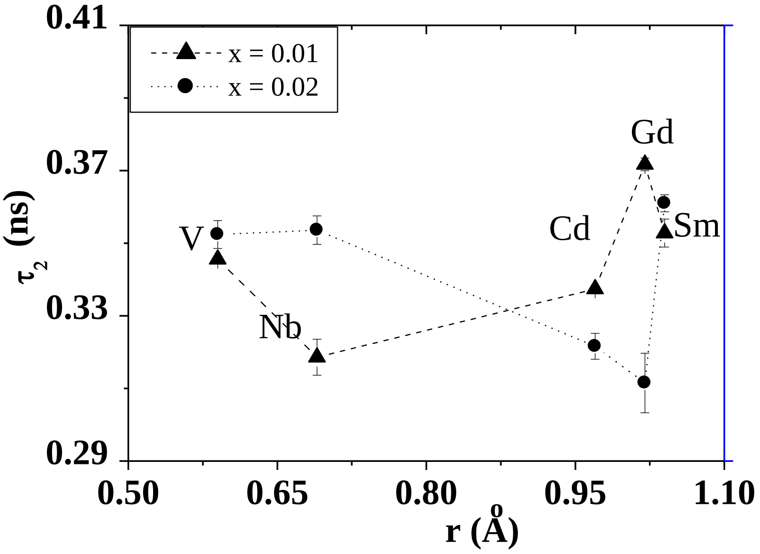

Fig. 9. Dependence of the lifetime τ_1 with the ionic radii for x = 1 % and 2 %

Similar behavior was reported for Substituted Mn-Zn-ferrite [Samy 2006]. Then the variation in grain growth of ferrite samples due to the change in the concentration of substitution ions affect on the lifetime parameters result from the positron annihilation lifetime technique.

4. CONCLUSIONS

For Li ferrite samples substituted with 2 % ions concentration:

1) The defect concentration is increased at grain boundaries with increasing the ionic radii of substituted ions. The exception for Sm ferrite sample is due to the formation of SmO_2 inside the bulk.
2) For V-Li-sample the increase of I_2 relative to the Nb sample is attributed to its smaller grain size.
3) I_1 is mostly decreased with increasing the ionic radii of substituted ions due to the dominated effect of intragranular porosity except for Sm – Li sample
4) The electrical resistivity is increased with increasing the ionic radii due to the increase of the intergranular porosity.
5) The initial permeability is increased with the ionic radii due to the decrease of intragranular porosity except for Gd-sample and Sm one. These exceptions attributed to the concentration of intragranular pores at the walls of the domains for Gd –sample and the formation of vacancies in the bulk for Sm sample.

Li ferrite with substitution 2 % grow slower than that substituted with 1 % under the same preparation condition. In general, Lifetime τ_1 is increased with intragranular porosity due to the decrease of the hopping electrons at B-sites in bulk sample. (PAS) is a good technique that helps to know a qualitative distribution of intragranular and intergranular pores. Also, gives a qualitative distribution of intragranular pores at the walls of the domains and inside them.

The novels of this work for substituted Li ferrite are:

1) The correlations between the lifetime of positrons and the hopping of the electrons at B- sites.
2) The correlation between the initial permeability and relative intensity I_1.
3) The variation in grain growth due to the change of concentration of the substituted ions that affects on lifetime parameters for Li ferrite.

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