HYDROTHERMAL SYNTHESIS OF SINGLE PHASE MONOCLINIC ZrO_2 NANO CRYSTALS: STRUCTURAL AND OPTICAL STUDIES

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Abstract

Single phase monoclinic ZrO_2 nano crystals prepared by hydrothermal process. The products were processed from Zirconyl Nitrate Hydrate as the precursor. X-ray diffraction, Scanning Electron Microscopy, Fourier Transform Infrared Spectroscopy, Photo Luminescence and UV are studied exhaustively. The XRD patterns reveals as prepared ZrO_2 have perfect monoclinic phase. The crystalline size is found to be approximately 9.5 nm. The average particle size displayed by the SEM is 35 nm. The observed vibrational bands at 418, 489, 733 cm confirms the monoclinic structure of as prepared ZrO_2. The PL emission spectrum excited at 246 nm consist of intense band centered at 452 nm along with four weak emission bands 482 nm, 575 nm, 608 nm, 650 nm. Band gap of ZrO_2 measured to be 4.7 eV.

Keywords: Monoclinic ZrO_2, Nano crystal, Hydrothermal, Band gap.

1. Introduction

Zirconia nano crystals have attracted very much interest recently due to their specific optical, electrical and potential properties, including transparent optical devices and electrochemical capacitor electrodes, oxygen sensors, fuel cells, catalyst [1], advanced ceramics, electronic nano devices and bio active coatings on bone implants [2]. ZrO_2 has three polymorphic phases: monoclinic, tetragonal and cubic, among these ZrO_2 phases the monoclinic structure which is thermodynamically stable below 1170°C, where control of crystalline phase and the crystalline size of its critical importance. For the synthesis of ZrO_2 nano crystals such as Sono chemical method, combustion method, sol-gel and surfactant templating method, however these processes required complicated procedures, such as sequential addition of the reagents and pretreatment of the precursors, because of the difficulty in controlling the crystal structure and size of the products. Using hydrothermal method, we can synthesis metal oxide and their corresponding nano crystals. This method enables to prepare surface modified metal oxide with nano crystalline structure. Nano sized ZrO_2 nano crystals were successfully prepared using hydrothermal method. In this case ZrO_2 was prepared with or without organic molecules as a surface modifier; the advantage of this approach is the simplicity of the process. Only Zirconyl nitrate was used as a precursor, and no other reagents were added in this procedure. The crystallization of ZrO_2 under hydrothermal conditions and the phase composition strongly depend on the solubility of the precursor in water. Greater solubility of the precursor in water results in a greater volume fraction of the monoclinic phase.

2. Experimental

The Zirconyl nitrate was used as a precursor in a hydrothermal method. The solution was prepared using the precursor (2.32 g) and distilled water (50 ml precursor concentration of 0.2 M) stirred using magnetic stirrer for

one hour. The prepared solution was placed in a Teflon inner bottle set inside a stainless steel vessel with an inner volume of 100 ml. The hydrothermal reaction was performed using an electric furnace at 200°C for 24 h. After the reaction the vessel was cooled to room temperature inside the furnace. The precipitate was centrifugated, washed with water and absolute ethanol for five times, and then dried in hot air oven at 60°C for 10 h.

X-ray diffraction analysis (XRD) was used to study the crystal phase of the samples. The XRD measurements were performed with the Cu Kα radiation (λ = 1.5406 A°) at 10°/min scanning speed in the 2θ range from 10° to 80°. Scanning Electron Microscope (SEM) micrograph is recorded using JEOL instrument. Fourier transform infra-red (FT-IR) spectra were recorded in MB 102 Spectrometer. Photoluminescence emission (PL) and excitation spectra were obtained from F4500 fluorimeter.

3. Results and Discussion

3.1 X-Ray Diffraction analysis

Fig.1 shows the XRD pattern of pure ZrO_2 nano crystal within the range of 10 to 80°. X-ray diffractogram of the material was confirmed the polycrystalline structure of the ZrO_2. It is clearly indicates the presence of monoclinic ZrO_2 (JCPDS No. 830944). The strongest peak observed at 27.9069 (-111), 31.2945(111) and 50(220). The average particle grain size of ZrO_2 was determined using Debye-Scherrer's formula and was estimated that 7 nm.

$D = 0.9 \lambda / \beta \cos\theta$

Where λ is wave length of X-ray Cu Kα radiation in Å (1.542 Å) and β is the full width half maximum in radian.

Dislocation Density is found to be 20×10^{15} m^{-2} calculated using the formula, $\delta = 1/D^2$

microstrain is found to be 5.3×10^{-3} calculated using the formula, $\mu = \beta \cos\theta/4$

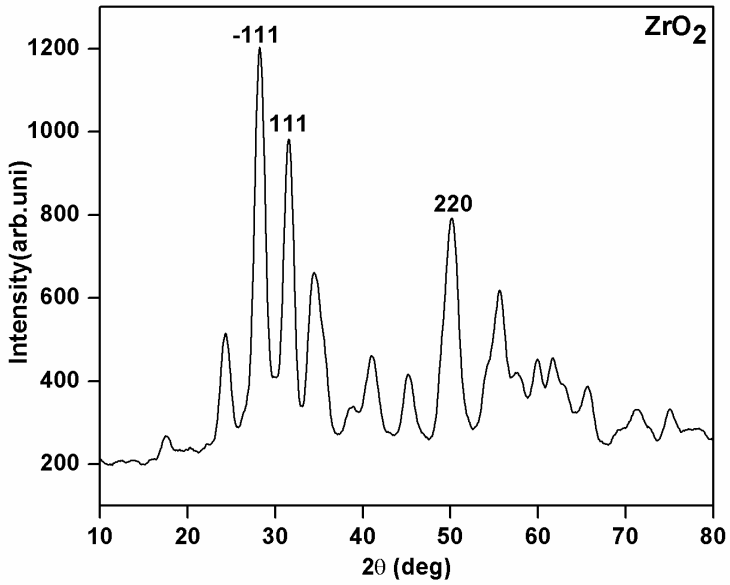

Fig.1 XRD pattern of ZrO_2 Nano Crystal

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3.2 Scanning Electron Microscope analysis

The SEM micrograph of the ZrO_2 Fig.2 shows porous, agglomerated and uniform spherical shaped particles. The voids observed can be ascertained due to the evolution of gases formed at the process of smoldering combustion. The average particle size of the ZrO_2 particles is observed to be 35 nm.

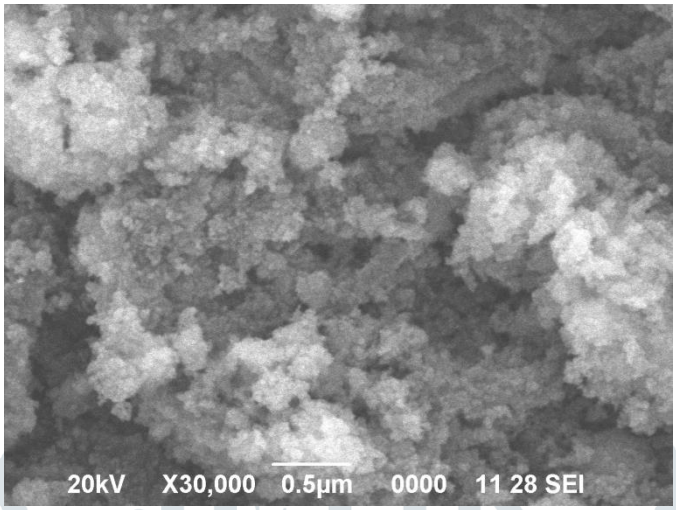

Fig.2 SEM Image of ZrO_2

3.3 Fourier transform infrared (FT-IR) analysis

FT-IR spectroscopy was used to study the surface interaction of adsorbed water in dynamic equilibrium with the gas phase on the ZrO_2 surface. Fig.3 shows the FT-IR spectra ZrO_2. The FT-IR spectra of ZrO_2 nano crystals were recorded in the range of 700 to 3500 cm^{-1}. well known that H_2O and CO_2 molecules are easily chemisorbed onto the ZrO_2 surface when exposed to the atmosphere. The dominant absorption band centered at 735 cm^{-1} is due to the deformation mode of Zr-O-Zr bond. The peaks centered at 1000 cm^{-1} and 1141 cm^{-1} can be associated to stretching vibrations of $Zr\text{-}O^-$ terminal groups [3]. Weak band centered at 1530 cm^{-1} assigned to symmetric bending of H_2O and the band at 2308 cm^{-1} is due to stretching vibrations of C-O in adsorbed $CO_2$from atmosphere. The wide band centered at 3390 cm^{-1} is ascribed to the stretching of O-H group of water. The observed vibrational bands at 418, 489, 733 cm^{-1} confirms the monoclinic structure of as prepared ZrO_2 [4,5]

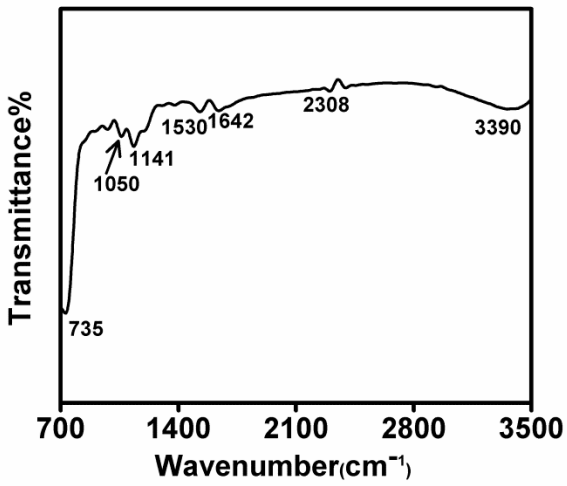

Fig.3 FTIR Spectra of ZrO_2

3.4 UV and PL analysis

Fig.4 shows the absorption spectra of the as prepared nanocrystalline ZrO_2 powder. The sharp of the absorption edge suggests a single phase. The band gap energy is calculated from the absorption spectra is 4.7 eV [6.7].

Fig.5 shows the photoluminescence emission spectra obtained from the sample under excitation wave length 262 nm. The fluorescence emission at 450 nm [8] and very weak two fluorescence emissions at 484, 576 nm could be observed respectively.

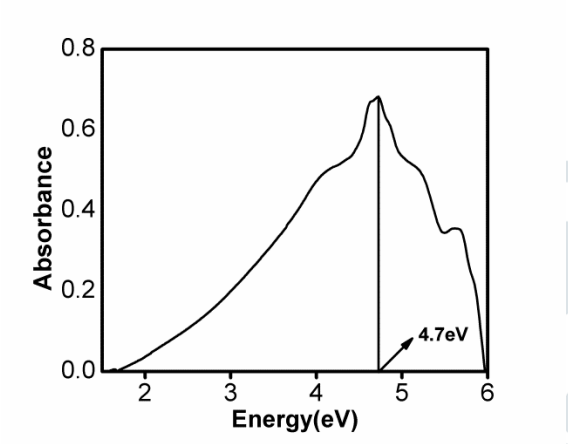

Fig.4 UV Spectra of ZrO_2

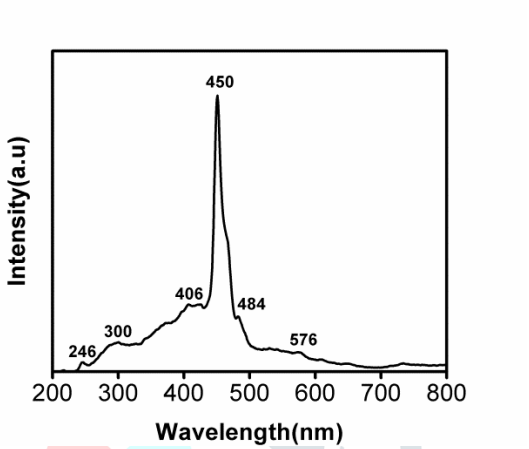

Fig.5 PL Spectra of ZrO_2

4. Conclusion

ZrO_2 nano-crystals have been successfully synthesized by simple hydrothermal method. XRD pattern indicate that the pure monoclinic phase and crystallite size is found to be 7 nm. The SEM image shows to be the average particle size is equal to 35 nm. From FT-IR the wide band centered at 3390 cm^{-1} is ascribed to the stretching of O-H group of water. The band gap is found to be 4.7 eV and two weak fluorescence bands are observed in PL.

References

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