

## CHAPTER PHASE AND OPTICAL ANALYSIS OF SYNTHESIZED DYSPROSIUM DOPED ZIRCONIA

S.Divya<sup>1</sup>, M.Prema Rani<sup>2</sup>

**Abstract-**Zirconia and Dysprosium doped Zirconia ( $Zr_{1-x}Dy_xO_2$ ,  $x=0, 0.01, 0.02, 0.03, 0.04$ ) nanostructures have been synthesized using sol-gel process. From the XRD data, undoped Zirconia had monoclinic structure and Dy doped  $ZrO_2$  had tetragonal structure. Additional case found in the case of pure Zirconia is stabilized in the case of Dy doped  $ZrO_2$ . The crystallite size was calculated using the full-width-at-half-maximum (FWHM) of the diffraction peaks and found to increase with the doping of Dy which may be due to the high ionic radius of Dy. Rietveld refinement was done and the cell parameters were determined. Structural morphology was observed from the TEM analysis. The chemical composition was verified and confirmed using EDAX.  
**Keywords:**Nanostructures, Sol-gel process, Rietveld refinement, TEM, Crystallite size

### 1. INTRODUCTION

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. Materials with structure at the nano scale often have unique optical, electronic, or mechanical properties [1]. Zirconium dioxide ( $ZrO_2$ ), a white crystalline inorganic metal oxide of Zirconium, is one of the most studied materials. They exhibit increased strength and ductility, enhanced diffusivity, all beneficial to applications in sensors, electronics, medicine etc., Three phases of Zirconia are known, monoclinic, tetragonal and cubic. It adopts a monoclinic crystal structure at room temperature and transitions to tetragonal and cubic at higher temperatures [2]. The transformation from tetragonal to monoclinic is rapid and is accompanied by a 3 to 5 percent volume increase that causes extreme cracking in the material [3]. This behavior destroys the mechanical properties of fabricated components during cooling and makes pure Zirconia useless for any structural or mechanical application. When the zirconia is blended with some other oxides, the tetragonal phase is stabilized [4, 5].

Dysprosium, a member of the lanthanide group of elements [6] are widely used in making laser materials, neutron absorbing control rods in nuclear reactors [7], studying nuclear reactors [8], data storage applications [9] etc. It is well known for its luminescence property [10].  $Dy^{3+}$  ions shows emission spectra:  ${}^4F_{9/2} - {}^6H_{13/2}$  transition at 492 nm and  ${}^4F_{9/2} - {}^6H_{15/2}$  at 580 nm [11]. The present work is to prepare and study the properties of zirconia with dilute doping of Dy in zirconia which would be a stabilized material suitable for optical applications.

### 2. EXPERIMENTAL PROCEDURE

The  $ZrO_2$  and Dy doped  $ZrO_2$  ( $Zr_{1-x}Dy_xO_2$ ,  $x=0, 0.01, 0.02, 0.03, 0.04$ ) were synthesized by the Sol-gel process. 5 grams of Zirconium oxychloride ( $ZrOCl_2$ ) was mixed with urea, which was used as a catalyst. The mixture was dissolved in 20ml of deionized water and the solution was stirred at  $50^\circ C$  for 10 minutes and then heated upto  $130^\circ C$ . A gelation was formed which was dried out by further heating. The product thus formed was ground and sintered at  $600^\circ C$ . The same procedure was repeated with the addition of 0.05, 0.10, 0.15, 0.20 grams of Dysprosium chloride with 5 grams of  $ZrOCl_2$  and urea. The resultant product formed was Zirconia.

### 3. RESULTS AND DISCUSSION

#### 3.1 X-Ray analysis

The structural characterisation was done using X-Ray diffraction. X-Ray powder diffraction measurements were performed using XPERT-PRO at SAIF, Cochin, using  $CuK\alpha_1$  with a  $2\theta$  range from  $10^\circ$  to  $120^\circ$  and  $0.02^\circ$  step size. The XRD patterns showed well defined peaks, which was compared with the JCPDS data from the JCPDS Card No. 01-0750 for pure Zirconia and Card No. 24-1164 for the doped concentrations that confirmed that the undoped and doped Zirconia had monoclinic and tetragonal phases respectively.

<sup>1</sup> Research Centre and PG Department of Physics, The Madura College, Madurai-11, Tamil Nadu, India

<sup>2</sup> Research Centre and PG Department of Physics, The Madura College, Madurai-11, Tamil Nadu, India,

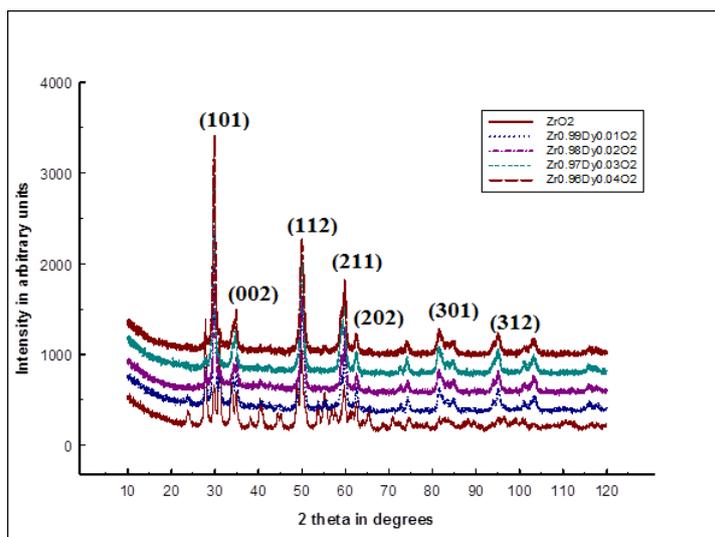


Fig 1 Raw XRD Profile of  $(Zr_{1-x}Dy_x)O_2$ ,  $x=0.0, 0.01, 0.02, 0.03, 0.04$

### 3.2 Crystallite size

From XRD, crystallite size of the samples was calculated. The crystallite size was calculated from full-width-at-half-maximum (FWHM) of the diffraction peaks. The particle size was calculated using Debye-Scherrer formula,  $D = k\lambda/\beta \cos\theta$  where  $D$  is the crystallite size,  $\lambda$  is the wavelength of X-ray (1.54056 Å),  $\beta$  is the full width at half maximum for the prominent intensity peak,  $k$  is the constant usually taken as 0.9 for a sample and  $\theta$  is the Bragg angle of reflection.

The crystallite size of the samples ranged from 15 nm – 45 nm approximately. The crystallite sizes of the samples are shown in table 1.

Table 1. Determination of Crystallite size by Debye- Scherrer formula

Sample	CRYSTALLITE SIZE (nm)
ZrDyO <sub>2</sub>	15.157
Zr <sub>0.99</sub> Dy <sub>0.01</sub> O <sub>2</sub>	30.251
Zr <sub>0.98</sub> Dy <sub>0.02</sub> O <sub>2</sub>	24.775
Zr <sub>0.97</sub> Dy <sub>0.03</sub> O <sub>2</sub>	31.533
Zr <sub>0.96</sub> Dy <sub>0.04</sub> O <sub>2</sub>	45.961

### 3.3 Rietveld refinement

The Rietveld technique [12] was used for refining structural parameters using software JANA 2006 [13] which is used to fit in the experimental and calculated diffraction patterns by considering the tetragonal structure which belongs to the space group P42/nmc. The atomic coordinates for Zr, Dy and O atoms were set as (0 0 0), (0 0 0) and (0.25 0.25 0.25) respectively. Using JANA 2006, the structural parameters, lattice parameters, background profile were refined. The principle of Rietveld Method is to minimize the difference between the calculated and the observed profiles. The raw XRD profile of Zirconia and other concentrations of Dy doped Zirconia is shown in figure 1. The refined powder profile of ZrO<sub>2</sub> and Dy doped ZrO<sub>2</sub> are shown in figures 2a-2d.

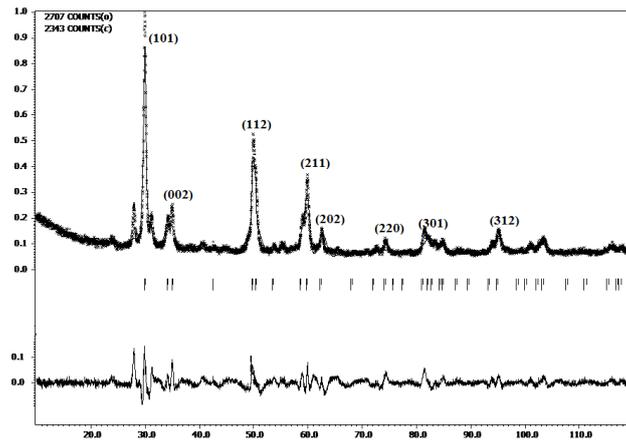


Fig 2a Refined Profile of  $Zr_{0.99}Dy_{0.01}O_2$

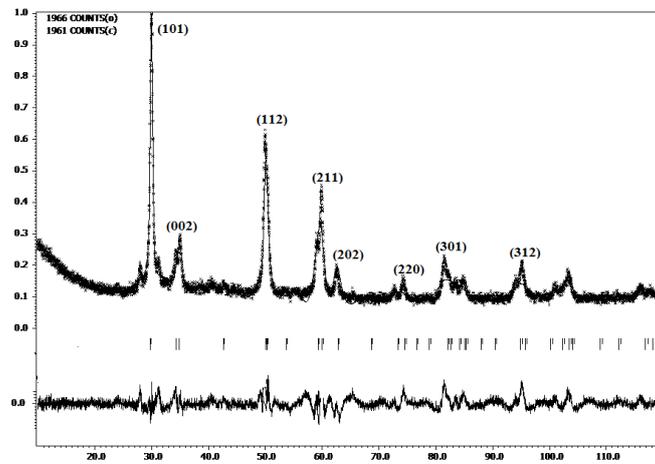


Fig 2b Refined Profile of  $Zr_{0.98}Dy_{0.02}O_2$

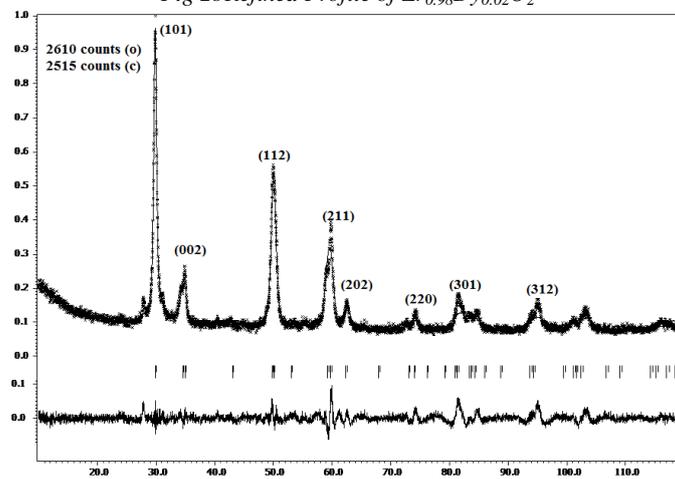


Fig 2c Refined Profile of  $Zr_{0.97}Dy_{0.03}O_2$

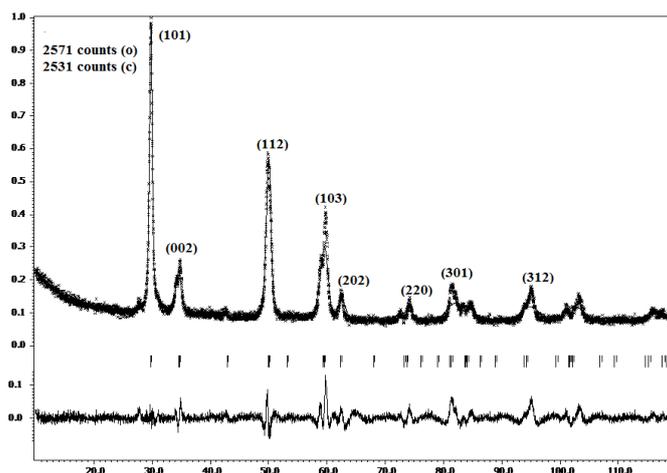
Fig 2d Refined profile of  $Zr_{0.96}Dy_{0.04}O_2$ 

Table 2 Structural parameters from JANA 2006

PARAMETERS	$Zr_{0.99}Dy_{0.01}O_2$	$Zr_{0.98}Dy_{0.02}O_2$	$Zr_{0.97}Dy_{0.03}O_2$	$Zr_{0.96}Dy_{0.04}O_2$
Cell constant(Å)	a=b=3.59688 (0.278018) c=5.253784 (0.191799)	a=b=3.68256 (0.271650) c=5.214565 (0.190498)	a=b=3.6999 (0.264820) c=5.1644 (0.190459)	a=b=3.7110 (0.270299) c=5.1353 (0.193574)
$F_{(000)}$	146	146	146	146
Volume (Å <sup>3</sup> )	69.83	69.83	69.83	69.83
$B^*$ for Zr	1.892481	0.199736	0.723511	2.122180
$R_{obs}$	0.37	2.63	1.02	1.59
$WR_{obs}$	0.56	2.98	1.53	2.34
$R_p$	9.54	8.07	8.47	6.86
$WR_p$	11.36	10.66	10.43	9.72

\* Debye Waller factor

### 3.4 Photoluminescence (PL):

Photoluminescence is light emission from any form of matter after the absorption of photons. It is one of many forms of luminescence and is initiated by photo excitation. Following excitation various relaxation processes typically occur in which other photons are re-radiated. Observation of photoluminescence at a certain energy can be viewed as indication that excitation populated an excited state associated with this transition energy [14].

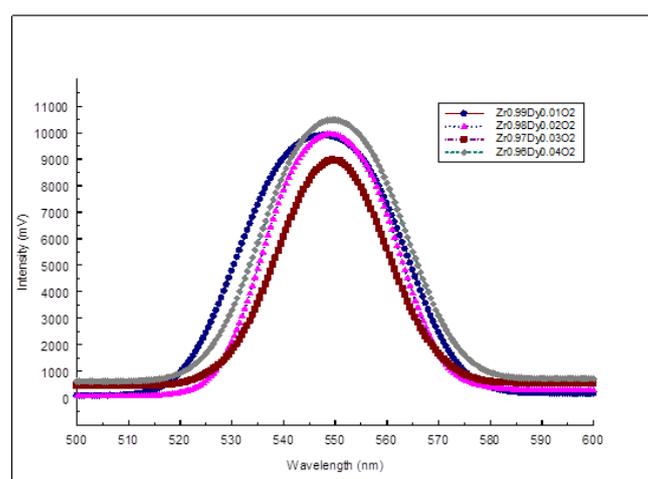
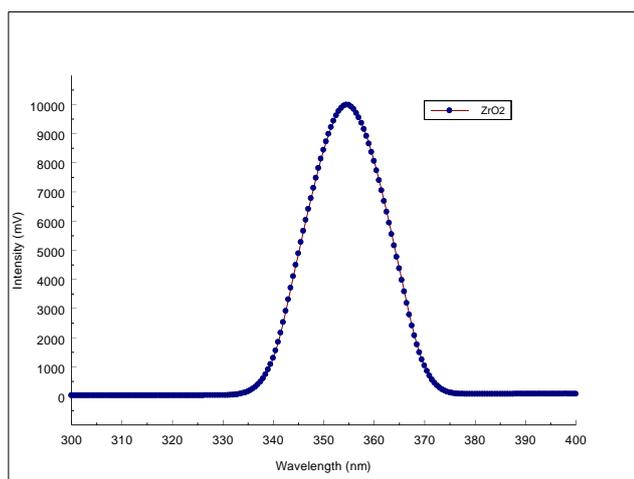


fig 3a shows the PL spectrum of  $ZrO_2$  and 3b shows the PL spectrum of  $Zr_{1-x}Dy_xO_2$  ( $x=0.01, 0.02, 0.03, 0.04$ )

### 3.5 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is a microscopy technique in which a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through it. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such

as a charge-coupled device. TEMs are capable of imaging at a significantly higher resolution [15]. The TEM pictures showing the surface morphology of the samples are shown in figures 3a-3e.

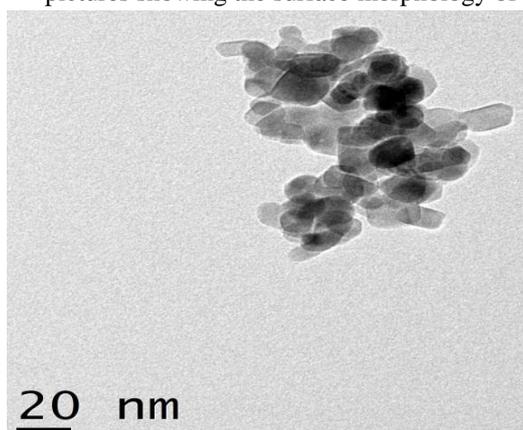


Fig 4a TEM image of  $ZrO_2$

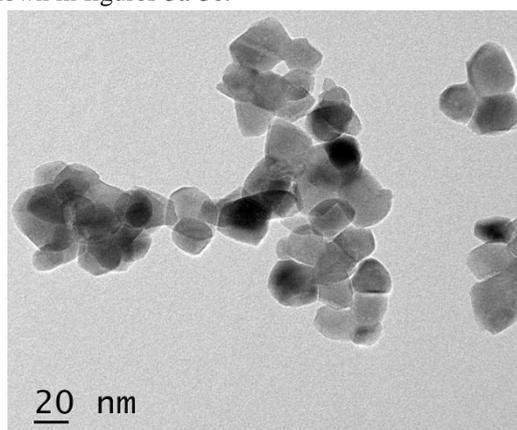


Fig 4b TEM image of  $Zr_{0.99}Dy_{0.01}O_2$

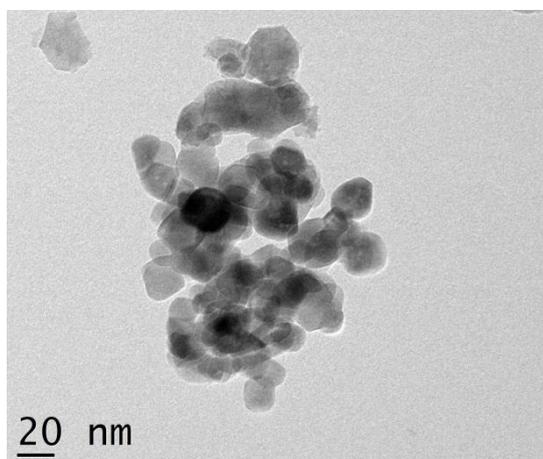


Fig 4c TEM image of  $Zr_{0.98}Dy_{0.02}O_2$

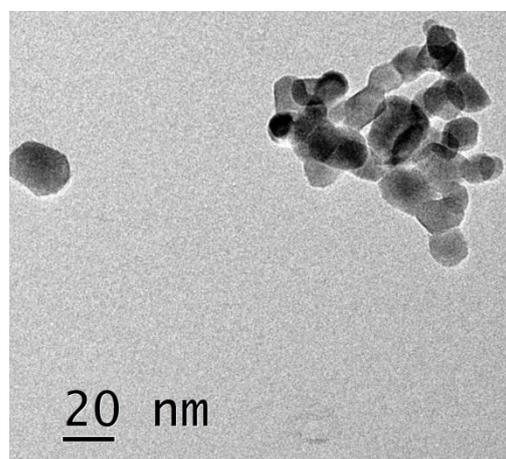


Fig 4d TEM image of  $Zr_{0.97}Dy_{0.02}O_2$

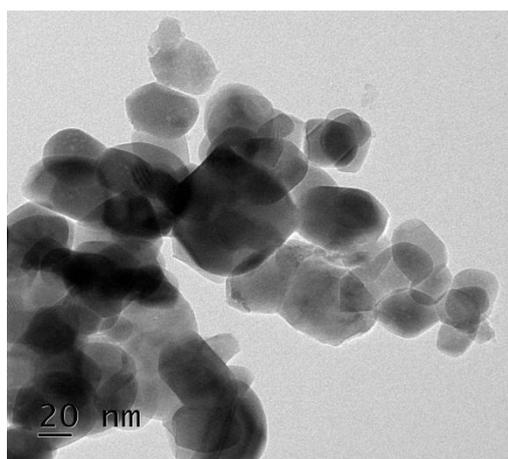
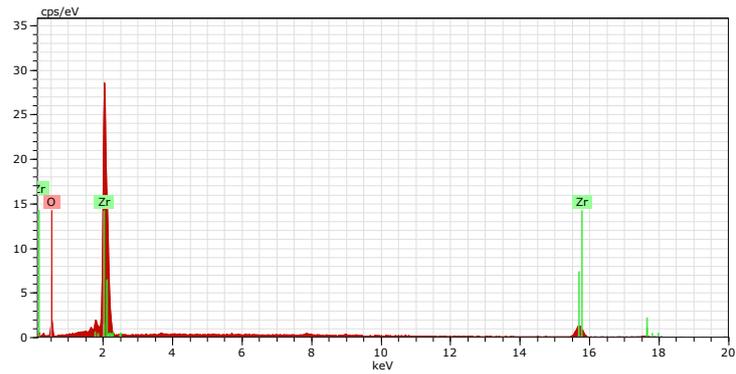
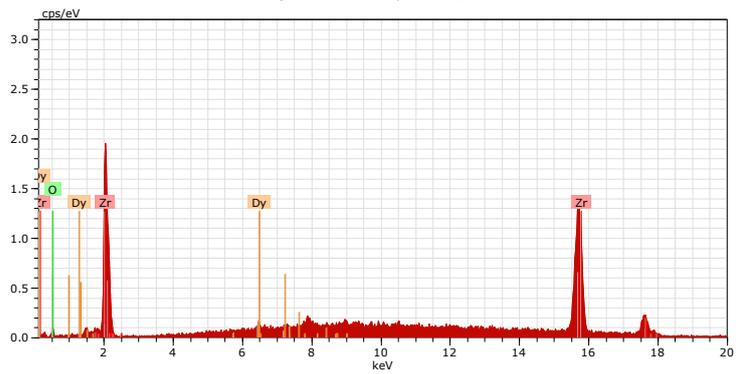
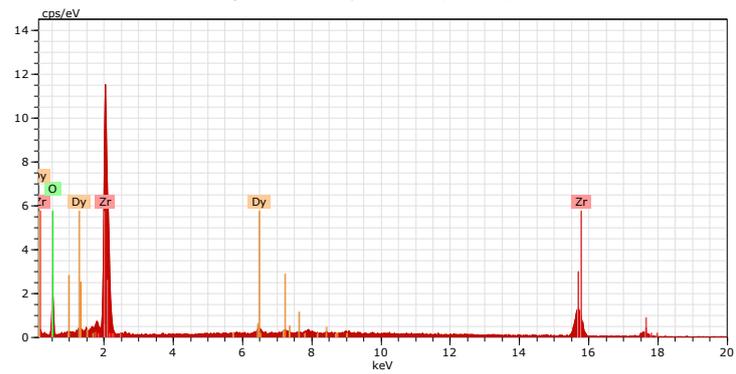
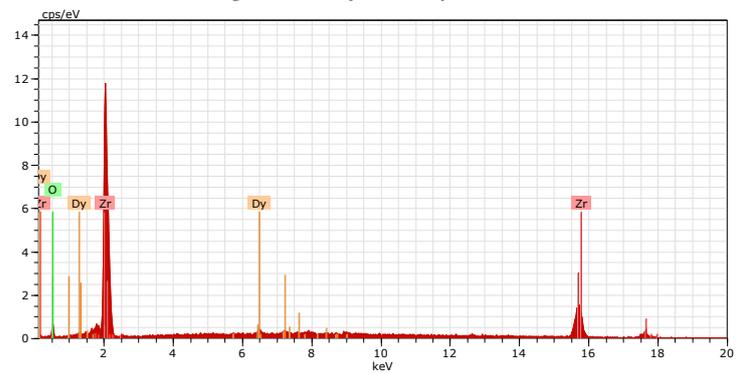
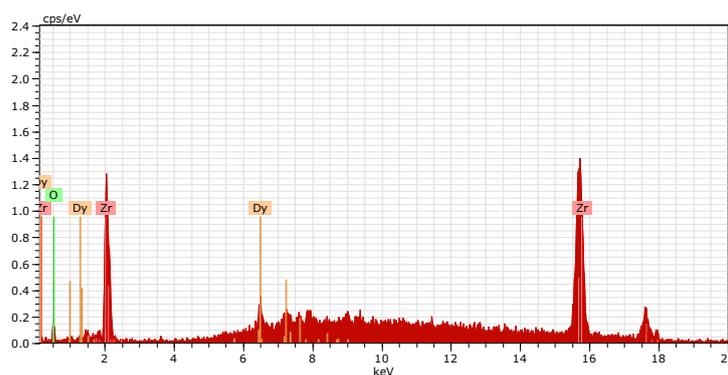


Fig 4e TEM image of  $Zr_{0.96}Dy_{0.04}O_2$

### 3.6 ENERGY DISPERSIVE ANALYSIS OF X-RAY SPECTROSCOPY

Dispersive X-ray spectroscopy (EDS) is an analytical technique used for the elemental analysis of the sample. It relies on an investigation of sample through interaction between electromagnetic radiation and matter in response with charged particle. The EDS analyses of the samples were taken in order to find the elemental composition of the EDS spectrum of the sample. The EDS graph is shown in the figures 4a-4e.

*Fig5a EDS of ZrO<sub>2</sub>**Fig 5b EDS of Zr<sub>0.99</sub>Dy<sub>0.01</sub>O<sub>2</sub>**Fig 5c EDS of Zr<sub>0.98</sub>Dy<sub>0.02</sub>O<sub>2</sub>**Fig 5d EDS of Zr<sub>0.97</sub>Dy<sub>0.03</sub>O<sub>2</sub>*

Fig 5e EDS of  $Zr_{0.96}Dy_{0.04}O_2$ Table 3 Elemental composition of  $Zr_{1-x}Dy_xO_2$ ,  $x=0.0, 0.01, 0.02, 0.03, 0.04$ 

SAMPLE	Zr	O	Dy
$ZrO_2$	56.74	43.26	-
$Zr_{0.99}Dy_{0.01}O_2$	94.78	5.22	0.01
$Zr_{0.98}Dy_{0.02}O_2$	54.61	44.99	0.39
$Zr_{0.97}Dy_{0.03}O_2$	71.14	28.30	0.56
$Zr_{0.96}Dy_{0.04}O_2$	90.14	9.17	0.69

## RESULTS AND DISCUSSION

Zirconia and Dysprosium doped Zirconia ( $Zr_{1-x}Dy_xO_2$ ,  $x= 0, 0.01, 0.02, 0.03, 0.04$ ) nanoparticles were synthesised by sol-gel process. From the XRD profile, the crystallite sizes of the samples were found to be 15-45 nm. Also it was found that there is a phase change from monoclinic in the undoped Zirconia to tetragonal in the doped Zirconia. From the rietveld refinement data, it is seen that the cell constant increases in the case of Dysprosium doped Zirconia. The ionic radii of Dy (105.2 pm) is higher than Zirconium (80 pm) which may be the reason for the increase in cell constant with doping of Dy. From the PL analysis, the wavelength changes towards the red shift is observed in the case of the doped Zirconia which verifies the decrease in the band gap of the material. This verifies the increase in the conductivity with increase in the concentration of the dopant. The structural morphology changes were observed from the TEM analysis. The variation in elemental composition due to doping was verified using EDAX.

## REFERENCES

- [1] <http://en.wikipedia.org/wiki/nanomaterials>
- [2] R. Stevens, 1986. Introduction to Zirconia. Magnesium Elektron Publication No 113.
- [3] Platt, P.; Frankel, P.; Gass, M.; Howells, R.; Preuss, M. (November 2014). "Finite element analysis of the tetragonal to monoclinic phase transformation during oxidation of zirconium alloys". *Journal of Nuclear Materials* 452 (1-3): 290-297.
- [4] Porter, D.L., Evans, A.G., Cannon, R.M. (1986). "Toughening of brittle solids by martensitic transformations". *Acta Met.* 34: 761. doi:10.1016/0001-6160(86)90052-0.
- [5] Bradsher, Keith (December 25, 2009). "Earth-Friendly Elements.Mined Destructively.*The New York Times*.
- [6] <https://www.google.co.in/amp/amp.livesscience.com/38292-dysprosium.html>
- [7] Jackson, Mike (2000). "Wherefore Gadolinium? Magnetism of the Rare Earths". *IRM quarterly* (Institute for Rock Magnetism).
- [8] Emsley, John (2001). *Nature's Building Blocks*. Oxford: Oxford University Press. pp. 129-132. ISBN 0-19-850341-5.
- [9] "What is Terfenol-D?". ETREMA Products, Inc. 2003. Retrieved 2008-11-06.
- [10] <https://www.google.co.in/amp/thirdworld.nl/amp/efficiency-of-Dy3-activated-phosphors?>
- [11] [aip.scitation.org/doi/10.1063/1.1849829](http://aip.scitation.org/doi/10.1063/1.1849829)
- [12] H.M. Rietveld, The Rietveld Method, *J. Appl. Crystallogr.* 2 (1969) 655-697.
- [13] V. Petricek, M. Dusek, L. Palatinus Jana, The crystallographic computing system Institute of Physics, Praha, Czech Republic, (2006).
- [14] [http://en.wikipedia.org/wiki/transmission\\_electron\\_microscopy](http://en.wikipedia.org/wiki/transmission_electron_microscopy).
- [15] <http://en.wikipedia.org/wiki/photoluminescence>.