A study of some properties for substituted Li-ferrite using positron annihilation lifetime technique

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ABSTRACT

Positron annihilation lifetime spectroscopy (PALS) is used to investigate polycrystalline substituted Li-ferrite samples. The dray ceramic technique was used to prepare all investigated samples. The variation of positron annihilation parameters $I_1\%$, $I_2\%$, τ_1, and τ_2 has been demonstrated with porosity and the initial permeability against the ionic radii of substituted ions for Li ferrite. The grain size (G.S.) increased with increasing the ionic radii of the substituted ions for Li-ferrite. The correlation between I_2 and τ_2 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.

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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 ceramics [1]. Due to the well-known sensitivity of positrons toward 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 and semiconductors [2], alloys [3], as well as ceramics [4–7]. A positron implanted in this type of materials can have different lifetimes depending 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 at grain boundaries. Thus, information about the size, type and relative concentration of various defects/vacancies can be given by a positron lifetime spectroscopy.

Ferrites have been used as inductor cores at high frequencies 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 [8–10]. In this work we concentrated on the distribution of pores at different sites of substituted Li-ferrite, and its effect on the electrical resistivity as an electrical parameter, and the initial permeability as magnetic parameter. By using positron annihilation spectroscopy (PAS), it is possible to obtain meaningful characteristic for the distribution of pore defects for polycrystalline substituted Li ferrite. 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 (nanoscale defects) and investigate the effect of substitution with ions of different radii and concentration (1% and 2% concentration) 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 [9,11–15].

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

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study. With a channel constant of 6.5 ps, lifetime spectra were recorded for each sample with about 5×10^6 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 [16] with the best fit $\chi^2 < 1.1$. The two lifetime components 382 ps/11% and 1500 ps/0.7%, which were attributed to annihilation in kapton and at the surfaces, were kept fixed during the analysis. The measured PAL spectrum analyzed as two lifetime components τ_1 and τ_2, order of a few hundred picoseconds, which have relative intensities I_1 and I_2. The respective intensities indicate the relative number of positrons that annihilate with different annihilation processes. On the basis of the two-state trapping model [17], the shorter-lived component τ_1 and 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 monovacancy defects. The positron lifetime reflects the geometrical three dimensional opened volume in a defect at grain boundaries. A lifetime value of about 300 ps corresponding to small voids (monovacancies) and about 500 ps corresponding to vacancy clusters.

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 $Li_{0.5+2x}Fe_{2.5-(4/3)x}Cd_xO_4$ [$x = 0.01$ and 0.02; M = V or Nb and R = Gd or Sm]. The polycrystalline samples were prepared by a dray 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. [11]. The X-ray analysis indicated the formation of one single spinel phase, diffractometer type X"Pert Graphics & Identified with CuK_α radiation. 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 [18]. Scanning electron microscope (SEM), type JEOL JEM 1200 EXII, used to investigate the microstructure of Li-ferrite samples substituted with 2% ions. Drawing random lines are being made on the obtained photographs and counting the number of grain boundaries, n. Then the grain size, G.S. (μm) was calculated by dividing the length of the line over n. More details for measurements of the initial permeability and the electrical resistivity are reported in Ref. [11].

3. Results and discussion

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. 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 nanoscale grain boundaries thickness and intergranular pores. (Table 1) indicates the increase of the average grain size with increasing the ionic radii of substituted ions. Similar result was reported for Mn–Zn ferrite [19].

Accordingly, these mean the increase of the grain boundaries defect and intergranular pores concentration with the increasing of the ionic radius of substituted ions. The slight increase in I_2 for V sample relative to Nb ones could attribute to the smaller
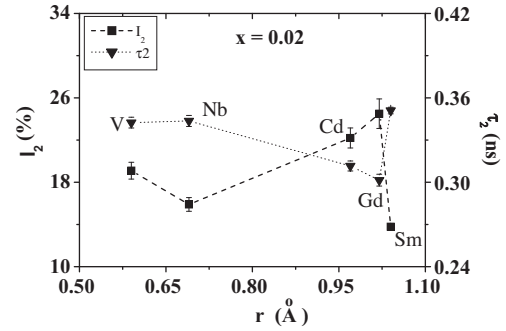

Fig. 1. The variation of relative intensity I_2 and the lifetime τ_2 with the ionic radii of the ions substituted Li-ferrite.

Table 1
Relation between the ionic radii of the substituted ions and the G.S. for Li-ferrite.

Ions	R(Å)	G.S. (μm)
V	0.59	1.45
Nb	0.69	2.1
Cd	0.98	3.81
Gd	1.02	5.32
Sm	1.04	5.51

ionic radius of V^{5+} than that for Fe^{3+}, $r(V^{5+}) = 0.59$ Å and $r(Fe^{3+}) = 0.63$ Å. Furthermore, V sample has smaller (G.S.) than that for Nb one. Dong et al. [20] reported that when the grain size is decreased the thickness of the grain boundaries is increased. The relative intensity I_1 might decrease for V-sample relative to Nb-one. Meanwhile, an opposite (reverse) behavior appears for τ_2 values. This behavior of τ_2 indicates that the small ionic radii of substituted ions (same concentration) permit the positron to reside at defect sites with longer life time. 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 [21], this causes the concentration of Sm ions to be less than 0.02 [19,22]. These 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. 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
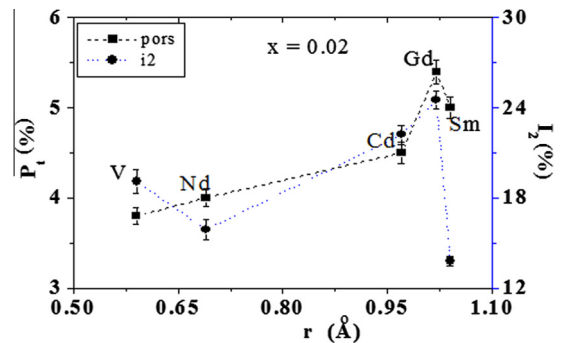

Fig. 2. Variation of the total porosity and I_2% as a function of the ionic radii of the substituted ions.