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#### **Order – disorder transformation and its effect on the properties of**

#### (Lanthanide)<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> functional nanoceramics

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#### **Graphical abstract**



- Nanoceramics of  $Ln_2Zr_{1.5}Hf_{0.5}O_7$  (Ln = Pr, Nd, Sm, Gd, Dy and Er) are prepared through the modified combustion method.
- Structure gradually changes from the pyrochlore to the defect fluorite as the Ln ions changes from Pr to Er.
- Hafnium substitution improves the densification of the bulk ceramics.
- Maximum ionic conductivity is observed at Pyrochlore fluorite phase boundary.

#### ABSTRACT

Order disorder transformations and its effect on the structural, optical and ionic transport properties of the cubic pyrochlore – defect fluorite structures are the prime focus of this study. Nanoceramics of  $Ln_2Zr_{1.5}Hf_{0.5}O_7$  (Ln = Pr, Nd, Sm, Gd, Dy and Er) are prepared

through the modified combustion technique. X – ray diffraction analysis and electron microscopic studies show the cubic nano crystallite nature of the materials. Vibrational studies reveal the pyrochlore–fluorite phase transformation in the series. Highly dense bulk ceramics are prepared from the nano particles at relatively low temperatures. The gradual replacement of  $Ln^{3+}$  ions in  $Ln_2Zr_{1.5}Hf_{0.5}O_7$  changes the pyrochlores (Ln= Pr-Sm) to defect fluorite (Ln=Er) through the weakly ordered defect fluorites (Ln=Gd and Dy). Impedance spectroscopic analysis carried on the bulk ceramics shows the influence of phase transformation on the oxide ion conduction of bulk materials. The peak oxide ion conduction is observed for the Ln=Dy ceramic, which is at the pyrochlore fluorite phase boundary.

Key words: A. ceramics, B. Optical properties, C. Impedance spectroscopy, D.ionic conductivity

#### 1. INRODUCTION

The recent development in nano technology attracted the researchers to develop novel materials with unique properties. In the field of ceramic processing, nanocrystalline ceramics are expected to exhibit improved optical, magnetic, mechanical and electrical characteristics due to their larger surface to volume ratio as compared to the conventional ceramic materials [1]. Tailoring of these multifunctional properties in technologically important structures will lead to multifunctional materials with improved characteristics. The  $A_2B_2O_7$  pyrochlore structure was considered as a potential material in many fields due to the wide variety of chemical substitution at the A (A<sup>2+</sup> or A<sup>3+</sup>) and B (B<sup>5+</sup> or B<sup>4+</sup>) sites [2]. Hence these are widely used as catalysts, host for fluorescence centers, transparent ceramics, solid electrolytes, nuclear waste encapsulates and thermal barrier coatings [3–7]. The unique

electrical properties make them potential candidates for solid oxide fuel cells (SOFCs) applications.

Among the  $A_2B_2O_7$  Pyrochlores,  $Ln_2Zr_2O_7$  (Ln= lanthanides) were widely studied due the variety of lanthanide elements at the Ln sites and the intrinsic oxide ion vacancies in the structure. Depending on the cationic radius ratio and processing methods the Ln<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> pyrochlores show different structural disorders [8]. Pyrochlore structure can be considered as an ordered defect fluorite structure. In the Ln<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> pyrochlore structure, the rare earth ion  $Ln^{3+}$  is located at the 16c site,  $Zr^{4+}$  ion at the 16d site, and  $O^{2-}$  oxide ions at 8a and 48f sites, respectively. The 8b site is vacant in the completely ordered pyrochlore structure [9]. The disorder in the structure increases as the oxide ions randomly occupies the 8b site. The ordering process in the 8b site depends on the cationic radius ratio in the Ln<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> pyrochlore structure. By considering the 8 fold coordination to  $Ln^{3+}$  cations and 6 fold coordination to  $Zr^{4+}$  cations,  $Ln_2Zr_2O_7$  compounds with cationic radius ratio  $(r_A^{3+}/r_B^{4+})$  less than 1.46 will form a disordered fluorite structure, between 1.46 and 1.78 will adopt an ordered pyrochlore structure and greater than 1.78 it will have a layered perovskite structure [10]. That is, the substitution of a larger cation in the A site or smaller cation in the B site on a disordered fluorite structure will increase the oxide ion ordering, which in turn converts the defect fluorite to pyrochlore structure. In this study the A site cation is successively replaced by the  $Ln^{3+}$  ions and 25% of the B site cation is replaced by  $Hf^{4+}$  ions. Due to the fractional substitution of Hf<sup>4+</sup>, only a slight change was expected in the structural parameters of the well-known Ln<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> pyrochlore structure, since the ionic radius of Hf<sup>4+</sup> (0.71 Å) and Zr<sup>4+</sup> (0.72 Å) have similar values in the 6 coordination [11]. However the slight changes in the structural properties of the pyrochlore can create large amount of oxide ion vacancies in the structure, which in turn affects the optical and ionic transport properties of the materials. It was also reasonable to expect a different optical and ionic transport properties to the hafnium

substituted materials, since the electronic structure and density of  $Hf^{4+}$  ions are different from  $Zr^{4+}$  ions.

The order - disorder transition in the pyrochlore structure is closely related to the ionic transport properties of materials. H. Yamamura et al. studied the ionic transport properties of Ln<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and found that the highest value of conductivity occurs at the vicinity of pyrochlore – fluorite boundary [12]. Many researchers studied the order - disorder transitions by varying A site and B site cations, a steady increase in conductivity was observed at the pyrochlore - fluorite boundary [13–15]. The ionic transport properties of the dense ceramics also depend on the bulk density and final heat treatment temperature, which in turn depend on the preparation methods [16]. That is, there is an indirect dependency between the preparation methods and the ionic transport properties of the dense ceramics. Preparation of dense ceramic from the nanomaterials offers high density at low temperature as compared with the conventional solid state method [17]. Therefore an auto ignited combustion method is used for the preparation of nanoceramics in this study and then this powder is used for the preparation of the final dense ceramics.

#### 2. EXPERIMENTAL

In the combustion technique used for the preparation of  $Ln_2Zr_{1.5}Hf_{0.5}O_7$  (Ln = Pr, Nd, Sm, Gd, Dy and Er), the rare earth ions are prepared by dissolving their oxides (Pr<sub>6</sub>O<sub>11</sub>, Nd<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, Dy<sub>2</sub>O<sub>3</sub> and Er<sub>2</sub>O<sub>3</sub>) in concentrated HNO<sub>3</sub> whereas the Zr and Hf ions are prepared by dissolving ZrOCl<sub>2.8</sub>H<sub>2</sub>O and HfCl<sub>4</sub>, respectively in double distilled water. Then the stoichiometric amount of metal ions containing solution is mixed with citric acid solution, keeping the citric acid to cation ratio unity. The precursor complex is prepared by adding concentrated HNO<sub>3</sub> (oxidant) and ammonia solution (fuel), keeping the pH ~7. This

solution is stirred well for uniform mixing and then heated in a hot plate at ~250  $^{\circ}$ C. The solution boils and undergoes dehydration followed by decomposition leading to a smooth deflation producing foam. On persistent heating the foam gets auto-ignited, giving a voluminous fluffy powder due to self-propagating combustion. The obtained powder is heated in the oxygen atmosphere at 850  $^{\circ}$ C for 30 minutes to remove the organic impurities.

The structure of the prepared nanomaterials are analysed using X-ray diffractometer (D8 advance, Bruker, Germany) with CuKα radiation in the 2θ range of 20-70 in steps of 0.02. Additional information regarding the phase purity of the powder samples are examined using FTIR and confocal Raman studies. The infrared spectrum of the samples are recorded in the range 370 – 1100 cm<sup>-1</sup> on a FTIR Spectrometer (Spectrum2, Perkin-Elmer, Singapore) by using the KBr method. Raman spectra of the powder samples are recorded between 200 and 1000 cm<sup>-1</sup> using a confocal Raman spectrograph (alpha300RA, WITec GmbH, Ulm, Germany) with a 532 nm DPSS laser. Particulate properties of the prepared nanoparticles are imaged using high resolution transmission electron microscopy (Joel/JEM 2100, USA) operating at 200 kV. The diffuse reflectance spectra in the range of 200 to 700 nm of the samples are recorded by using a UV-Vis spectrometer (Lamda 35, PerkinElmer, Singapore) with an integrated sphere accessory (RSA-PE-20, Labsphere, USA). In this method Spectralon is used as the standard reference material for the samples. The photoluminescent emission of the prepared nanopowders are recorded using a spectrofluorometer (FP-846, Jasco, Japan). The phase pure powder samples are then ground in an agate mortar with polyvinyl alcohol as the binding medium. It is then uniaxially compacted into pellets of 2 mm thickness and 10 mm diameter at 20 MPa using a hydraulic press. The disc shaped pellets are sintered in a high temperature resistive heating furnace with molybdenum heating elements (TE-4050, Therelek, India). The relative density of the sintered pellets are calculated by using Archimedes method. The surface morphology of the thermally etched pellet samples is

examined by Field Emission Scanning Electron Microscope (Nova NanoSEM 450). Dielectric and impedance analysis are carried in an LCR meter (LCR HiTester 3532-50, Hioki, Japan) in the frequency range 100 Hz – 5 MHz at different temperatures from 500 to 850  $^{\circ}$ C. Before taking the measurements, disc shaped capacitors are made by applying silver paste on both sides of the pellets and fired up to 850  $^{\circ}$ C.

#### 3. RESULTS AND DISCUSSION

The X-ray diffraction (XRD) patterns of the prepared  $Ln_2Zr_{1.5}Hf_{0.5}O_7$  (Ln = Pr, Nd, Sm, Gd, Dy and Er) nano ceramics are shown in Fig. 1. The XRD pattern of the Ln = Prnanoceramic shows the pyrochlore structure with space group Fd3m whereas all the other prepared nano materials show the defect fluorite structure with space group Fm3m. ICDD files 19-1021 and 78-1299 are respectively used for indexing the pyrochlore and defect fluorite structures. The two low intensity super structure pyrochlore reflections (331) and (511) nearly at the  $2\theta$  values 37 and 45 degree, respectively are visible only in the XRD pattern of Ln= Pr. The absence of these peaks in the other diffractograms may be due to the broadening of the XRD peaks, which will results in the merging of low intensity peaks in the background data. It is known that one of the major causes of peak broadening in the diffraction pattern is the smaller size of the crystallites. Therefore the well-known Scherer's formula  $D = K\lambda/\beta \cos\theta$  can used to determine the size of the nanocrystallites [18], where D is the crystallite size,  $\lambda$  is the wavelength,  $\beta$  is the full width half maximum (FWHM) of the peaks and  $\theta$  is the angle of diffraction. The calculated crystallite size values for the prepared nanoceramics are shown in Table 1. It can be seen that the crystallite size decreases in the Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> series from Pr to Gd and then increases from Gd to Er. Also it is identifiable from the table that the lattice constant gradually decreases in the series as the lanthanides

changes from Pr to Er, which is due to the lanthanide contraction of  $Ln^{3+}$  ions. Here the lattice parameters of fluorite structures are shown as doubled values for comparing it with the pyrochlore structure.

Fig. 1.XRD patterns of Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> nanoceramics



Ln ceramics	Ionic radius Crystallite size (Å) (nm)		Lattice constant (Å)
Pr	1.126	8.93	10.70
Nd	1.109	6.45	10.69
Sm	1.079	4.96	10.64
Gd	1.053	4.80	10.58
Dy	1.027	5.73	10.48
Er	1.004	6.09	10.42
		(	

Table 1. Structural parameters and crystallite size of Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> nanoceramics

X- ray diffraction sometimes fails to show the exact pyrochlore – fluorite transitions in nanoceramics, since these structures are differed only by oxygen occupancy at the 8b site. The intensity of the X-ray reflections from the oxygen atoms is very weak as compared with the other metal atoms in the pyrochlore structure due to its relatively smaller size. Therefore vibrational studies are employed in the prepared nano materials, the metal oxygen vibrations are sensitive to the input frequencies of infrared and Raman studies. Factor group analysis predicts 13 active vibrational modes in pyrochlore structure as [19]

$$\Gamma = A_{1g} + E_g + 4F_{2g} + 8F_{1u}$$

For an ordered pyrochlore structure, the eight  $F_{1u}$  modes are IR active (seven optical and one acoustical) and the remaining six vibrational modes are Raman active. In the mid IR region the absorption spectrum of pyrochlore structure is characterised by two absorption bands whereas the fluorite structure is characterised by only one absorption band [17]. Fig. 2(a) shows the Fourier Transform Infrared (FTIR) spectra of the prepared materials between 370 and 1100 cm<sup>-1</sup>. The observed bands and the corresponding band assignments are tabulated in Table 2. The FTIR spectra of the Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> with Ln = Pr – Sm shows two

distinctly visible absorption bands, Ln = Er shows only one absorption band and Ln = Gd and Dy shows two faint broad absorption bands. That is Ln = Pr - Sm are purely pyrochlore structured materials, Ln = Er is formed as a defect fluorite material whereas Ln = Gd and Dy are defect fluorite structure with ordered pyrochlore domains. It is also clear from the table that the  $F_{1u}^{(1)}$  mode associated with the Zr/Hf- O bond gradually shift towards the lower wavenumber region with the replacement of Ln ions from Pr to Er. However the  $F_{1u}^{(2)}$  mode associated with the Ln - O' bond gradually shifted towards the lower wavenumber from Ln = Pr to Ln = Sm and then shifted towards the higher wavenumber region from Ln = Gd to Ln = Er. A broad shoulder peak around 600 cm<sup>-1</sup> in the defect fluorite structures is an indication of the presence of weakly ordered pyrochlore domains [16]. The broadening of peak around 600 cm<sup>-1</sup> in Ln = Dy is higher than Ln = Gd, which indicates that the former one is less ordered than the later.



Fig. 2 (a) FTIR spectra and (b) Raman spectra of the Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> ceramics

Sample name	FTIR s	FTIR spectrum		Raman spectrum			
	$F_{1u}^{(1)}$	$F_{1u}^{(2)}$	$F_{2g}^{(1)} + F_{2g}^{(2)}$	Eg	$F_{2g}^{(3)}$		
Pr	530 s	407 s					
Nd	517 s	383 s	502 wbr	386 mbr	294 s		
Sm	505 s	381 s	515 wbr	375 mbr	310 s		
Gd	490 s	395 s	520 wvbr	392 mbr	330 sbr		
Dy	481 sbr	407 s		398 wbr	335 vbr		
Er	420 sbr						

Table 2 Band assignments of FTIR and Raman spectra

Spectral intensity indications: s - strong, m - medium, w - weak and br - broad

The Raman spectra of  $Ln_2Zr_{1.5}Hf_{0.5}O_7$  (Ln = Nd, Sm, Gd and Dy) are shown in Fig. 2(b). Here Ln = Pr and Er are avoided from the Raman spectral analysis due to the fluorescence effect. The observed absorption bands and corresponding band assignments are shown in Table 2. From the figure and table it is clear that Ln = Nd and Sm shows three distinctly visible Raman active bands whereas Ln = Gd and Dy shows a similar spectra with broad Raman bands. The peak broadening in the Raman spectra is not only influenced by the nano size of the materials but also by the disorder in the structure. The translational periodicity in the pyrochlore lattice are be broken down due to the presence of disorder in the form of vacancy or defects in the crystal. This disordering allows more phonons to contribute to the optical spectra. Therefore phonons from all parts of the Brillouin zones starts to contributing to the vibrational spectra, which will creates broad, continuously spread weakintense Raman bands [20]. Thus six Raman active bands in a pyrochlore structure reduces to a single broad Raman band around 350 cm<sup>-1</sup> in the disordered defect fluorite structure [8]. However some defect fluorite structures usually shows weak intense peaks on their Raman spectra due to the presence of short range ordered pyrochlore domains in the structure. In this study, some weak intense shoulder peaks are observed on the broad Raman peak of Ln= Gd

and Dy, which indicates the presence of weakly ordered pyrochlore domains in the material. Therefore it can be concluded from the vibrational studies of  $Ln_2Zr_{1.5}Hf_{0.5}O_7$  that, the Ln = Prand Nd ceramics are perfect pyrochlores, Ln = Er is a perfect defect fluorite and Ln = Gd and Dy are defect fluorites with weak pyrochlore domains. Previous studies on the  $Ln_2Zr_2O_7$ shows that Ln = Gd is the phase boundary between pyrochlore and fluorite phase boundary [21]. The shift of phase boundary observed in this study is shifted to Ln = Dy, which is due to the substitution of isovalent  $Hf^{4+}$  ions in the  $Zr^{4+}$  sites.



Fig. 3 TEM images of (a) Pr<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub>, (b) Er<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> and (c) their SAED patterns

The size and morphology of the prepared powders are analysed by using Transmission Electron Microscopy (TEM). TEM images of Ln = Pr and Er are shown in Fig. 3 (a) and (b) respectively. It is clear from the images that, the nano ceramic particles are highly agglomerated with less than 10 nm size. This smaller size of the particles are comparable with the crystallite size calculated from the XRD. The high agglomeration observed in the image is the characteristic nature of combustionally derived nano particles. A further insight into the structure of the prepared nano particles are explored by using High Resolution Transmission Electron Microscopy (HRTEM), which are shown in the inset of Fig. 3(a) and (b). The HRTEM images shows the regularly ordered atomic arrangements in the materials. The interplanar spacing measured from the HRTEM images shows that Ln = Prforms the pyrochlore structure whereas Ln = Er forms as a fluorite type structure. In order to differentiate the pyrochlore and fluorite structure, a combined Selected Area Electron Diffraction (SAED) pattern is created as shown in Fig. 3(c). The ring nature of the materials indicates the polycrystalline nature of the fine nano powder. The slightly larger radius of the Ln = Er as compared with the Ln = Pr indicates the smaller d spacing of the former with respect to the latter, which is consistent with the X-ray diffraction analysis.

The UV-Visible diffuse reflectance spectroscopy (DRS) is a convenient method to analyse the absorption behaviour and optical properties of ceramic materials. The UV-Visible absorption spectra of the prepared nano ceramics between 200 and 700 nm are shown in Fig. 4(a). All the prepared lanthanide materials except Ln = Pr, shows high absorption in the UV region and then exponentially decreased towards the visible region. This exponential decrease is due to the defect states present in the forbidden region. However Ln = Pr shows a wide range of absorption, which starts from the visible region and extends up to the UV region. Balakrishna et al. reported that  $Pr^{3+}$  ions have several absorption bands near 400 nm corresponding to the transitions from the ground level (<sup>3</sup>H<sub>4</sub>) to the higher energy levels of the

 $Pr^{3+}$  ions [22]. However the defects states present in the forbidden energy gap may widen the absorption towards the forbidden gap region. A similar type of spectrum was reported in previous literature [23,24]. The absorption band edge (wavelength at which absorption starts) of the prepared nano ceramics can be identified by extrapolating the linear part of the absorption spectrum to the wavelength axis. The measured absorption band edge values are presented in Table 3. It is clear from the table that  $Ln_2Zr_{1.5}Hf_{0.5}O_7$  (Ln= Nd, Sm, Gd, dy and Er) nanoceramics shows the absorption band edge in the UV region, whereas Ln = Pr shows an absorption edge at the visible region (647 nm).



Fig. 4(a). UV-visible Absorption spectra of Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> ceramics



Fig. 4(b). Tauc's plots of Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> nanoceramics

Table 3 Absorption and emission	operties of Ln <sub>2</sub> Zr <sub>1.5</sub> HI <sub>0.5</sub> O <sub>7</sub> nand	ceramics

	UV visible s	pectroscopy	Photoluminescence spectroscopy		
Ln Ceramics	Absorption Band edge (nm)	Band gap (eV)	Excitation (nm)	Emissions (nm)	Transition levels
Pr	647	3.71	414	620	$^{1}\text{D}_{2} \rightarrow {}^{3}\text{H4}$
Nd	271	5.01	324	368 411	Due to the structure defects
Sm	261	5.21	404	605	${}^4G_{5/2} \rightarrow {}^6H_{7/2}$
Gd	243	5.33	278	301	${}^{6}P_{5/2} \rightarrow {}^{8}S_{7/2}$
Dy	258	5.43	386	471 578	${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$
Er	246	5.47	445	529 667	${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$

The electronic transitions in the forbidden gap obeys the Tauc's relation [25],

 $F(R).hv = A (hv - E_g)^m$ 

where A is a constant,  $E_g$  is the band gap energy, h is the Plancks's constant, F(R) is the Kubelka-Munk function, v is the frequency and m is an index, which assumes values between 1/2 and 3 depending on the nature of the transition mechanism responsible for absorption of photon in the energy gap. The exponent m = 1/2, 3/2, 2 and 3 are corresponding to the direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions respectively. The value of  $E_g$  can be evaluated by extrapolating the linear part of  $[f(R).hv]^{1/m}$ versus hv graph to the point  $[f(R).hv]^{1/m} = 0$ . Earlier studies on Ln<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> ceramics showed that these materials are direct band gap materials [21,26,27]. Therefore  $m = \frac{1}{2}$  is selected for the present study. The Tauc's plots for the prepared materials are shown in the Fig. 4(b) and the corresponding estimated band gap energy are presented in Table 3. The measured band gap values of these materials are not comparable with the energy values corresponding to the absorption band edge wavelength. This may be due to the presence of defect states in the band gap region. The band gap values reported in this study are much higher than the previous reports. Uno et al. studied the band gap of  $Ln_2Zr_2O_7$  (Ln = La, Ce, Nd and Sm) through the photochemical measurements and it was found that the band gap values of these ceramics lie between 2.53 and 3.52 eV [27]. The reported band gap of Dy<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> in the earlier study was also less than the Ln = Dy in the present study [26]. Moreover the measured band gap energy values in this study is higher than that of the previously reported band gap values of Ln<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> nanoceramics prepared by the same method [21]. That is the 25% of Hf ion substitutions at Zr sites of  $Ln_2Zr_2O_7$  (Ln = Pr, Nd, Sm, Gd, dy and Er) considerably increases the band gap energy of the materials.

The optical emission properties of the prepared nanomaterials are analysed by using Photoluminescence spectroscopy (PL). Fig. 5 shows the PL emission spectra of the prepared nanocreamics, the excitation wavelengths used for this emissions are included in Table 3. The absorption spectra of  $Ln_2Zr_{1.5}Hf_{0.5}O_7$  with Ln = Pr, Sm and Er shows several peaks in the

blue region. Therefore the PL emission spectra of these materials are monitored under the blue region excitations, all the three materials shows orange red or red emissions. By exciting under 414 nm, Ln = Pr shows the intense orange red emission (620 nm) of  $Pr^{3+}$ , the 404 nm excitation on Ln = Sm also shows an orange red emission (605 nm) of  $Sm^{3+}$  and the 445 nm excitation on Ln = Er shows an intense red emission (667 nm) of  $Er^{3+}$ . That is these materials are potentially useful in blue-based white LEDs. The electronic transitions corresponding to the emission spectra of these materials are also included in the Table 3, which agrees well with the previous reports [22,28,29]. The emission spectra of Ln = Nd shows two low intense broad emissions near 368 and 411 nm. Nd<sup>3+</sup> ion is well known for its near infrared (NIR) luminescence. Therefore the observed peaks cannot be simply attributed to the Nd<sup>3+</sup> transitions levels. A. Zhang et al. reported that the PL emission of Nd<sup>3+</sup> near 360 and 400 nm is due to the structure defects in the nano crystals [30]. The PL emission of Ln = Gd shows broad UV emission near 300 nm for an excitation of 278 nm. The observed spectrum is consistent with previously reported data [31]. However the PL emission spectra of Ln = Dyshows two peaks, one at the blue region (471 nm) and the other at the yellow region (578 nm). The  ${}^{4}F_{9/2} - {}^{6}H_{15/2}$  transition of Dy<sup>3+</sup> ions corresponding to the 471 nm is magnetically allowed, while the  ${}^{4}F_{9/2} - {}^{6}H_{13/2}$  transition corresponding to the 578 nm is a forced Electric Dipole Transition (EDT). The intensity of EDT transition depends on the local environment of the  $Dy^{3+}$  ions. When  $Dy^{3+}$  ions are located at low-symmetry sites with no inversion centers, the  ${}^{4}F_{9/2} - {}^{6}H_{15/2}$  transition is predominant [32]. The dominancy of the 471 nm peak in Ln = Dy in this study shows that  $Dy^{3+}$  ions are located at the low symmetric matrix



Fig. 5 PL emission spectra of Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> nanoceramics

The dielectric and ionic transport properties of the prepared materials can be studied in dense ceramic materials. For this, the prepared nano materials are thoroughly mixed with 5wt.% of poly vinyl alcohol (PVA) in an agate mortar until a uniform mixing is attained. These powder samples are then dried and again grinded in the agate mortar for half an hour.

Disc shaped pellets of 10 mm diameter and 2 mm thickness are then prepared from this power materials under a pressure of 20 MPa. The green compacts are then sintered in a resistive heated furnace at a constant heating rate of 5 °C/min and soaking time of 90 min. The sintering temperature and the density achieved by each ceramic material is tabulated in Table 4. The prepared bulk ceramics achieves a relatively higher density at the lower temperature as compared with the previous reports [21,33]. The homogeneous size distribution of the nano particles may be the cause of higher density and reduced sintering temperature in this study. Nano particles have a high surface to volume ratio and hence large surface energy. The tendency to reduce this excessively large surface area per unit volume of the nanocrystalline powders is the mechanism that drives the sintering process. Also the sintering stress in the 10 nm particle is 100 times larger than that of the 1 µm particles [34]. That is the sintering temperature of  $Ln_2Zr_{1.5}Hf_{0.5}O_7$  (Ln = Pr, Sm, Nd and Er) is considerably decreased as compared with the sintering temperature of undoped Ln<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> prepared by the same preparation method [21]. Thus the partial substitution of Hf ions in Ln<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> improves the density and decreases the sintering temperature. However the sintering temperature of Ln = Gd and Dy are slightly increased, which may be due to the improved density of these materials as compared with the previous report. The density of Hf<sup>4+</sup> ions is much larger than that of Zr<sup>4+</sup>, since Hf ions have larger atomic mass and comparatively similar ionic radius with the Zr ions. Therefore the presence of Hf ions may imposes additional stress to the nearby particles, which in turn improves the sintering density.

The surface morphology of the densified ceramics, Ln = Nd, Sm, Gd and Dy are examined by using field emission scanning electron microscopy (FESEM). The FESEM image of the thermally etched pellet samples are shown in Fig. 6 (a). A highly compacted grain structure with less porosity and well separated grain boundaries are visible in the

images. Some small black spots are observed on the FESEM images of Ln = Sm and Dy ceramics, which is due to the diffused silver during the impedance analysis (discussed later).

Ln ceramics	Sintering temperature ( <sup>O</sup> C)	Experimental density (g/cm <sup>3</sup> )	% of density
Pr	1420	6.29	93.54
Nd	1400	6.75	99.53
Sm	1420	6.99	99.22
Gd	1485	7.18	98.32
Dy	1475	7.36	96.05
Er	1470	7.85	99.29

Table 4 Sintering density of Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> ceramics

It is clear from the images that the grain size of Ln = Gd and Dy are higher than that of the Ln = Nd and Sm ceramics. The higher grain size of Ln = Gd and Dy are due to its higher sintering temperature as compared with the others. The grain size distribution in these images are collected by using imageJ software. A histogram is plotted by taking grain size along the x-axis and grain counts along the y- axis as shown in Fig. 6 (b). The average grain size in from this histogram data is measured by fitting Gaussian curve to this histogram. The average grain size measured for the Ln = Nd, Sm, Gd and Dy ceramics are, respectively,  $0.21 \pm 0.06$ ,  $0.26 \pm 0.07$ ,  $1.35 \pm 0.26$  and  $0.84 \pm 0.27 \mu m$ . The standard deviation measurements of Ln = Gd and Dy are higher than other material, which indicate that the particle size distribution of these ceramics are scattered to large extent. According to classical sintering theories, during the sintering process the grain boundary between two grains migrates form a larger grain to a

smaller grains due to the atomic diffusion [35]. Therefore the grain boundary diffusion and the grain size of the ceramics gradually increases with increase of temperature.



Fig. 6 (a) SEM image of  $Ln_2Zr_{1.5}Hf_{0.5}O_7$  ceramics (Ln = Nd, Sm, Gd and Dy)



Fig. 6 (b) Histogram of grain size distribution in  $Ln_2Zr_{1.5}Hf_{0.5}O_7$  ceramics (Ln = Nd, Sm, Gd and Dy)



Fig. 7(a). Cole-Cole plot of Sm<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub>

Impedance spectroscopy can be used to determine the electrical properties of the prepared dense ceramic materials. Fig. 7(a) shows the Cole-Cole plots of Ln = Sm ceramics between 500 and 850  $^{\circ}$ C. The impedance plot at 500  $^{\circ}$ C is characterised by a single semicircular arc whose centre lies below the x axis, above 600  $^{\circ}$ C an inclined spike is appeared along with the semi circles. The spike at the low frequency region on the right side of the plot is due to the space charges between the pellet and the electrode and the arc at the high frequency region on the left side of the plot is due to the combined effect of grain and grain boundary [36]. Due to the instrument's limitation, the semicircle corresponding to the grain and grain boundary effect is not completely visible at high temperature. It can also be seen that with the increase of temperature the size of the semicircle gradually reduces and shift towards the origin. This indicates that the conduction process in the material is thermally activated. Other prepared materials in this study (Ln = Nd, Gd, Dy, and Er) also shows a similar impedance behaviour as that of Ln = Sm.



Fig. 7(b). Cole-Cole plot of Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> ceramics at different temperature.

Fig. 7(b) shows the variation of impedance with the substitution of Ln ions. It can be seen that impedance of the  $Ln_2Zr_{1.5}Hf_{0.5}O_7$  (Ln = Nd, Sm, Gd, Dy, and Er) gradually decreases as the Ln ions changes from Nd to Dy and a sudden increase is observed for Ln = Er. It is identified from the vibrational studies that the oxide ion disorder in the pyrochlore structure increases as  $Ln^{3+}$  ion changes from Nd to Er with pyrochlore to defect fluorite transition at Ln = Dy. That is the impedance of the  $Ln_2Zr_{1.5}Hf_{0.5}O_7$  pyrochlore decreases with

the increase of disorder in the structure up to the pyrochlore-fluorite boundary and then increases with the increase of disorder. This is due to the fact that the number of mobile charge carriers increases with the increase of disorder and hence the impedance decreases. However the large increase of impedance in Ln = Er, irrespective of the increase of disorder is due to the increased ion- ion interaction in the material. Another interesting observation from the Fig. 7(b) is that the impedance of the Ln = Er ceramic is three times larger than that of the impedance of Ln = Nd ceramic at 500 °C. This large difference in impedance is gradually decreased with increase of temperature and it became comparable (but impedance of Ln = Er is greater than Ln = Nd) at 750 °C. This behaviour of the Ln = Er ceramic indicate that the number of mobile oxide ions liberated from the ion- ion interaction drastically increases due to thermally activated conduction.

The total electrical conductivity of the bulk ceramic materials are calculated by using the formula  $\sigma = G.t/A$ , where G is the measured conductance, t is the thickness and A is the area of the ceramic material. The temperature dependence of electrical conductivity of the dense materials can be studied by using Arrhenius relation

$$\sigma.T = \sigma_0 \exp(-E_a / K_B T)$$

where the pre-exponential number  $\sigma_0$  is a measure of number of mobile charge carriers in the material,  $E_a$  is the activation energy,  $K_B$  is the Boltzmann constant and T is the absolute temperature. Fig. 8 shows the Arrhenius plot of the ceramic materials, the straight line fit to points on the plot shows that the ionic conduction of the materials is thermally activated. The higher slope observed in the straight line fit of Ln = Er confirms the sharp variation of impedance observed in the Cole – Cole plot. The values of  $\sigma_0$  and  $E_a$  can be respectively evaluated from y-intercept and slope of the straight lines. Table 5 shows the

variation of activation energy and pre-exponential number with the variation in ionic radius ratio  $r(Ln^{3+})/r(B_{av}^{4+})$ . The average ionic radius of B site cation ( $Zr^{4+}/Hf^{4+}$ ) is calculated as

$$B_{av}^{4+} = 0.75 r (Zr^{4+}) + 0.25 r(Hf^{4+})$$

Díaz-Guillén reported that the activation energy of defect fluorites are less than that of the pyroclore structures and their reported values are comparable with the present study [37]. Activation energy values of Ln<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> reported by Yamamura et al. [9] are slightly less than that of the activation energy values presented in the Table 5, which are be due to the smaller grain size of the materials in the present study. However the variation of activation energy with average cationic radius ratio in the present study is similar to the previous reports [15,21].



Fig. 8. Arrhenius plot for  $Ln_2Zr_{1.5}Hf_{0.5}O_7$  ceramics

Ln <sup>1</sup> Ceramics	Radius ratio $r(I n^{3+})/r(B)$	Activation	Pre- exponential	Conductivity (Scm <sup>-1</sup> )		
	$\left( \frac{4+}{v} \right)$ (eV)		number $\times 10^4$	at 750 <sup>O</sup> C ×10 <sup>-4</sup>	at 850 <sup>o</sup> C ×10 <sup>-3</sup>	
Nd	1.55	1.09	3.62	1.49	0.49	
Sm	1.50	1.07	6.41	3.31	1.08	
Gd	1.47	0.89	1.11	3.92	1.30	
Dy	1.43	0.88	1.31	5.03	1.63	
Er	1.40	1.18	10.30	1.47	0.61	

Table 5 variation of ionic transport pr	properties with Ln	$^{3+}$ ions
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The A<sub>2</sub>B<sub>2</sub>O<sub>7</sub> pyrochlores contains an intrinsic oxide ion vacancy at the 8b site. The activation energy required for the oxide ion conduction in this pyrochlore structure is higher than that of the proton conduction [38]. The activation energy values reported in this study varies between 1.18 and 0.88 eV, which agrees with oxide ion migration in the pyrochlore crystal lattice [38,39] Also, it is clear from the table that the decrease of radius ratio gradually decreases the activation energy of Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> up to Ln = Dy and then increases for the Ln = Er. That is the oxide ion movement in disordered fluorite structure requires more activation energy than that of ordered pyrochlore structure. The  $\sigma_0$  value of the ceramics shows an increase with the decrease of radius ratio except for Ln = Gd and Dy. That is the number of mobile charge carriers present in the materials increases with decrease of radius ratio, since the  $\sigma_0$  value is a measure of mobile charge carriers present in the sample. The decrease of E<sub>a</sub> will facilitate an easy path for the oxide ion hoping conduction and increase of  $\sigma_0$  will increase number of mobile oxide ions in the crystal lattice. Both of the factors will try improves the oxide ion conductivity of the materials. Thus conductivity of the

 $Ln_2Zr_{1.5}Hf_{0.5}O_7$  ceramics gradually increases with the replacement  $Ln^{3+}$  ions from Ln = Nd to Dy. Instead of increasing the ionic conductivity with the increase of oxide ion concentration, Ln = Er ceramic material shows a decrease in its conductivity. This contrary behaviour of Ln = Er ceramic is due to the ion - ion interaction and increase of activation energy. When the number of mobile oxide ions increases, a weak ion - ion interaction is developed between the oxide ions and it will restricts the hopping motion of charge carriers [40]. Thus the available number of charge carriers participating in the conduction process will decreases. Therefore the ionic conductivity of defect fluorite structured Ln = Er shows the lowest conductivity value in the series. The maximum ionic conductivity observed at 800 °C in this study is 1.63  $\times 10^{-3}$  Scm<sup>-1</sup> for the Ln = Dy ceramic with radius ratio 1.43. Yamamura et al. reported that the maximum oxide ion conductivity in the  $Ln_2Zr_2O_7$  is at the pyrochlore fluorite phase boundary (Ln = Gd) with radius ratio 1.26, ionic radius values of the B site cations are in the 8 fold coordination [12]. By considering the 6 fold coordination for the B site cations, the corresponding radius ratio value in this study is 1.46. Earlier conductivity studies on the  $Ln_2Hf_2O_7$  series also show that Ln = Gd has the maximum conductivity with cationic radius ratio 1.48 [41]. In this study the maximum conductivity is observed at the vicinity of pyrochlore to fluorite transition (Ln = Dy) but the average cationic radius ratio of the phase boundary is shifted to 1.43. That is the oxide ion conductivity of the prepared materials in the present study is not only depending on the oxide ion disorder but also the preparation methods. The measured conductivity values in this study are slightly less than that of the previously reported conductivity values of  $Ln_2Zr_2O_7$  prepared by the same method [21]. This slight decrease observed in the oxide ion conductivity is due to the reduced grain size of the bulk ceramics as compared with the above reported study. The grain conductivity of bulk ceramics usually decreases with the decrease of grain size of the materials. The structural analysis performed in this study shows that Ln = Dy ceramic is neither an ordered pyrochlore

nor a disordered defect fluorite structures. It can be considered as a defect fluorite structure with weakly ordered pyrochlore domains. That is the partial substitution of  $Hf^{4+}$  ions at the  $Zr^{4+}$  sites shifts the order disorder transformation boundary and peak ionic conduction point from Ln = Gd to Ln = Dy in Ln<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>.



Fig. 9 shows the fitted curve and the equivalent circuit of the Ln = Gd ceramic at 500  $^{O}C$ 

Table 6 Equivalent circuit	parameters for	r grain and	grain boundary	v effects.
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	Range of capacitance		Resistance values at selected temperatures					
Cermics	Runge of e		500	°C	600	°C	700	0 <sup>o</sup> C
	C <sub>g</sub> ×10 <sup>-11</sup> F	$C_{gb}  imes 10^{-10}$ F	$egin{array}{c} R_{ m g} \ \Omega \end{array}$	${f R_{gb}}{\Omega}$	$egin{array}{c} R_{ m g} \ \Omega \end{array}$	$egin{array}{c} R_{gb} \ \Omega \end{array}$	$egin{array}{c} R_{ m g} \ \Omega \end{array}$	$egin{array}{c} R_{gb} \ \Omega \end{array}$
Nd	4.91 – 7.35	4.84 - 5.56	81628	54513	10821	7999	2548	1209
Sm	0.82 - 8.17	3.41 - 7.20	28273	25350	4368	3745	926	847
Gd	10.8 - 14.0	2.10-5.19	15403	6923	3129	1525	679	618
Dy	12.1 – 18.9	4.58 - 9.17	13030	5426	2196	1283	577	390
Er	3.35 - 6.82	1.0 - 2.7	295610	183910	19343	17900	4041	893

The grain, grain boundary and electrode contribution to the electrical properties of the bulk ceramic material are further analysed by fitting suitable circuit elements. In this study the Cole-Cole plot of the Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> shows a depressed semicircle with an inclined spike. The depressed semicircle at the intermediate and high frequency region is due to the combined effect of grain and grain boundary, it can be fitted with a series combination of two parallel resistance - capacitance elements. Fig. 9 shows the fitted curve and the equivalent circuit of the Ln = Gd ceramic at 500  $^{\circ}$ C. In this study, Z-view 3.2 software is used for the curve fitting analysis. The calculated values of grain resistance (Rg), grain boundary resistance (R<sub>gb</sub>), grain capacitance (C<sub>g</sub>) and grain boundary capacitance (C<sub>gb</sub>) for selected temperatures are shown in the Table 6. It is clear from the Table 6 that Rg is higher than that of R<sub>gb</sub> at all temperatures and chemical compositions. This may be due to the smaller grain size of the bulk ceramic material. The grain resistance of a material usually increases with decrease of grain size. It is also clear from the table that the Rg and Rgb values decreases with increase of temperature in accordance with the Arrhenius law of thermally activated ionic conduction. Fig. 10 shows the Arrhenius plot for the grain conduction. The linear behaviour of the Arrhenius plot shows that the grain conduction is thermally activated. Variation of the activation energy (E<sub>ag</sub>) and pre-exponential values ( $\sigma_{0g}$ ) of the Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> grain conduction is graphically shown in the Fig. 11 The  $E_{ag}$  and  $\sigma_{0g}$  values of the grain conduction of Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> shows a similar behaviour as that of the total electrical conductivity (discussed earlier). That is, the  $E_{ag}$  value decreases gradually with the decrease of  $r(Ln^{3+})/r(B_{av}^{4+})$  ratio, reaches a minimum for Ln = Dy and then increases with the decrease of radius ratio. The capacitance values evaluated for the material are shown in Table 6. From this table it can be identified that C<sub>gb</sub> is always greater than the C<sub>g</sub> value of the bulk ceramics. The  $C_g$  and  $C_{gb}$  values are of the order of  $10^{-11}$  and  $10^{-10}$  F, respectively, which are comparable with the grain and grain boundary capacitance in the previous studies [14,42].

The Cole-Cole plots of Ln= Gd and Dy at higher temperature shows an incomplete semicircles in the low frequency region instead of inclined spike. The capacitance values corresponding to these semicircles are of the order of  $10^{-6}$  F, which confirms the accumulation of charges at the electrode region.



Fig. 11 Variation of activation energy and pre-exponential number of  $Ln_2Zr_{1.5}Hf_{0.5}O_7$ grains with average cationic radius ratio

#### CONCLUSION

Partial Substitution of  $Hf^{4+}$  ions in the  $Zr^{4+}$  sites of  $Ln_2Zr_2O_7$  alters its structural, optical and ionic transport properties. Nano crystallites of  $Ln_2Zr_{1.5}Hf_{0.5}O_7$  (Ln = Pr, Nd, Sm, Gd, Dy and Er) ceramic are prepared through the modified combustion technique. Materials with Ln = Pr – Sm are purely pyrochlores, Ln = Er is a defect fluorite and Ln = Gd and Dy are neither pyrochlores nor defect fluorites. Ln = Dy with cationic radius ratio 1.43 is observed as the pyrochlore - fluorite phase boundary in the present study. Optical studies shows that most of the prepared nano ceramics are wide band gap materials with sharp emissions in the visible region. The bulk ceramics derived from the nano powders achieves high density at relatively low temperatures due to the additional stress from the hafnium ions. The oxide ion migration in the bulk ceramics shows a dependency on the order - disorder transformations. As the disorder increases in the series, the oxide ion conductivity first increases, attains a maximum at the phase transformation boundary and then sharply decreases. Measured values of activation energy and oxide ion conductivity suggests that the prepared materials are suitable for intermediate temperature SOFCs (ITSOFCs)

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#### **Table titles**

Table 1. Structural parameters and crystallite size of Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> nanoceramics

Table 2 Band assignments of FTIR and Raman spectra

Table 3 Absorption and emission properties of Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> nanoceramics

Table 4 Sintering density of Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> ceramics

Table 5 variation of ionic transport properties with Ln<sup>3+</sup> ions

Table 6 Equivalent circuit parameters for grain and grain boundary effects

#### **Figure titles**

Fig. 1 XRD patterns of Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> nanoceramics

Fig. 2(a) FTIR spectra and (b) Raman spectra of  $Ln_2Zr_{1.5}Hf_{0.5}O_7$  ceramics

Fig. 3 TEM images of (a) Pr<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub>, (b) Er<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> and (c) their SAED patterns

Fig. 4(a) UV-visible Absorption spectra of Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> ceramics

Fig. 4(b) Tauc's plots of Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> nanoceramics

Fig. 5 PL emission spectra of Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> nanoceramics

Fig. 6 (a) FESEM image of  $Ln_2Zr_{1.5}Hf_{0.5}O_7$  ceramics (Ln = Nd, Sm, Gd and Dy)

Fig. 6 (b) Histogram of grain size distribution in  $Ln_2Zr_{1.5}Hf_{0.5}O_7$  ceramics (Ln = Nd, Sm, Gd and Dy)

Fig. 7(a) Cole-Cole plot of Sm<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub>

Fig. 7(b) Cole-Cole plot of Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> ceramics at different temperature.

Fig. 8 Arrhenius plot for Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> ceramics

Fig. 9 Fitted curve and the equivalent circuit of the Ln = Gd ceramic at 500  $^{O}C$ 

Fig. 10 Arrhenius plot for the grain conduction

Fig. 11 Variation of activation energy and pre-exponential number of Ln<sub>2</sub>Zr<sub>1.5</sub>Hf<sub>0.5</sub>O<sub>7</sub> grains

with average cationic radius ratio