Defect evolution in trivalent and pentavalent ion doped, and codoped CeO_2 nanoparticles: A combined PALS and PL study

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Defect engineering via aliovalent doping in technologically important oxide materials like ceria is an evolving field of research in order to explore its wide variety of applications such as gas sensors, redox catalysts, SOFCs etc. [1,2]. Several experimental and theoretical studies have been reported on trivalent rare earth doped ceria investigating the two important governing factors viz., oxygen vacancy concentration and variation in Ce^{3+}/Ce^{4+} ratio [3-5]. However, despite number of studies the exact nature and concentration of defects with various dopants and their correlation with the ionic size of the dopants are not completely understood. In this study we have employed Positron Annhilation Lifetime Spectroscopy (PALS) as a technique to understand the creation of vacancies in La^{3+} doped and La^{3+},V^{5+} codoped CeO_2:Eu^{3+} nanoparticles and their distribution around the dopants has been revealed by photoluminescence studies. The objective of codoping with pentavalent V^{5+} ion was to understand the effect of charge compensation on oxygen vacancy evolution.

All of the ceria samples were prepared by gel-combustion synthesis, followed by calcination and heating at 800 °C. Rietveld refinement of the acquired powder XRD patterns of phase pure samples showed larger lattice constants for all the La doped samples than that of the undoped one indicating lattice strain caused due to size and charge mismatch. PALS complimented by photoluminescence (PL) of Eu^{3+} ions which gives symmetry around the ion were used to understand the defect evolution in these systems. The studies showed the formation of oxygen vacancies with La^{3+} ion less strongly associated with the oxygen vacancies than Eu^{3+}. Codoping with pentavalent ions removed the vacancies as shown both by PALS and PL emission studies. The results show the usefulness of PALS as a technique in tuning oxygen vacancy concentration in rare earth doped ceria keeping eyes on its novel technological applications. The PALS studies on CeO2 with various trivalent and pentavalent ion doping will be discussed. The studies are complemented by PL and XRD studies.

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