Positron annihilation spectroscopic studies of multiferroic Bi$_{1-x}$Pr$_x$FeO$_3$ nanocrystalline compounds

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Abstract. Positron lifetime (PL) and coincidence Doppler broadening spectroscopic (CDBS) experiments were carried out on BiFeO$_3$ samples doped with Pr (in place of Bi) in concentrations ($x$) = 0, 0.05, …, 0.35. In the initial stages of doping, the existing Bi$^{3+}$ vacancies are occupied by Pr$^{3+}$ ions and positron trapping is reduced. From $x$ = 0.15 to 0.35, more number of positrons diffused to the surfaces of the nanocrystallites. The CDBS ratio curves showed enhancement of the peak at $p_L = 10.2 \times 10^{-3}$ m/s due to positron annihilation with the 2$p$ electrons of oxygen. It suggested increased trapping of positrons in newly created cationic vacancy-type defects due to the mismatch of ionic radii of Pr$^{3+}$ substituting Bi$^{3+}$ ions. The lattice parameters decreased (3.9661-3.9248Å) while the nanocrystallite sizes reduced and increased (28.6-34.2nm) during the doping.

1. Introduction
In the era of multiferroic nanocrystalline materials being rigorously looked into for their promising properties for physical and technological applications [1], BiFeO$_3$ has got the maximum attention because of the ability to tune its properties by adding or “substituting” trace amounts of lanthanide elements in place of a fraction of Bi so that the desired application can be performed without seriously compromising on its basic structure and/or ionic distribution. Still, defects are invariably bound to play a decisive role in controlling some of the useful properties down to even an atomic scale. The defects, especially of the vacancy-type, can result from either one or more out of a few factors such as charge imbalance, mismatch of ionic radii and lattice expansion or contraction. Positron annihilation spectroscopy is especially useful to investigate them and has been proved to be successful in a number of similar studies in the past [2, 3]. In this work too, we focus on the defects-related variations of the positron lifetimes and intensities and the coincidence Doppler broadened spectral line shapes in praseodymium (Pr) - doped BiFeO$_3$ and tried to understand the specific features responsible for such changes.
2. Experimental details
The synthesis of Bi$_{1-x}$Pr$_x$FeO$_3$ ($x = 0.0, 0.05, \ldots 0.35$) samples was performed through the sol-gel route using hydrogenated bismuth nitrate (Bi(NO$_3$)$_3$.5H$_2$O), ferric nitrate (Fe(NO$_3$)$_3$.9H$_2$O) and praseodymium nitrate (Pr(NO$_3$)$_3$.6H$_2$O) as precursors and polyvinyl alcohol (PVA) as chelating agent. For the synthesis of the undoped bismuth ferrite (BiFeO$_3$), 0.1M solutions of Bi(NO$_3$)$_3$.5H$_2$O and Fe(NO$_3$)$_3$.9H$_2$O in 70%-concentric nitric acid and water respectively were mixed and sonicated for 20 minutes. PVA was added to the mixed solution with a weight equal to the weight of the metal ions (Bi$^{3+}$) and was stirred until it was completely dissolved. After the complete dissolution of PVA, the solution was evaporated at 333K till it gradually turned into a viscous sol and then to dark brown gel. The dried gels were calcined at 873K for 2 hours. Similar procedure was repeated for the synthesis of the other samples, the differences being the change in the molarity of the precursor solutions including Pr(NO$_3$)$_3$.6H$_2$O in water and the weight of the PVA in order to keep the stoichiometry and nanocrystalline nature of the product (Table 1).

**Table 1.** Details of the amounts of the reagents used for the synthesis of the samples.

| Samples          | Bi(NO$_3$)$_3$.5H$_2$O (g) | Fe(NO$_3$)$_3$.9H$_2$O (g) | Pr(NO$_3$)$_3$.6H$_2$O (g) | Bi (g) | Fe (g) | Pr (g) | PVA (g) |
|------------------|-----------------------------|-----------------------------|-----------------------------|--------|-------|-------|--------|
| BiFeO$_3$        | 4.851                       | 4.04                        | 0                           | 2.090  | 0.558 | 0     | 2.648  |
| Bi$_{0.95}$Pr$_{0.05}$FeO$_3$ | 4.608                       | 4.04                        | 0.218                       | 1.985  | 0.558 | 0.070 | 2.614  |
| Bi$_{0.90}$Pr$_{0.1}$FeO$_3$  | 4.366                       | 4.04                        | 0.435                       | 1.881  | 0.558 | 0.141 | 2.580  |
| Bi$_{0.85}$Pr$_{0.15}$FeO$_3$ | 4.123                       | 4.04                        | 0.653                       | 1.776  | 0.558 | 0.211 | 2.546  |
| Bi$_{0.80}$Pr$_{0.20}$FeO$_3$ | 3.881                       | 4.04                        | 0.870                       | 1.672  | 0.558 | 0.282 | 2.512  |
| Bi$_{0.75}$Pr$_{0.25}$FeO$_3$ | 3.638                       | 4.04                        | 1.088                       | 1.567  | 0.558 | 0.352 | 2.478  |
| Bi$_{0.70}$Pr$_{0.30}$FeO$_3$ | 3.395                       | 4.04                        | 1.305                       | 1.463  | 0.558 | 0.423 | 2.444  |
| Bi$_{0.65}$Pr$_{0.35}$FeO$_3$ | 3.145                       | 4.04                        | 1.525                       | 1.359  | 0.558 | 0.494 | 2.410  |

The samples were checked for their purity and characterized by x-ray diffraction. For positron annihilation measurements, a $^{22}$Na source of strength ~ 400 kBq deposited on a thin (~ 2 mg.cm$^{-2}$) annealed (at 1273K for 2 hours in vacuum ~ 10$^{-6}$ mbar) Ni foil is kept embedded in the sample (in powder form) taken in a glass tube. The glass tube is continuously evacuated to maintain the sample and source under moisture-free atmosphere throughout the experiments. For positron lifetime measurements, BaF$_2$ scintillators coupled with XP2020Q photomultiplier tubes were used as detectors and the slow-fast gamma-gamma coincidence spectrometer had a time resolution of 170 ps. The HPGe detectors used for the coincidence Doppler broadening (CBD) measurements had energy resolutions 1.27 and 1.33 keV at 511 keV. More than a million counts were collected under each positron lifetime spectrum and the data were analyzed using the PALSfit program [4]. About 20 million coincidence events were generated in each CDB spectrum and the analysis was done using the LAMPS software [5].
3. Results and discussion

The sizes of the nanoparticles were obtained from the x-ray diffraction patterns via the peak width analysis and using the well-known Scherrer equation [6]. Further, the lattice parameters were estimated from the Bragg diffraction formula and combining it with the lattice constant. These are shown in figures 1(a) and (b). The initial decrease of the particle sizes is attributed to the reduction of strain brought in by the occupancy of the Bi$^{3+}$ vacancies by the Pr$^{3+}$ ions and the subsequent increase to the strain developed by the substitution in place of Bi$^{3+}$ ions by Pr$^{3+}$ ions of slightly larger radii (1.013 Å in place of 0.96 Å).

![Figure 1](image1.png)

Figure 1. (a) The size of the nanocrystallites and (b) the lattice parameter versus the concentration of Pr in the samples.

![Figure 2](image2.png)

Figure 2. Peak-normalized positron lifetime spectra of all the samples.

There are a number of aspects of nanocrystalline material systems that can affect the values of the measured positron annihilation parameters. First and foremost is the ability of thermalized positrons to diffuse through the interstitial regions of the material over distances of the order of 10-100 nm to reach the crystallite surfaces during their lifetimes. If the crystallites are of sizes less than these thermal diffusion lengths and devoid of any positron trapping defects in their interior, the positrons will eventually diffuse out and annihilation will therefore take place on the crystallite surfaces or within the intercrystallite regions (as positronium in the latter case). It is therefore prudent to attribute positron lifetimes of the order of 400-600 ps to the diffused vacancy clusters on the crystallite surfaces. Often this gets admixed with the defect-specific positron lifetime and, as a result, lower values for $\tau_2$ are obtained. The identity of the defects that trap positrons within the crystallites is often lost or difficult to retrieve in such cases.

The peak-normalized positron lifetime spectra of the samples shown in figure 2 are indicative of the sensitivity of this technique to identify the changing electronic environment within the samples due to doping and of the presence of extended vacancy-type defects of diverse nature and size in the samples. The positron lifetimes and their intensities are given in the figures 3(a) and 3(b). Lattice contraction results into the atoms coming closer and the sizes of the vacancy-type defects too can have a proportionate decrease. The resulting enhancement in the local electron density will therefore normally decrease the positron lifetime and the initial trend of variation of $\tau_2$ is in agreement with this interpretation. An anomaly is observed as the subsequent rise in $\tau_2$ which is remarkable and is indicative of an enhancement in the number of positrons reaching the nanocrystallite surfaces, thereby tilting the admixed lifetime $\tau_2$ to higher values. The intensity $I_2$ decreases with doping concentration, which signifies the cancellation of a number of
Bi$^{3+}$-vacancies by the doped Pr$^{3+}$ ions. Continued substitution results into strain being developed due to the larger ionic radii of the Pr$^{3+}$ ions which replace the Bi$^{3+}$ ions. The immediate consequence is the increase in size of the crystallites, as indicated in figure 1(a), and the probable increase in the number of positrons annihilating within the defect-free regions of the crystallites. In other words, the fall of $I_2$ can be well thought of as an independent and opposite change in $I_1$ and the initial fall and following near-constancy of $\tau_1$ supports this argument. It should be mentioned that the shortest lifetime $\tau_1$ incorporates in it the lifetime of positrons undergoing “free” annihilation and the Bloch state residence time of the trapped positrons. In nanocrystalline solids, the concept of “free” annihilation is a misnomer as the positrons would have by then thermally diffused to the crystallite surfaces and got trapped there. We however could not eliminate such a lifetime component in the data analysis and it should have a definite physical origin. We therefore attribute the term “free” to positrons getting annihilated in flight during the thermal diffusion to the crystallite surfaces. Although the orthopositronium lifetimes ($\tau_3$) and intensities ($I_3$) do show similar changes, considering the negligibly small values of $I_3$, they are not further discussed.

![Figure 3](image_url)

**Figure 3.** (a) Resolved positron lifetimes and (b) their relative intensities versus the concentration of Pr in the samples.

The results from coincidence Doppler broadened spectra support these explanations. The ratio curves generated with respect to well annealed (at 1273K for 2 hours in vacuum ~ 10$^{-6}$ mbar) single crystalline Al (99.999% pure) are shown in figure 4. The peak observed at an electron momentum $p_L = 10.2 \times 10^{-3} \text{ m}_0c$ results from the annihilations with the 2$p$ electrons of oxygen ions and its amplitudes are shifted upward after an initial decrease till the doping concentration $x = 0.15$ (figure 5). For annihilation with the oxygen electrons, the positrons are to be trapped in cationic vacancies and the initial trend of variation are consistent with the cancellation of such vacancies by the doped Pr$^{3+}$ ions. That the intensity of annihilation with the oxygen electrons thereafter enhances is an indication of new vacancy type defects generated due
to the lack of effective substitution by Pr$^{3+}$ ions which have got larger radii compared to the Bi$^{3+}$ ions. Intriguingly, this feature was not reflected in the variation of the intensity component $I_2$.

We also calculated the lineshape parameters $S$ and $W$ from the counts under the usual energy intervals of the projected one-dimensional spectra and their variations too indicated changes taking place in the samples due to doping (figures 6(a) and (b)). For positrons to be sensitive to the changes in electronic environment due to the substitution of Bi$^{3+}$ by Pr$^{3+}$ ions, they should have got trapped and annihilated at the lattice sites vacated by the oxygen ions. Normally such a possibility is ruled out because of the positive charge associated with the oxygen vacancies. But

![Figure 4](image)

**Figure 4.** The ratio curves generated with respect to Al from the CDB spectra.

![Figure 5](image)

**Figure 5.** The amplitude of the peak at $p_L = 10.2 \times 10^{-3} m_0 c$ of the ratio curves versus the Pr$^{3+}$ doping concentration in the samples.

the situation is favorable for positron trapping when the defects are vacancy clusters composed of neighboring anionic and cationic monovacancies in numbers such that the resultant vacancy clusters are either neutral or negatively charged. Since, in this study, we have been not able to separately resolve the positron lifetime in the defects, it can only be postulated that the vacancy clusters are either divacancies of the form $V_{Bi+O}$ (neutral) or trivacancies $V_{Bi+O+Bi/Fe}$ (negatively charged).

![Figure 6](image)

**Figure 6.** (a) $S$ and (b) $W$ versus Pr$^{3+}$ doping concentration in the samples.

Bi$^{3+}$ has the electronic configuration $[Xe]4f^{14}5d^{10}6s^26p^0$ whereas Pr$^{3+}$ has got partially filled $4f$ and $5d$ orbits in it due to the $[Xe]4f^25d^06s^0$ structure. As Pr$^{3+}$ ions continue to substitute for the Bi$^{3+}$ ions, the absence of the $6s^2$ electrons will be increasingly felt by the positrons and the $W$ parameter will decrease. The $S$ parameter consequently increases reflecting further as a linear fall
with the $W$ parameter in the $S$-$W$ plot (figure 7). The empty 5$d$ orbit in Pr$^{3+}$ will further facilitate improved ferromagnetic properties for the multiferroic samples and can be a topic of independent studies in future.

![Figure 7. The $S$-$W$ plot.](image-url)

4. Summary and conclusions
Doping by Pr$^{3+}$ ions in place of Bi$^{3+}$ in multiferroic nanocrystalline BiFeO$_3$ resulted in a gradual decrease of the lattice parameter whereas the average crystallite size initially decreased and then increased. An interplay between the strain associated with vacancy type defects and the surface stress due to substitutional effects is the deciding factor on the sizes of the doped crystallites [7]. The role of the defects is reflected in the positron lifetimes and intensities. A number of Bi$^{3+}$ vacancies, originally present due to the non-stoichiometry of the compound, got filled up by the Pr$^{3+}$ ions. Further doping led to substitutional effects and resulted into strain and strain-induced defects whereby the defect-specific lifetime increased. CDBS results also supported the concept of fresh cationic vacancies being the dominant trapping centres for positrons. Positronium formation, although of small intensities, cannot be ignored totally as the lifetimes and intensities often exhibit systematic variation with grain size, doping concentration, temperature etc. These information can be highly useful in studies involving defect-related properties such as magnetism, heat treatment, cold-work, metallurgy etc of similar samples.

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