

Positron annihilation spectroscopic studies on Nd-doped ceria

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Abstract

We report a new result on the characterization of Nd-doped ceria, $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-x/2}$ ($x = 0.075-0.675$) using positron lifetime spectroscopy (LTS) and coincidence Doppler broadening (CDB) measurements. A systematic increase in lifetime that is attributed to formation of Nd-oxygen vacancy associates is seen from $x = 0.075-0.4$ followed by a sharper increase up to $x = 0.5$. The change in profile of lifetime around $x = 0.4$ suggests drastic increase in the concentration of these associates. Discontinuity in lifetime around $x = 0.5$ is ascribed to ordering of oxygen vacancies. Coincidence Doppler broadening measurements indicate reduction in the overlap of positron wavefunction with oxygen core electrons due to trapping of positrons. Low-temperature (50–300 K) lifetime measurements indicate the presence of Rydberg-like positron states associated with Nd^{3+} sites.

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1. Introduction

Rare-earth-doped oxides have attracted considerable interest in view of their potential applications in solid oxide fuel cells and oxygen concentration cells [1,2]. Doped ceria, in particular is an attractive material due to its high ionic conductivity at relatively low temperature (below 800 °C) [3]. Several divalent alkaline and trivalent rare-earth oxides form extensive solid solutions with ceria [4,5]. Doping ceria with lower valent oxides introduces oxygen vacancies in the lattice. The local structure of these vacancies plays an important role in determining the properties such as ionic conductivity of doped oxides. Thus, there is a need to study the vacancy structure of these oxides using a probe that can provide information at atomic level.

Positron annihilation spectroscopy (PAS) is a well-established technique to study the electronic structure and defects in materials [6–9]. The lifetime of positrons depends on the electron density at the annihilation site.

Positrons have high affinity for open volume defects and in the presence of defects, the electron density experienced by positrons is reduced leading to increase in its lifetime. Thus, positron lifetime spectroscopy is capable of giving information about the size, type and relative concentration of various defects/vacancies even at ppm level concentration. Doppler broadening technique, on the other hand, measures the momentum distribution of the annihilating electrons. The low momentum part of the Doppler spectrum (511 keV gamma line) arises mainly from the annihilation with the valence electrons and the core electrons that can be taken as signature of an element, contribute to the high momentum part of the spectrum. A very small fraction of positrons annihilate with core electrons due to the repulsion of positron by the positively charged nucleus. The amplitude of the high momentum or core electron component is, therefore, low and it is buried in the Compton background in conventional Doppler spectrum. Coincidence Doppler broadened (CDB) technique using two HPGe detectors [10], is capable of eliminating the background to a great extent, e.g., peak to background ratio of $\sim 10^6$ can be obtained as compared to a few

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hundreds in conventional Doppler technique. This enables unambiguous extraction of the shape and magnitude of the high momentum part of the Doppler spectrum. The chemical surrounding of the annihilation site or elemental specificity is obtained from the shape/magnitude of the high momentum core component, which carry the signature of the element. Since the core electron momentum distribution is not influenced by the physical or chemical state of the element, the CDB technique is capable of identifying the elements at the annihilation site irrespective of its physical or chemical state in the sample. Therefore, combined use of lifetime spectroscopy (LTS) and CDB technique can provide valuable information about the vacancy structure.

In doped oxides, where vacancies play a dominant role in influencing its properties, PAS studies can help to characterize the vacancy structure at atomic level. Although, PAS has been extensively utilized to study the defect structure in ceramics, barring few reports [11–13] the interest has been limited to high-temperature superconductors [14,15]. To the best of our knowledge, there is no PAS investigation carried out on doped ceria. In view of this, positron lifetime and coincidence Doppler broadening measurements have been carried out in Nd-doped ceria by systematically changing the Nd concentration. In addition, temperature dependence of the lifetime (50–300 K) has been measured on pure and doped ceria. The objective of these studies has been to characterize the vacancy structure as well as understand the positron behavior in these doped oxides.

2. Experimental

Commercially available Nd_2O_3 and CeO_2 (99.9% pure) were used to prepare various compositions of solid solution. These oxides were characterized by powder XRD before use. Appropriate amounts of starting

materials to give the nominal composition $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-x/2}$, ($0.0 \leq x \leq 0.675$) were ground, and pressed into pellets and conventional solid state reaction methodology was followed as illustrated in Ref. [16]. XRD patterns of the doped oxides of different composition were recorded on a Philips X-ray diffractometer (Model PW 1710) with monochromatized $\text{Cu-K}\alpha$ radiation. Silicon was used as an external standard. XRD patterns were analyzed by comparing with reported ones of the end members. The phase and lattice parameters for various compositions prepared are presented in Table 1.

Positron annihilation lifetime measurements on these oxides were performed with a ^{22}Na positron source in sandwich configuration using a fast–fast coincidence spectrometer. The fraction of positrons annihilating in the source was estimated to be 5%. The lifetime spectra ($\sim 10^6$ counts) were analyzed using PATFIT program [17]. Analysis of lifetime spectra gave a single component that shows variation with composition of doped oxide.

CDB spectra of pure ceria and various compositions ($x = 0.0–0.6$) of doped oxide were measured using two HPGe detectors. The energies of the annihilating γ -ray pairs denoted by E_1 and E_2 were simultaneously recorded by the two detectors located at an angle of 180° relative to each other. The difference in energies of the two γ -rays $\Delta E = E_1 - E_2$, is expressed as cP_L and the total energy $E_T = E_1 + E_2$ is expressed as $2m_0c^2 - E_B$ (neglecting the thermal energies and chemical potentials), where P_L is the longitudinal component of the positron–electron momentum along the direction of the γ -ray, c is the velocity of light, m_0 is the electron rest mass and E_B is the electron binding energy. Coincidence events were selected with the following condition; $2m_0c^2 - 2.8 \text{ keV} < E_T < 2m_0c^2 + 2.8 \text{ keV}$, which resulted in a peak to background ratio $> 5 \times 10^5$. This enabled us to observe the high-momentum component of positron annihilation spectra. All CDB spectra were normalized

Table 1
Nominal compositions, corresponding phases and phase parameters in $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-x/2}$ (partly from Ref. [16])

Sl. no.	Nominal composition	Mol% of $\text{NdO}_{1.5}$	Phase (s) present	a (Å)
1.	$\text{Ce}_{1.00}\text{Nd}_{0.00}\text{O}_{2.0}$	0.0	F	5.411(1)
2.	$\text{Ce}_{0.925}\text{Nd}_{0.075}\text{O}_{1.963}$	7.5	F	5.424(1)
3.	$\text{Ce}_{0.85}\text{Nd}_{0.15}\text{O}_{1.925}$	15.0	F	5.437(1)
4.	$\text{Ce}_{0.775}\text{Nd}_{0.225}\text{O}_{1.888}$	22.5	F	5.448(1)
5.	$\text{Ce}_{0.70}\text{Nd}_{0.30}\text{O}_{1.85}$	30.0	F	5.462(1)
6.	$\text{Ce}_{0.625}\text{Nd}_{0.375}\text{O}_{1.813}$	37.5	F	5.475(1)
7.	$\text{Ce}_{0.55}\text{Nd}_{0.45}\text{O}_{1.775}$	45.0	F	5.484(2)
8.	$\text{Ce}_{0.525}\text{Nd}_{0.475}\text{O}_{1.763}$	47.5	F	5.486(2)
9.	$\text{Ce}_{0.50}\text{Nd}_{0.50}\text{O}_{1.75}$	50.0	F	5.490(1)
10.	$\text{Ce}_{0.475}\text{Nd}_{0.525}\text{O}_{1.738}$	52.5	C	10.992(4)
11.	$\text{Ce}_{0.45}\text{Nd}_{0.55}\text{O}_{1.725}$	55.0	C	10.994(6)
12.	$\text{Ce}_{0.40}\text{Nd}_{0.60}\text{O}_{1.70}$	60.0	C	11.009(3)
13.	$\text{Ce}_{0.325}\text{Nd}_{0.675}\text{O}_{1.663}$	67.5	C	11.021(1)

F, cubic (fluorite)-type; C, C-type cubic.

with respect to a reference spectrum (CeO_2 in the present case) to highlight the differences in the high-momentum region of spectra. Each spectrum was normalized to unit area and divided by ceria curve. All measurements were repeated to check the reproducibility of the data.

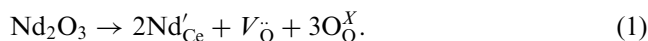
In addition to room temperature measurements, low-temperature positron lifetime measurements in the temperature range of 50–300 K were carried out on pure ceria and two different compositions ($x = 0.3$ and 0.5) of doped oxide using a closed cycle helium refrigerator (APD, cryogenics).

3. Results and discussion

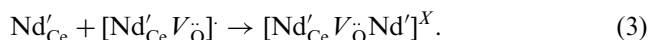
Analysis of lifetime spectra showed single lifetime component and extraction of two components failed. Positron lifetime in pure ceria was found to be 189 ps that increased with Nd doping. Fig. 1 shows the variation of lifetime with Nd concentration in the doped samples. The lifetime is seen to increase monotonically up to $x = 0.4$, followed by a sharper increase up to $x = 0.5$ beyond which there is discontinuity as seen at $x = 0.525$. On further increase of Nd concentration, there is a decreasing trend at least up to $x = 0.675$. Beyond $x = 0.675$, a biphasic region (Cubic and Hexagonal phase) appears and was not studied by positron annihilation spectroscopy.

CeO_2 is a fluorite-type structure, with Ce^{4+} forming the FCC lattice and oxygen occupying all the eight tetrahedral sites in the unit cell. In doped oxide

($\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-x/2}$), Nd^{3+} replaces Ce^{4+} and in order to balance the electronic charge, oxygen vacancies are created. Each Nd^{3+} doped in the lattice necessitates introduction of half oxygen vacancy as illustrated in the following equation:



Thus with the increase in Nd content, the oxygen vacancy concentration is expected to increase. It may be mentioned that oxygen vacancies are positively charged and they are not effective trapping centers for positrons due to electrostatic repulsion. In view of this, the observed increase in lifetime cannot be explained on the basis of oxygen vacancy concentration. It has been suggested [18] that Nd^{3+} doped at Ce^{4+} site would carry an effective negative charge and may be associated with the positively charged oxygen vacancies giving rise to the following type of vacancy associates:



In the event of formation of such vacancy associates (Eq. (3)), the positively charged oxygen vacancies will be rendered neutral. This would lead to positron trapping and consequently increase in lifetime with Nd concentration. Such trend is observed upto $x = 0.4$, beyond which the change in lifetime is sharper. We suggest that at $x = 0.4$, there is a drastic increase in concentration of such associates which persists upto $x = 0.5$ leading to observed changes. It may, however, be mentioned that only a small fraction of Nd incorporated into the lattice forms vacancy associates. This is evident from the trend in the positron lifetime i.e., in the event of all the doped Nd ions forming vacancy associates, the number of oxygen vacancies accessible to positron would be large enough to cause saturation trapping of positrons [19]. This would manifest as saturation of lifetime, i.e., a single life-time corresponding to oxygen vacancy would be observed that would remain unchanged with increase in Nd concentration unlike that is seen in our experiment. It may be mentioned that although the present experimental data suggests formation of neutral oxygen vacancy associates (Eq. (3)), the possibility of interaction between these associates leading to formation of dimers, trimers or clusters cannot be ruled out.

A sharp discontinuity in lifetime (Fig. 1) is seen above $x = 0.5$. This is followed by a gradual decrease in lifetime, upto $x = 0.675$. This sharp discontinuity can be ascribed to ordering of oxygen vacancies manifested as super-lattice peaks as seen in the XRD pattern of the composition with $x \geq 0.525$ [16]. The decreasing trend in the positron lifetime from $x = 0.525$ at least up to 0.675 can be interpreted as a reduction of the Nd-oxygen vacancy associates. It is logical to argue that the ordering of oxygen vacancies in C-type structure would

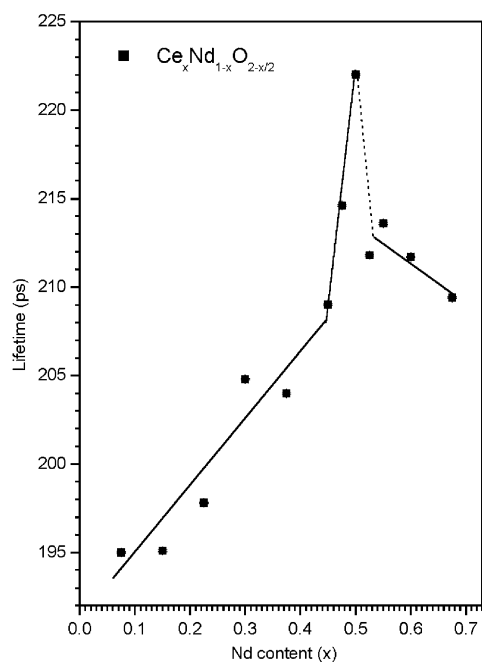


Fig. 1. Positron lifetime as a function of Nd content in Nd-doped ceria. The lines are guides to the eye.

affect the formation of Nd-oxygen vacancy associates. Concomitant reduction in such associates would produce isolated and charged oxygen vacancies that are less suitable for positron trapping leading to a reduction in positron lifetime.

In order to probe the electronic environment of positron trapping centres in these doped oxides, CDB studies were carried out on pure ceria and composition with $x = 0.45, 0.5, 0.525$ and 0.6 . The ratio spectrum of various compositions of doped oxide with respect to pure ceria is shown in Fig. 2. While the profile of all the doped samples are identical, there is a significant reduction in the magnitude of high momentum component in doped samples as compared to pure ceria. It is known that in an ionic crystal, majority of positrons from the delocalized state annihilate with electrons of the negatively charged ion. In pure ceria, the high momentum component of the CDB spectra is thus representative of annihilations with core electrons of oxygen. A reduction of this component in doped samples is due to localization of positrons in vacancies in the doped samples leading to reduction in the overlap of positron wavefunction with oxygen core electrons. In order to quantify the fraction of positrons annihilating with the low (valence) and high momentum (core) electrons, S and W parameters, defined as the counts in the momentum range $0 \times 10^{-3} m_0 c < P_L < 3 \times 10^{-3} m_0 c$ and $10 \times 10^{-3} m_0 c < P_L < 25 \times 10^{-3} m_0 c$, respectively were evaluated. Fig. 3 shows the S - W plot for all the compositions of doped oxide and pure ceria. All the doped samples fall in a single line indicating the fact that the trapping centers are identical, i.e., Nd-oxygen vacancy associates in the doped sample. It is interesting to note that the point for pure ceria which generally does

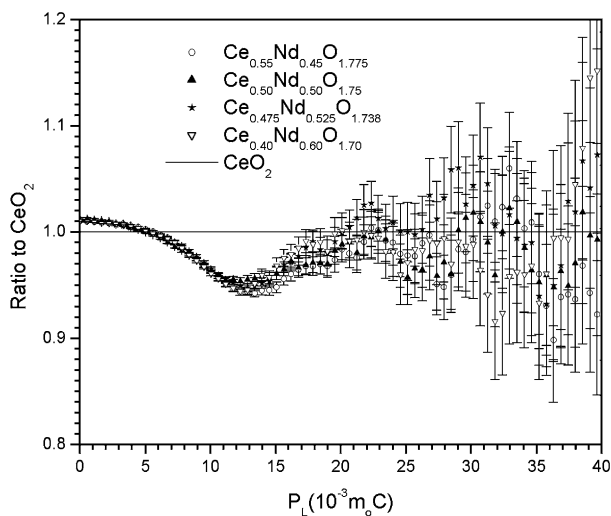


Fig. 2. Ratio curve of CDB spectra of $\text{Ce}_{0.55}\text{Nd}_{0.45}\text{O}_{1.775}$, $\text{Ce}_{0.50}\text{Nd}_{0.50}\text{O}_{1.75}$, $\text{Ce}_{0.475}\text{Nd}_{0.525}\text{O}_{1.738}$ and $\text{Ce}_{0.40}\text{Nd}_{0.60}\text{O}_{1.70}$ relative to CeO_2 .

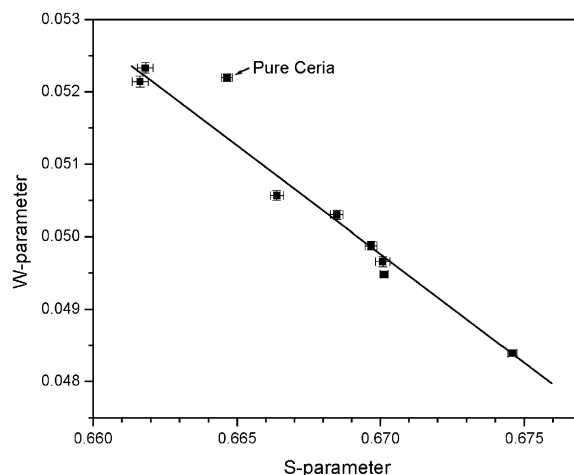


Fig. 3. S - W plot for various compositions of doped oxide. The solid line is guide to the eye.

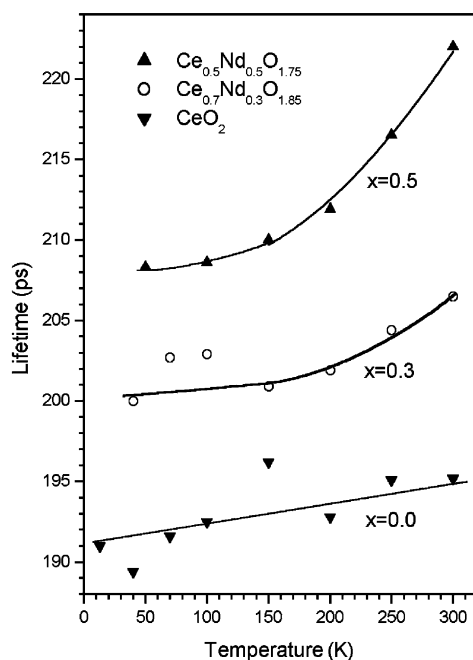


Fig. 4. Temperature dependence of positron lifetime in pure ceria, $\text{Ce}_{0.7}\text{Nd}_{0.3}\text{O}_{1.85}$ and $\text{Ce}_{0.5}\text{Nd}_{0.5}\text{O}_{1.75}$. The solid lines are guide to the eye.

not have oxygen vacancies lies outside the line as shown in Fig. 3.

We performed low-temperature (50–300 K) positron lifetime measurements on these oxides, viz., pure ceria and Nd-doped samples with $x = 0.3$ and 0.5 . The temperature dependence of lifetime is shown in Fig. 4. The lifetime is seen to decrease in a non-linear manner from room temperature down to the lowest temperature in doped samples. In pure ceria the decrease is linear, which can be explained due to the effect of thermal expansion alone. The observed temperature dependence

in doped samples is similar to that seen in semiconductors, where the non-linear changes are attributed to trapping of positrons in Rydberg-like states around the negative charge centres [20]. These Rydberg-like states are weak trapping centres for positrons and the lifetime in these centres is almost equal to the lifetime in the bulk rendering them indistinguishable [21]. In doped ceria, neodymium site (Nd'_{Ce}) and oxygen ions in the lattice are potential sites providing Rydberg-like positron states. Since, pure ceria does not show any temperature dependence, formation of such Rydberg-like positron states around oxygen ion can be ruled out. The temperature dependence arises due to the competition between negative charge centres, Nd'_{Ce} and the Nd-oxygen vacancy associates, $[\text{Nd}'_{\text{Ce}}\text{V}'_{\text{O}}\text{Nd}'_{\text{Ce}}]^X$. At sufficiently low temperature, positrons are trapped at both the sites. As the temperature is increased, detrapping from Rydberg-like positron states (at Nd^{3+} site) to Nd-oxygen vacancy associates that are deeper positron traps occur leading to the observed increase in lifetime. The differences in magnitude of change in lifetime from room temperature to lowest temperature studied in $\text{Ce}_{0.7}\text{Nd}_{0.3}\text{O}_{1.85}$ and $\text{Ce}_{0.5}\text{Nd}_{0.5}\text{O}_{1.75}$ can be attributed to the concentration of doped Nd, i.e., higher Nd concentration ($x = 0.5$) shows larger change in lifetime compared to $x = 0.3$. This result can be taken as a direct evidence of Rydberg-like positron states due to residual negative charge on the doped Nd ions in the doped oxides.

4. Conclusion

We have reported a new result on defect characterization in $\text{Ce}_{1-x}\text{Nd}_x\text{O}_{2-x/2}$ for $x = 0.075-0.675$. Evidence for the formation of Nd-oxygen vacancy associates is obtained, the concentration of which increases monotonically from $x = 0.075$ to 0.4. A drastic increase in the concentration of such associates is seen at $x = 0.4$, which persists upto $x = 0.5$. A sharp discontinuity in lifetime above $x = 0.5$ has been ascribed to oxygen vacancy ordering. The ordering of oxygen vacancy is

seen to have detrimental effect on the formation and stability of Nd-vacancy associates. Coincidence Doppler broadening studies indicate reduction in the overlap of positrons with oxygen core electrons due to trapping. Low-temperature studies indicate the presence of Rydberg-like positron states confirming the presence of residual negative charge on doped Nd ions.

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