

Positron Annihilation Spectroscopic Studies of Sr-substituted Lanthanum Ferrite ($La_{1-x}Sr_xFeO_3$)

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Abstract. Lanthanum Ferrite is a perovskite ferromagnetic insulator with wide areas of applications such as electrode material in solid oxide fuel cells, gas sensors and in high temperature atmospheric studies. However, achieving cent percent success of substitution is always a challenge. Incomplete substitution can result in a high concentration of structural defects like of Lanthanum by Strontium. The effects of vacancies on different physical properties have been investigated by different types of probes which unfortunately have not been able to yield conclusive results. Positron annihilation spectroscopy (PAS) is a well established spectroscopic probe to investigate defects. Its success in the investigation of defects and defect-related processes in a variety of solids has enriched the subject of solid state physics. Over the years, it has been recognized as the most sensitive and reliable among analytical probes that provide information on defects. In the present work, this technique has been used to extract information on the effects of substitution of *La* by *Sr* ions in $LaFeO_3$. The results are discussed in detail.

Keywords: Ferrites, Defects, Positron annihilation.

1. INTRODUCTION

1.1 Positron Lifetime Measurement

Positron being an antiparticle of electron, its lifetime and stability are very short. Whenever it comes in contact with an electron, it gets annihilated. The processes involved during the annihilation are discussed below.

The process starts with the decay of the radioactive sources like the one used in this work Na^{22} isotope emitting a positron and the daughter nucleus (Na^{22} , in this case) transiting from its excitation level to the ground state with the prompt emission of the difference in energy (1.276 MeV, in this case) as a gamma ray. This gamma ray serves as the birth signal of the positron. There is an emission of two gamma rays after the annihilation of the positron with energy 0.511 MeV each, either of which serves as the death signal of the positron. The time interval between these two signals is called the lifetime of the positron.

The annihilation of positrons is directly related to the density of electrons at the site of annihilation.

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The decay rate of positron is given by [1]

$$\lambda = \pi r_0^2 c \zeta n_e \quad (1)$$

where r_0 is the classical electron radius, c the velocity of light and ζ is the enhancement factor which accounts for the local increase in the density of electrons (n_e) due to Coulomb attraction by the positron. The equation determining ζ is given as

$$\zeta = 1 + 1.23r + 0.8295r^{\frac{3}{2}} - 1.26r^2 + 0.3826r^{\frac{5}{2}} + 0.167r^3 \quad (2)$$

where r is the radius of a sphere whose volume equals the average volume per conduction electron of the solid. Also, $\lambda = \frac{1}{\tau}$ where τ is the positron lifetime.

In solid containing defects, the annihilation of positrons is governed by the following rate equations.

$$\frac{dn_b}{dt} = -\lambda_b n_b - \kappa_d n_b \quad (3)$$

$$\frac{dn_d}{dt} = -\lambda_d n_d + \kappa_d n_b \quad (4)$$

where n_b is the number of positrons in the bulk n_d is the number of positrons in the defects at any instant of time t and κ_d is the rate of trapping of positrons from the bulk into the defects.

The above two equations are solved to give positron lifetime spectrum as

$$N(t) = n_b + n_d = I_1 \exp\left(\frac{-t}{\tau_1}\right) + I_2 \exp\left(\frac{-t}{\tau_2}\right) \quad (5)$$

where, for simplicity we define the following relations between the various useful physical parameters.

$$I_1 = \frac{\lambda_b - \lambda_d}{\lambda_b - \lambda_d + \kappa_d} \quad (6)$$

$$I_2 = \frac{\kappa_d}{\lambda_b - \lambda_d + \kappa_d}$$

Further it can be shown that $\tau_1 = (\lambda_b + \kappa_d)^{-1}$ and $\tau_2 = \lambda_d^{-1}$ It may be further noted that $I_1 + I_2 = 1$, i.e., 100% when the relative intensities are expressed in percentage.

1.2 Coincidence Doppler Broadening Spectroscopic Measurements

Whenever electron-positron annihilation takes place, two gamma rays each of energy 0.511 MeV are emitted in the opposite directions. The positron loses its kinetic energy and linear momentum to the material due to inelastic collisions through several energy dissipative processes whereas the annihilating electron has a finite linear momentum. Therefore, according to the law of conservation of linear momentum, the total momentum after the annihilation cannot reduce to zero. Hence the gamma rays will be moving away from each other with a slightly different direction and also the energies will be shifted by magnitudes $E_{\gamma_1} - E_{\gamma_2} = 2\Delta E = p_L c$ which gives $\Delta E = \frac{p_L c}{2}$,

where p_L is the longitudinal component of the electron momentum. This shift in the energies of the gamma rays is known as Doppler shift [1]. It gives an overall broadening to the 0.511 MeV gamma ray spectrum and it is monitored and the changes as functions of the changing parameters of the samples are carefully evaluated.

1.3 Angular Correlation

There is a loss of the kinetic energy and hence the linear momentum of the positron when it enters a material, by virtue of processes like electronic excitation, ionization of atoms, phonon interaction and plasmon excitation. Conservation of linear momentum demands that the non-zero momentum of the electron needs to be conserved. Hence, the two gamma rays move apart making an angle (θ) with the axis passing through the sample and the detector. The annihilation cross section (σ) given by Eq. (7) below dominates over the other processes only at very low velocities (v) of the positron

$$\sigma = \frac{\pi r_0^2 c}{v} \quad (7)$$

As already mentioned, in order to conserve the linear momentum, the annihilation gamma rays move in opposite directions with an angle θ , which is given by the equation

$$\theta = \frac{p_z}{m_0 c} \quad (8)$$

where m_0 is the mass of either the electron or the positron. The momentum distribution in two dimensions (p_y and p_z) can also be recorded in this way in two-dimensional angular correlation of annihilation radiations (2d-ACAR) measurements.

Angular correlation studies have not been carried out in the present work being reported here.

2. EXPERIMENTAL DETAILS

The positron lifetime spectra were recorded using a slow-fast gamma ray spectrometer [2]. The data was analyzed using the PALSfit program [3]. This is done in two stages, RESOLUTIONFIT and POSITRONFIT. In RESOLUTIONFIT, the program is used to calculate the instrumental resolution function which consists of a number of Gaussians with respective FWHMs, intensities and displacements and deconvolutes it from the recorded positron lifetime spectrum. The resultant spectrum, after the background subtraction, is a true multi exponential decay spectrum. The POSITRONFIT program is then used for fitting the resultant spectrum with a number of decaying exponentials and also incorporates the source correction for contributions from the source backing materials which otherwise interfere with the spectrum of the samples. The program continues the iteration procedure till the best reduced chi-square is obtained. Typically values between 0.9 and 1.2 are accepted as good fit. The corresponding positrons lifetimes and intensities are considered as the final results. The coincidence Doppler broadening spectroscopy data are analyzed with the help of the OriginPro 8.5 software.

3. RESULTS AND DISCUSSION

3.1 Results of analysis of positron lifetime spectra

The peak normalized positron lifetime spectra of all the samples are shown in Fig. 1. The nature and shape of the curves indicate the multi exponential decaying nature of the spectra and which is a clear evidence to the presence of large positron lifetimes. The large positron lifetimes within the samples show the presence of defects in the samples. The positron lifetimes and intensities obtained from the PALSfit analysis are given in Table 1.

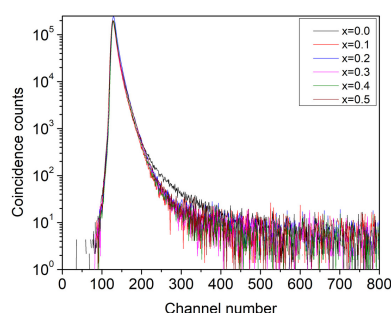


Figure 1. Peak normalized positron lifetime spectra of the samples

The nature of variation of the different positron lifetime parameters with different concentration of Sr is rather smooth and makes the interpretations easy and straightforward. The initial decrease of τ_1 is due to the diminishing contribution of positron annihilation in the bulk, which happens when more number of positrons are trapped in defects. For this to happen, the defect concentration needs to have increased. This is confirmed by the increase of the intensity I_2 at this stage.

Table 1: The positron lifetimes and relative intensities obtained from the PALSfit analysis and the calculated mean lifetime and the bulk lifetime in the different samples.

Concentration of Sr^{3+}	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	I_1 (%)	I_2 (%)	I_3 (%)	τ_m (ns)	τ_b (ns)
0	0.1434	0.4781	2.7979	87.6567	11.3974	0.9459	0.20666	0.15737
0.1	0.131	0.3604	3.9904	75.066	24.6401	0.2939	0.19887	0.15589
0.2	0.1383	0.3838	3.9628	76.0649	23.6214	0.3137	0.20829	0.1635
0.3	0.1452	0.401	4.2581	78.1673	21.5506	0.2821	0.21193	0.16888
0.4	0.1437	0.3825	4.6498	79.2838	20.4311	0.285	0.20533	0.16523
0.5	0.1417	0.3725	3.0733	67.4171	32.0733	0.3947	0.22713	0.17793

The sharp decrease in τ_2 in the initial stages of strontium incorporation indicates a reduction in

the sizes of the vacancy type defects which trap positrons. One more reason for the substantial drop in τ_2 can be as follows. Initially, in the undoped sample, the positrons were able to diffuse till the surfaces of the nanocrystallites and get annihilated on the surfaces. But, complete replacement of La^{3+} with Sr^{2+} does not take place and, on the other hand, as we keep on increasing the percentage of doping, this factor keeps on decreasing. The process also results in the formation of vacancies with virtual negative charges and the positrons are strongly trapped in these vacancies and get annihilated before reaching to the surface.

The intensity I_2 shows a sharp increase which indicates that additional defects are created due to non-occupancy of the vacant lattice sites by the ions of the elements with which doping is done. Thus, we see more defects in doped sample as compared to undoped one.

The behaviour of τ_3 and I_3 are explained as follows. This lifetime and intensity is due to the formation of orthopositronium atoms in the intercrystalline regions. Orthopositronium is a metastable bound state of an electron and a positron with their spins oriented in the same direction to give a triplet configuration. The annihilation of orthopositronium in a material normally occurs through the pick-off process where an electron with opposite spin takes away the positron and forms the spin singlet parapositronium, which has a much reduced lifetime. The effective lifetime is therefore a few nanoseconds only. The increase is basically due to the increase in the intercrystallite separation. This happens when cations of higher radii are doped to replace existing host cations. Due to the increased ionic radii, strain is developed within the crystallite. One way to get rid of the strain is to accommodate the substituted cations at sites closer to the surfaces of the crystallites. As concentration of substitution is increased, more ions are to be accommodated at the surfaces. This implies more surfaces are required and hence the sizes of the crystallite are reduced to enhance the surface to volume ratio. As the crystallite sizes are reduced, their separation increases and is reflected in the increase of τ_3 .

The decrease in I_3 is explained as follows. The actual substitution decreases on increase in the known incorporated substitution and hence we have more number of free Sr^{2+} ions in the intercrystallite region and hence it reduces the probability of positronium formation.

Both the mean positron lifetime and the bulk positron lifetime increases with substitution. The increase of τ_m reflects the dominance of τ_3 which increases due to the increase in the intercrystallite separation. The reason of the increase in τ_b is not clearly understood at this stage but will be discussed elsewhere.

3.2 Coincidence Doppler Broadening Measurements

For Doppler Broadening measurements, energy sensitive detectors with high energy resolution are required. So we have used High Purity Germanium detectors (HPGe) with an energy resolution of

about 1.3 keV at 0.511 MeV. The HPGe detectors are operated with the crystal at liquid nitrogen temperature to minimize the leakage of current due to thermally generated charge carriers. A digitally stabilized multi-channel analyzer (MCA) has also been used for data acquisition and storage. The signal is generated here through the process of electron-hole pair production by the absorbed gamma ray energy and collecting the charge carriers so produced across an electric field by giving high operating voltages to the detectors. The signals are then processed using a series of nuclear electronic modules like timing filter amplifiers (TFAs), constant fraction discriminators (CFDs), delays, a TAC/SCA, gate and delay generator (GDG), linear gate and stretcher (LGS) etc. The signals from the GDG+LGS serve as the master-gate for the amplifier signals to get registered within the multichannel analyzer (MCA). The advantage in using the coincidence system is that the high nuclear gamma ray background which may submerge the core electron momentum events can be almost fully eliminated.

The ratio curves of the CDB spectra are generated by dividing the one-dimensional projection of the events parallel to the $\Delta E = E_1 - E_2$ axis within a window of $1.022 + / - 0.00087$ MeV with the corresponding spectra of pure and defect-free aluminium and are shown in Fig. 2(left). The prominent peak around $p_L(10^{-3}m_0c) = 9.66$ indicates the annihilation of positrons with the $2p$ electrons of oxygen ions [4]. This means positrons are getting trapped at the vacancies of the cations. As vacancies of the La^{3+} and Fe^{3+} cations are negatively charged, positrons will be strongly attracted towards these vacancies.

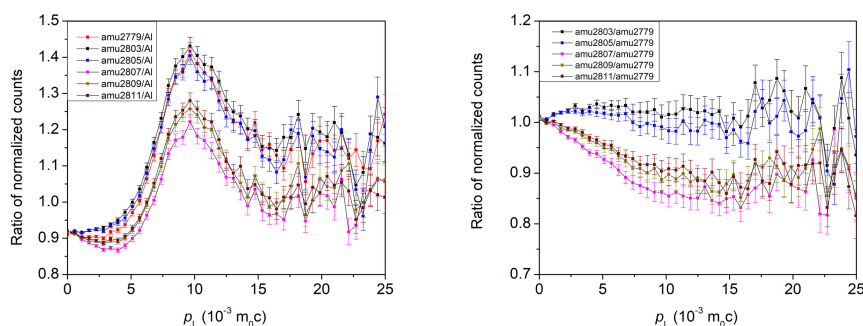


Figure 2. The ratio curves generated from the CDB spectrum of the samples with respect to reference aluminium (left) and the $x = 0$ samples (rightF).

On the other hand, since the vacancies of the O^{2-} ions are positively charged, positrons will be repelled by these vacancies. Still, in order to see the effect of substitution, another set of ratio curves are generated with the $x = 0$ sample as reference and these results are presented in Fig. 2(right). The curves are showing a broad peak around $p_L(10^{-3}m_0c) = 1216$ which perhaps indicates the substitution effects [4].

The CDBS peak ratios at $p_L(10^{-3}m_0c) = 9.66$ plotted against the doping concentration (Fig.

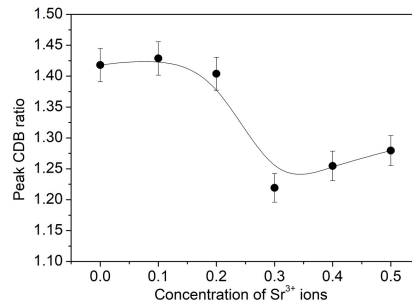


Figure 3. The CDBS peak ratios at $p_L(10^{-3}m_0c) = 9.66$ plotted against the doping concentration of strontium ions.

3) shows a drastic decrease between 0.2 and 0.3, which indicates the effects of substitution. There should have been a continuous increase due to the increase in defect concentration (as indicated by I_2). The fact that the CDBS peak ratio decreases indicates a reduction of positron trapping in cationic vacancies. In other words, some of the cationic vacancies are indeed getting occupied by strontium ions.

4. SUMMARY AND CONCLUSION

In this work, we have carried out positron lifetime and CDBS measurements on $LaFeO_3$ samples in which La^{3+} are progressively substituted by Sr^{2+} ions. We have been able to show from this study that the evolution of structural changes in the parent compound with changes in external parameters such as doping concentration can be directly seen through positron annihilation measurements.

While it is always desirable to support the findings through other techniques such as X-ray diffraction, PAS studies can give information on certain aspects of substitutions.

We summarize the main parts of our findings.

- Up to $x = 0.4$, a number of fresh vacant lattice sites are being created as a significant fraction of the replaced La^{3+} sites are not getting occupied by the Sr^{2+} ions due to the mismatch of the ionic radii of La^{3+} and Sr^{2+} .
- Positronium formation within the intercrystallite region is significantly reduced on introducing Sr^{2+} ions due to dispersion of a fraction of them in the intercrystallite region. At the same time, due to the increase in the intercrystallite separation, the lifetimes of positronium increases. The decrease in crystallite sizes occurs due to strain minimisation through a process of near-surface atomic substitution that necessitates an increased surface to volume ratio and consequently a decreased crystallite size.

- Above $x = 0.4$, it is conjectured that additional phases are being formed because of which the positronium lifetime drastically reduces. We need to perform complementary experiments like XRD or transmission electron microscopy (TEM) to confirm these arguments.
- The results from CDB experiments also support these findings.

In conclusion, the substitution of La^{3+} ions by Sr^{2+} ions results in the creation of more defects in the compound due to ionic radii mismatch. However, it is still possible to alter the properties for better use and applications. Beyond $x = 0.4$, it is advisable to restrict the substitution of the parent compound and explore improved methods of reducing the defect concentration and the phase instabilities.

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