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Effect of Excitation Energy on Photoluminescence Properties of Ti Doped ZrO_2 Phosphors

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Abstract— *Present paper reports the Photoluminescence properties of Ti doped ZrO_2 phosphors prepared by two different synthesis roots such as Combustion Reaction and Solid State Reaction method. For the characterization of the sample XRD and FTIR study were carried out, the XRD pattern shows the variation in intensity, due to this variation the estimated grain size was also vary with synthesis temperature. The FTIR spectra reveal the presence of conventional impurities in both the samples. Through the PL study we try to explain the surface morphology of the prepared sample.*

Highlights— *Photoluminescence, Combustion Reaction, Solid State Reaction*

Keywords— *Photoluminescence, Combustion Reaction, Solid State Reaction*

1. INTRODUCTION

Zirconia is an extremely refractory material and has a variety of applications in catalysis and many other areas such as oxygen sensors, fuel cells, automobile parts and thermal barrier coatings on metal compounds due to its versatile structural and surface chemical properties as well as good thermal stability [1-3]. Zirconia is a IV group member,in periodic database table and the main source of zirconia is Baddeleyite (ZrO_2) and zircon (zirconium ortho-silicate $ZrSiO_4$). Hafnium, Hamatite (Fe_2O_3) Fe and Ti are the major impurities found in a commercial zirconia due to closeness in their crystal radii (Zr^{4+} 0.79A^0, Hf^{4+} 0.78 A^0) [4].There are various procedures to produce pure as well as doped ZrO_2, but possessing desired structure and composition is still a big challenge to scientists and engineers. At room temperature pure zirconia has a monoclinic structure and with increasing temperature the phase changes to tetragonal to cubic phase, with the change in phase structure of the material its mechanical, electrical, chemical properties and hence the optical properties also changed.

Excitation is basically an addition of a discrete amount of energy to a system, by absorbing this extra amount of energy (i.e electromagnetic energy) the matter is heated or ionized by the impact of charged particles. In atoms the orbiting electrons absorbed the excitation energy and jump/raised to higher distinct energy levels. In molecules the excitation energy is absorbed not only by electrons but also by the whole molecules which excited to discrete modes of vibration and radiation. Photoluminescence spectroscopy is a noncontact, non destructive method of probing electronic structure of the material. PL intensity provides information about the surface quality and interfaces of the prepared sample [5,6]. In present study we try to explain the photoluminescence behavior at different excitation wavelength of Ti doped ZrO_2 Yon Cong et al reported the PL properties of Ti doped ZrO_2 prepared by Sold State reaction method, under 471 nm emission the sample shows two broad band centered at 255 nm and 292 nm, an excitation spectra showed a broad band at 471 nm under 254 nm excitation. Laxmi J. Tomar et al reported the PL properties of hydrothermal synthesized ZrO_2 doped with varying concentration of TiO_2. All the sample showed similar PL spectra accept the intensity of the sample changes with the increase of TiO_2 concentration. In short, lot of work has been done on the PL properties of Ti doped ZrO_2 but no one explains the effect of excitation on PL properties of Ti doped ZrO_2. On the basis of PL spectra we try to explain the surface morphology of the material.

2. EXPERIMENTAL

Synthesis process plays an important role for the design of nanostructure with required properties. Method of synthesis affects not only the type and impurities but also has an effect of crystalline size which in turn has a strong influence on the intensity of luminescence. Combustion synthesis is quite simple and quick to obtain fine particles; with high purity homogenous crystalline products also have desired composition and structure, whereas solid state reaction is most widely used method for the synthesis of polycrystalline bulk materials. It provides wide range of starting material such as oxides, carbonates etc. At room temperature solids do not react with each other and hence it is necessary to heat them at temperature up to 1500^0C.

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3. COMBUSTION METHOD (SAMPLE C1)

To prepare Ti doped ZrO_2 phosphors high purity zirconium oxynitrate [$Zr(NO_3)_2.5H_2O$], Titanium oxide TiO_2 and Urea [H_2NCONH_2] from Aldrich Chemicals were used as starting material, to convert TiO_2 into its nitrate form HNO_3 is mixed into TiO_2 drop wise and stirred at 60^0C for 5 to 10 minutes. After that the calculated amount of metal nitrates and urea are mixed homogeneously through magnetic stirrer for 30 minutes. An aqueous concentrated paste is kept in a preheated furnace maintained at 500^0C. Urea was used s a fuel and its amount was calculated using total oxidizing and reducing valances. Urea is a source of C and H, which at the time of combustion form CO_2 and H_2O and liberates heat.

4. SOLID STATE REACTION (SAMPLE S1)

In Solid State reaction method high purity ZrO_2 and TiO_2 from sigma Aldrich were used as starting material, all the samples are mixed and ground thoroughly with agate mortal for 3 to 4 hours and heated at 1200^0C for 3 hour in an air atmosphere. The basic mechanism of solid state reaction is diffuse control reaction. The controlled atmosphere is necessary to master the valance of the activators.[4]

For characterization and optical studies of the prepared sample FTIR, XRD and photoluminescence study were carried out. The FTIR spectra were taken through Shimadzu IR-Affinity between IR region i.e 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}, before taking FTIR spectra samples are mixed and ground with IR grade KBr powder with a ratio of 1: 100 mg. The crystal structure and phase purity is conformed through X-ray powder diffraction (XPD). The patterns were collected with a Bruker D-2 Phaser (Table Top Model) with CuKα radiation 1.5405 A^0. The 2θ values are 20^0 to 60^0 and the increment is 0.02^0.PL properties of the samples is taken through shimadzu spectrophotometer RF-5301PC equipped with xenon light source.

5. CHARACTERIZATION OF THE SAMPLE

5.1 FTIR

Fig (1) shows the FTIR spectra of both the samples prepared by combustion synthesis (C1) and solid state reaction (S1). IR spectra are a plot between percent transmissions of the radiation versus the wavenumber of the radiation. A downward peak represents absorption at a specific wavenumber. If we have low transmittance at specific wavenumber it implies large absorption at that wavenumber. Areas that do not have peak show that photons are not being absorbed at that frequency. In another words it indicates that the specific bond at that frequency does not exist in the molecule.[6]

The FTIR spectra revealed the presence of conventional impurities (NO^{3-}, OH^-)[7] as well as it is useful in determining chemical bonds because the absorption peaks found at specific wavenumbers allows us to identify various functional groups within a molecule.for the interpretation of the IR spectra we split IR region (4000cm^{-1} to 400 cm^{-1}) into Functional group region (4000cm^{-1} to 1450 cm^{-1}) and Finger print region (1450 cm^{-1} to 500 cm^{-1}).

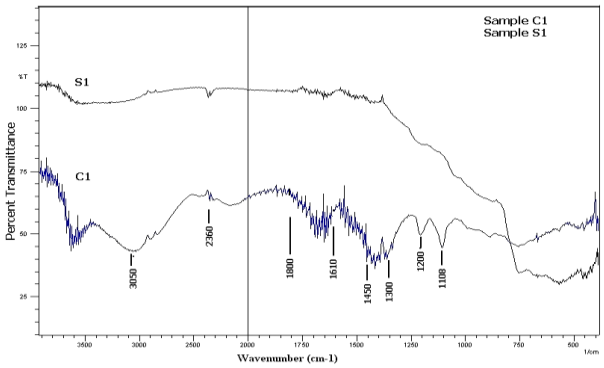

Fig. 1: Figure shows the FTIR spectra of C1:Combustion synthesized ZrO_2:Ti (0.1 %); and S1: Solid State Reaction ZrO_2:Ti (0.1%) sample.

Table 1

Wavenumber (cm^{-1})	*Functional Groups*
3050	O-H Stretching
2360	Asymmetric Stretching of O=C=O
1800-1610	C=O Stretching
1450-1300	Combination of C-O Stretch and O-H bend
1200	C-O Stretching
1108	O-H Bend

6. X-RAY DIFFRACTION STUDIES

The XRD pattern of sample C1 prepared by Combustion synthesis method and S1 through Solid State Reaction method is shown in the fig.(2), pattern shows the formation of monoclinic phase in both the sample, which is conformed through Crystallography Open database (COD) 9007485 with sub group P1 21/ C1 (14). Peak centered at 28.19, 31.49, and 34.23 degree are due to (-1,-1,1), (-1,-1,-1) and (0,0,-2) reflections. In sample S1 we found high intense peaks as compared to sample C1, this is due to the high temperature synthesis.The average crystalline size was calculated from the diffraction data by using Scherrer formulae. In Combustion synthesized sample the particle size is 50.6 nm whereas in SSR synthesized sample we found 53.5 nm, which indicates that with increasing temperature the crystal size increases due to growth of particles. [7]

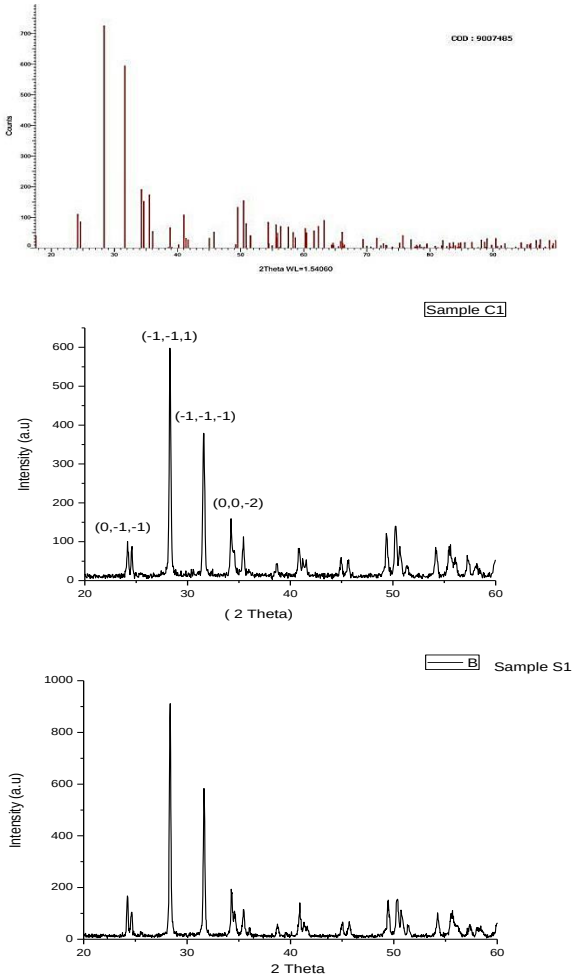

Fig. 2: XRD pattern of C1: Combustion synthesized ZrO_2: Ti (0.1 %); and S1: Solid State Reaction ZrO_2: Ti (0.1%) sample.

7. PHOTOLUMINESCENCE STUDY

Photoluminescence properties of the sample depends not only the surface quality of the material but also depends on the nature of the optical excitation. Timothy H. Gfroerer reported that when surface structure is poor, the PL spectrum changes with increasing excitation energy whereas the PL spectrum of a high-quality surface is independent of excitation energy.

Fig (3) shows the PL emission spectra of sample C1 under 220,250,295and 320nm excitation. We found broad peak centered at 471 nm which shows the blue emission of Ti doping, also conforms the presence of Ti in the prepared sample. As we increase the excitation energy the PL intensity will increase, also the peak is slightly shifted towards the higher wavelength. Maximum PL intensity is found at 295 nm excitation after that the PL intensity diminish for higher excitation this clearly showed that the number of interfaces and impurity states is finite in the sample due to this the recombination at these sites will saturate at higher excitation, similar result is found in sample S1 (Fig 4) only the intensity of the sample reduces as compared to sample C1.

Figure (5) shows the excitation spectrum of both the sample C1& S1 under 470 nm emission. Spectra shows a broad band with single peak at 281 nm and another hump at 294 nm for clear visualization of the peaks when Gaussian component is taken in sample C1 both the peaks is separated and shows smooth peak at 284 nm and 327nm whereas Sample S1 shows only one peak at 278nm.

The mechanism behind the photoluminescence spectra is not clear at al but it is supposed to be, due to the Oxygen vacancy created. When Ti is mixed in to the Zirconium, and prepared at different temperature mixture valance states of Ti [Ti^{4+}, Ti $^{3+}$] ions coexist in the sample with different ratios. The ionic radii of Ti^{3+} (0.76 A^o) is much closer to that of Zr^{4+} (0.79 A^o) rather than Ti^{4+} (0.68 A^o) and hence the Ti^{3+} ions substituting for Zr^{4+} are assumed to be the luminescence centers[9]. Two Ti^{3+} ions substituting for a Zr^{4+} ion produces one oxygen ion vacancy for charge compensation, these anion vacancies are effective and deep traps for electrons generated in the conduction band during excitation. A traping center is formed between the Ti/Zr ion and an oxygen vacancy[10]. When the excitation energy greater than the band gap of ZrO_2 is given it produces electron- hole pairs. Some electrons are trapped by the oxygen vacancies creating F centers. Hence the electron trapped at F centers when transfer to ground level it gives broad band emission centered at 471nm under 220,250,295,320 nm excitation. The emission is strongly depends on the concentration of F centers and the crystallinity of the prepared sample [9, 10] and if the number of impurity states or interface is finite then the recombination of these site will saturate at high excitation [11] and hence due to the saturation we found highest emission intensity at 295 nm excitation after that for higher excitation the intensity will decreases continually.

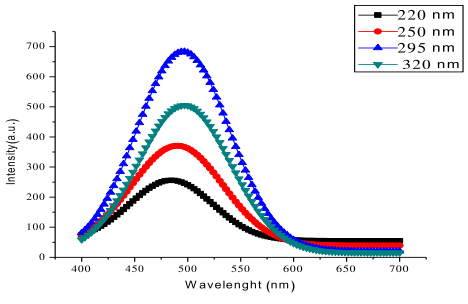

Fig. 3: The Emission spectrum of Combustion Synthesized (sample C1) ZrO_2:Ti (0.1%) λ_{exe}= 220, 250, 295, 320 nm.

8. SUMMARY AND CONCLUSION

In short, Ti doped ZrO_2 phosphor materials were synthesized by two different preparation root i.e combustion and solid state reaction method. The intensity

of PL emission spectra shows variation in both samples also we found variation in intensity as we increase the excitation energy and hence we conclude that the surface of the sample is poor in nature i.e the particles are irregular in shape and the growth is highly non-uniform.[12]

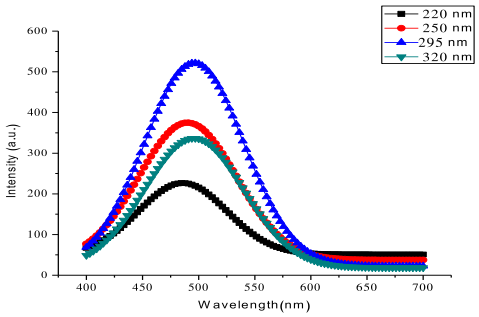

Fig. 4: The Emission spectrum of Solid State Synthesized (sample S1) ZrO_2:Ti (0.1%) λ_{exe}= 220, 250, 295, 320 nm.

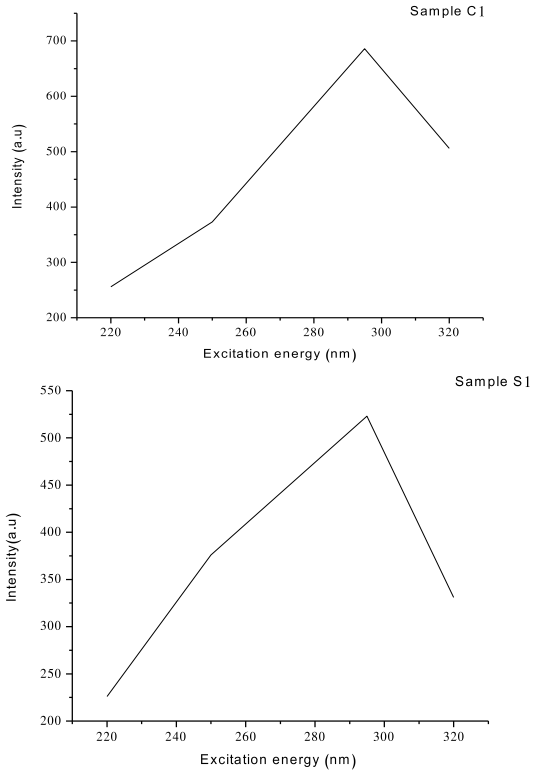

Fig. 5: Variation of intensity with excitation energy in sample C1 and sample S1.

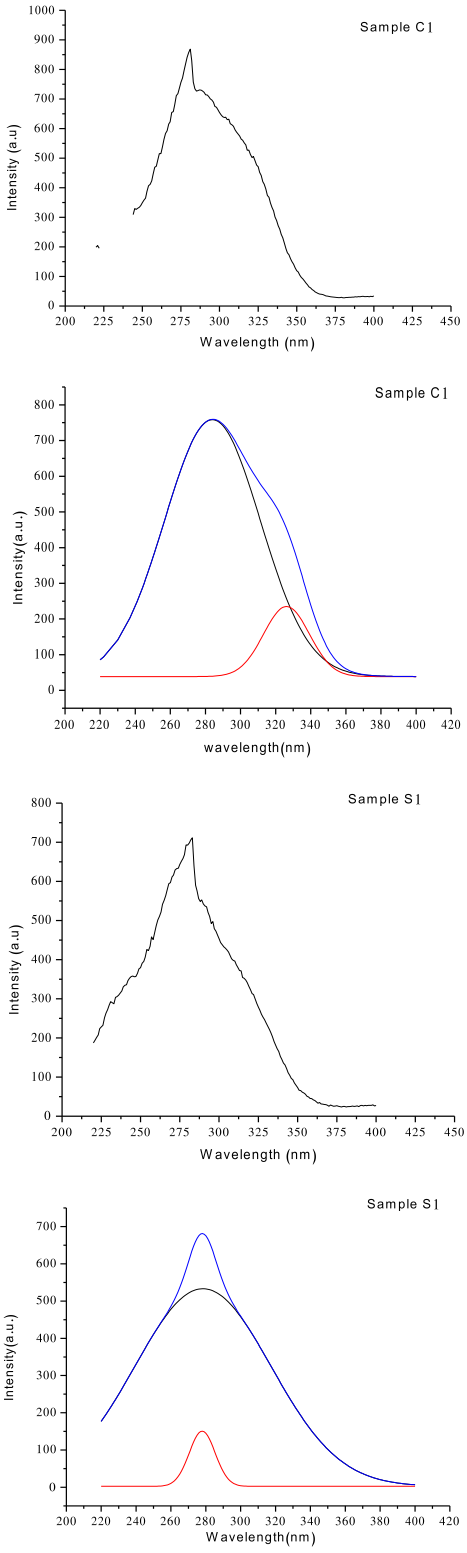

Fig. 6: The Excitation spectrum (λem= 470nm) and Gaussian component of the ZrO_2:Ti (0.1%) of sample C1 and sample S1.

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