



Photoluminescence Behaviour of Pure ZrO₂ Phosphor Prepared By Combustion Synthesis Method

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Abstract

Pure ZrO₂ is prepared by combustion synthesis method. The prepared phosphor has cubic phase which was confirmed by powder X-ray diffraction, scanning electron microscopic method. Elemental composition was determined by EDX analysis. Photoluminescence emission spectra was recorded under 235 nm excitation. The intense emission peak is present at 390 nm along with weak emissions at visible region in blue, green and red region. The visible emitted colour is identified by using CIE chromaticity programme.

Key words: ZrO₂ phosphor, combustion synthesis, X-ray diffraction, photoluminescence

1. Introduction

Photoluminescence property of phosphor material depends on various lattice defects. ZrO₂ is a very wide gap oxides with application in durable optical coatings such as high-index layers, chemical sensors etc [1,2]. ZrO₂ has three different phases monoclinic, tetragonal and cubic phase. Some useful characteristic of the pure ZrO₂ is found in stable tetragonal and cubic phase [3]. Pure ZrO₂ can show a number of different broad band photoluminescence (PL) emission depending on the preparation method and excitation wavelength [4,5]. At high temperature the oxygen becomes mobile and displaying substantial conductivity [6,7]. Due to its special characteristics and superionic properties ZrO₂ has many applications such as oxygen detector, ceramic storage heater, oxide thermistor etc [8]

In present work we have studied the synthesis of pure ZrO₂ by combustion synthesis method. The photoluminescence behaviour of the phosphor was also studied under 235 nm excitation.

2. Synthesis & Experimental detail:-

Analytical grade zirconium nitrate (Zr(NO₃)₄) purchased from sigma Aldrich was used as a precursor material for combustion synthesis of ZrO₂ phosphor material. Urea is used as fuel also purchased from sigma Aldrich. The aqueous solution of redox mixture is taken in an alumina crucible and placed in a preheated muffle furnace maintained at 400°C [9].

The X-ray powder diffraction data was collected by using Bruker D8 Advanced X-ray diffractometer using Cu K α radiation. Observation of particle morphology was investigated by FEGSEM (field emission gun scanning electron microscope) (JEOL JSM-6360). Energy dispersive X-ray analysis (EDX) was used for elemental analysis of the phosphor. Particle diameter and surface morphology of prepared phosphor determined by The PL emission spectra were recorded with a spectrophotofluorometer (SHIMADZU, RF-5301 PC), which was also used to record the excitation spectra.

2.1 Results and discussion

X-Ray Diffraction analysis:-

X-ray diffraction pattern of ZrO_2 phosphor. The observed patterns assigned to tetragonal phase and are in well agreement with JCPDS card no 81-1551 (figure 1). The average crystal size is calculated by Debye-Scherer's equation and it was found to be in the range 8-19 nm.

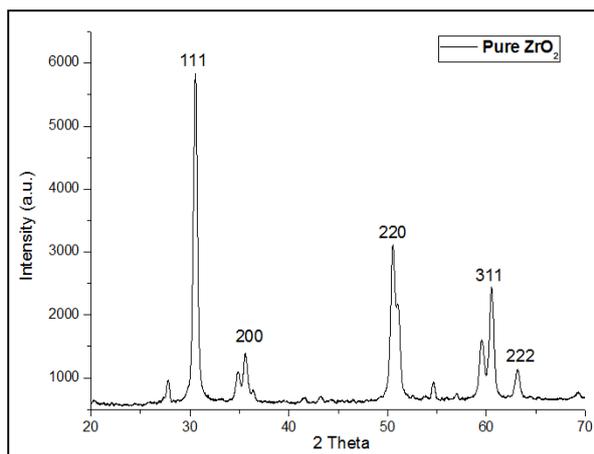


Figure 1. XRD pattern of pure ZrO_2

2.2 Scanning Electron Microscopic analysis:-

Figure 2 shows the SEM micrograph of the ZrO_2 . It shows that the particles are porous, agglomerated and irregular. The pores present in the surface are due to evolution of gases during the synthesis process.

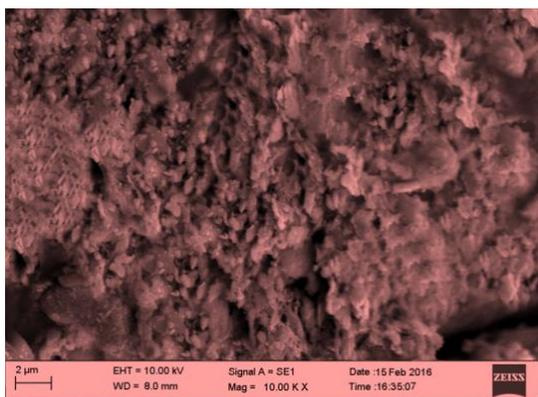


Figure 2. SEM image of ZrO_2

2.3 Energy Dispersive X-ray spectroscopy:-

EDX spectra recorded to determine the elemental composition of ZrO_2 . The spectra have peaks of Zr, O and C which confirms the formation of

ZrO_2 . The C is may be due to the carbon coated copper grid used for sample holding (figure 3).

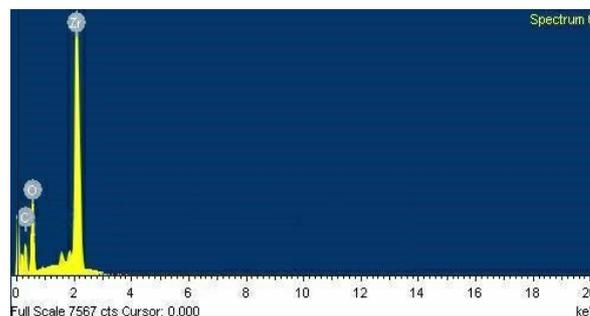


Figure 3. EDX spectra of ZrO_2

2.4 Photoluminescence (PL) studies:-

The photoluminescence emission spectrum was recorded under 235 nm excitation. The emission spectrum has peaks centred at 390, 475, 533, 588 and 610 nm. The luminescence behaviour of the ZrO_2 can be explained by using structure defect model [10]. According to this model the luminescence behaviour of ZrO_2 is due to the F-centres generated in the ZrO_2 crystal lattice due to oxygen vacancies [11].

The oxygen vacancies were generated due to the violent combustion process used in synthesis step. The emission peak at 390 is charge transfer band, which is assigned due to the transition of electron from conduction band to oxygen vacancy. The blue emission at 475 nm is due to extra oxygen vancy. The peak at 533 nm ascribed to the emission due to near band-edge transitions [12].

The red emission at 610 nm is due to transition between the 2p orbital of O to 4d orbital of Zr [13]. It may also be due to combination emission of electron and holes in oxygen vacancies in ZrO_2 [14]

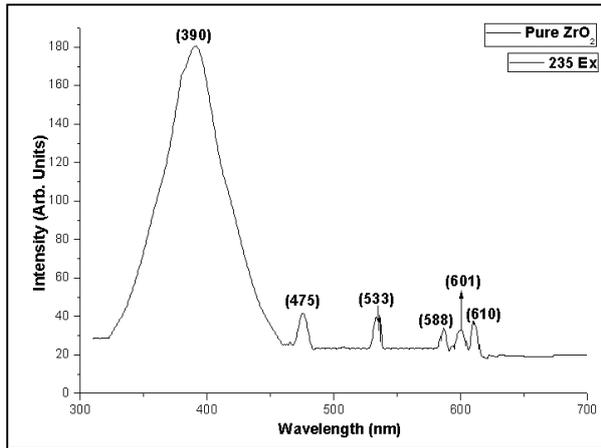


Figure 4. Emission spectra of pure ZrO₂ under 235 nm excitation

Figure 5 represents the effect of annealing on photoluminescence emission spectra. It is clear from the spectra that the emission spectrum increases after annealing. This increase in intensity is due to improved crystallinity after annealing. Due to this the surface to volume ratio decreases. Because of decreased surface area concentration of killer centres i.e. CO₂ and H₂O also decreases.

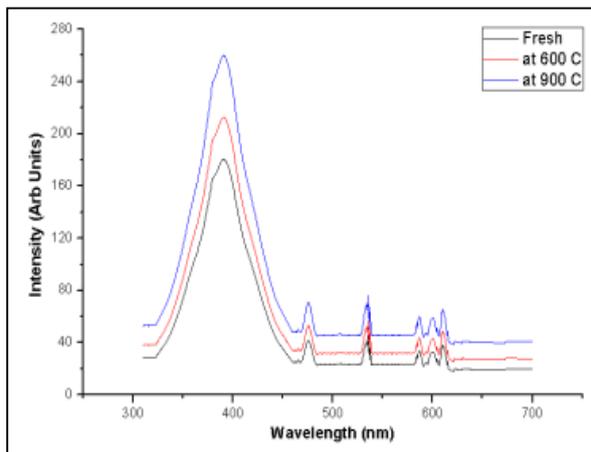


Figure 5. Effect of annealing on photoluminescence emission spectra

The emitted visible colour of the prepared phosphor is determined by CIE chromaticity diagram. The CIE coordinates X and Y have values 0.299 and 0.273 respectively which resembles with visible blue colour (Fig 6).

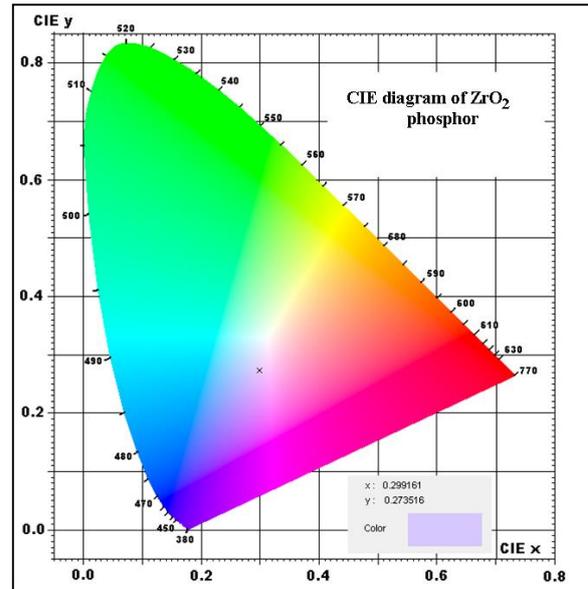


Figure 6. CIE diagram of ZrO₂ phosphor

Conclusion:

Tetragonal ZrO₂ is synthesized by using combustion synthesis method using urea as a fuel. The phosphor has crystal size around 8-19 nm and surface morphology was determined by scanning electron microscopy. Emission spectrum was recorded under 235 nm excitation which consists intense peak at 390 nm along with some weak visible emissions centered at green and red region. The overall visible emission colour determined by CIE chromaticity method is found blue.

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