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Variation in Morphology and Crystallinity of ZTO Ceramics

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Abstract

Higher electron mobility, interesting optical properties and their stability under extreme conditions made Zinc Stannate or zinc tin oxide (ZTO) a promising candidate for applications such as solar cells, gas sensing, photo catalysis etc. Among the different methods of synthesizing ZTO ceramics, the hydrothermal method is an attractive green process, carried out at relatively low temperatures. We report the characterisation of surfactant free hydrothermally prepared Zinc Stannate ceramics. The pH of the crystal growing medium is varied as 7, 8 and 10. The improvement of crystallinity of the samples with increase in basicity of the medium is clear from XRD (X-Ray Diffraction) results. Amorphous nature of the sample drastically changed and showed high crystalline nature while the pH of the medium increased to 10. The chemical composition of the samples was confirmed via EDS (Energy Dispersive Spectra). The pH variation has a prominent effect on the morphology of the sample. Perfect cubic shaped particles were observed for high pH sample in the SEM (Scanning Electron Microscopy) images. Diffuse reflectance spectra analysis showed that the UV absorption characteristic is also improved with the increase in basicity of the medium.

Keywords: Morphology, zinc stannate, crystallinity, basicity, hydrothermal.

Introduction

The immense interest in ternary oxide semiconductors such as cadmium stannate (CTO), and zinc stannate, often called zinc tin oxide (ZTO) etc. is due to the urgent need for novel functional materials to fulfill the requisites of the emerging material world. ZTO is well known for having high electron mobility, high electrical conductivity, and attractive optical properties that makes it suitable for a wide range of applications in solar cells, sensors for the detection of humidity and various combustible gases [1-6], negative electrode material for Li-ion battery and as photocatalyst for the degradation of organicpollutants[7–14]. ZTO has been successfully used as flame retardant and smoke suppressant[15]. The control of sizes and shapes of crystal structures is crucial as it may affect their electrical and optical properties[16–20]. The physical properties of ZTO depend on the method used for synthesis. Hydrothermal growth is an attractive and relatively simple method, since crystal growth occurs at mild temperatures and pressure. This method is becoming one of the most important tools for advanced material processing, particularly owing to its advantages in the processing of materials for a wide variety of technological applications such as electronics, optoelectronics, catalysis, ceramics and biophotonics. We report the variation of morphology and crystallinity of hydrothermally synthesized ZTO with the variation of pH of the precursor solution from7 to 10.The crystalline nature was studied using XRD and the morphological studies were carried out by SEM. The absorption characteristics were analysed by using UV-Visible spectroscopy. With the help of Energy Dispersive Spectra(EDS), the chemical composition was confirmed.

Materials and Methods

Zinc stannate particles were synthesized by low temperature hydrothermal method. 0.1M of $Zn(CH_3COO)_2.2H_2O$~99.9% purity and 0.1M of $SnCl_4.5H_2O$~99.9% purity in the ratio 60:40 were added to 80 ml of doubly distilled water to obtain a milky white solution. The desired pH was achieved by the controlled addition of KOH (1M) solution. The mixture was then transferred to a Teflon-lined stainless steel autoclave and fired in a hydrothermal furnace at 150^{o}C for 3 hours. After the reactions, the sample was cooled naturally to room temperature, the solid products were separated from liquid phase via centrifugation and washing with de-ionized water to remove trace impurities. Then, the final products were dried at 100^{0}C for 1 hour.

Results and Discussion

The crystallinity and structure of the synthesised samples were analysed by XRD recorded using Rigaku Miniflex 600 machine with Cu Kα radiation (1.5406 A^{o}). The intensity data was collected over a 2θ range of 10-90°. Figure-1 and 2 show XRD pattern of zinc stannate ceramics grown at pH 7 and 8 respectively. Both the figures indicate that the samples are not perfectly crystalline. But the prominent peak of zinc stannate is seen at 2θ of 33° corresponding to the (020) plane of zinc stannate. The crystallinity of the sample got improved when pH increases from 7 to 8.When the pH was further increased to10 (Fig.3) the perfect crystalline nature of the sample can be observed. All the peaks obtained are in well agreement with the ICDD database of zinc stannate (01-078-3428). Trace amounts of Sn_3O_4 were also observed from the XRD. In the course of hydrothermal growth, a hydrated form of zinc stannate develops at approximately 120–150°C, called zinc hydroxyl stannate $ZnSn(OH)_6$ or ZHS. It is reported that the transformation of ZTO from the precursors starts with the formation of ZHS followed by ZTO[20]. When KOH is used as the mineraliser, the hydroxyl (OH−) ions get consumed, favouring the formation of ZHS. The yield of pure ZTO can be increased through optimization of KOH concentration, reaction time, temperature, and other parameters.

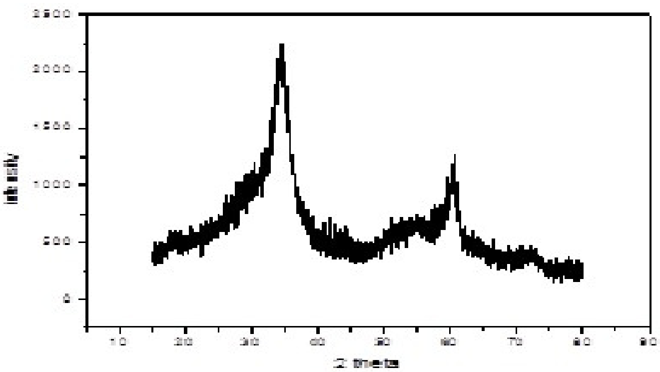

Figure-1
XRD Spectrum of sample with pH7

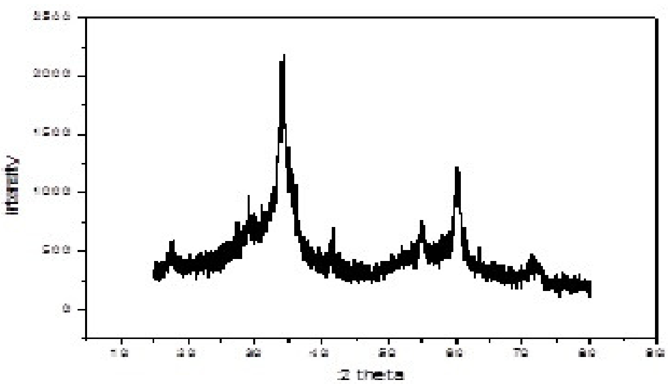

Figure-2
XRD Spectrum of sample with pH8

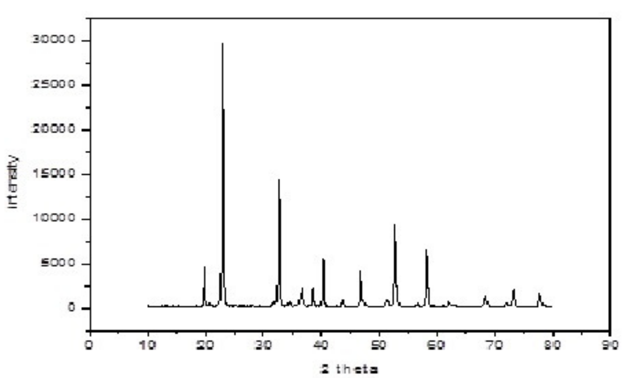

Figure-3
XRD Spectrum of sample with pH10

Figure-4, 5 and 6 show the SEM images of the zinc stannate samples prepared at pH 7,8 and 10 respectively. This is in complete agreement with the XRD results. Highly uniform cubic shaped particles were obtained at a precursor pH of 10. The minimum size of the particles is found to be ~707nm for this sample.

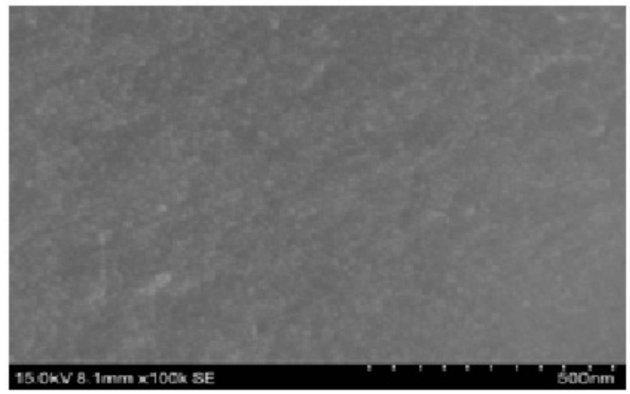

Figure-4
SEM micrograph of sample with pH7

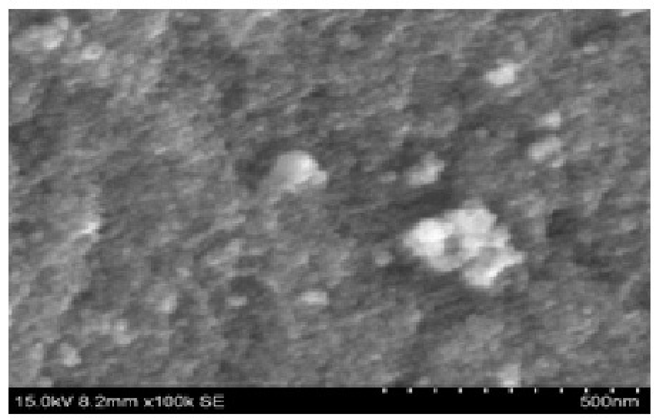

Figure-5
SEM Micrograph of sample with pH8

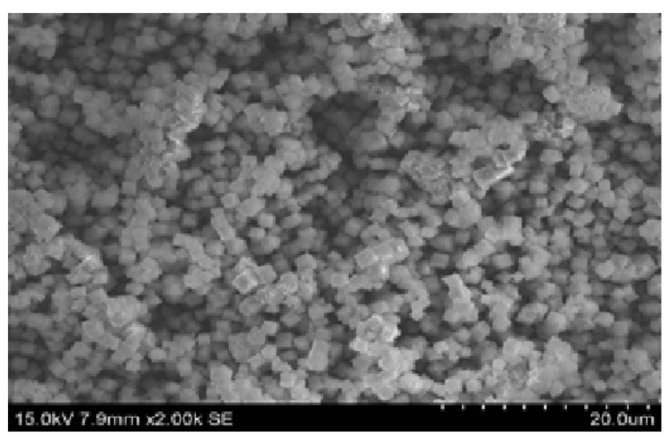

Figure-6
SEM Micrograph of sample with pH10

The UV-Visible spectra of the samples are shown in figure-7. It is seen that all the samples have high absorption in the ultraviolet region. The variation of absorbance with the pH of precursor is investigated. It is noted from the figure that sample prepared at pH 10 has high UV absorption as compared to other samples. This result leads us to suggest ZTO as a good candidate for UV absorption. The protection against harmful UVA (320–400 nm) and UVB (280-320nm) radiation is very important. The sunscreens used for the protection of human skin against the harmful effects of solar radiation must contain UV-absorbing substances like ZTO.

The chemical composition of the samples was confirmed with the help of Energy Dispersive Spectra. Figure-8, 9 and 10 indicate that the prepared three samples are pure zinc stannate.

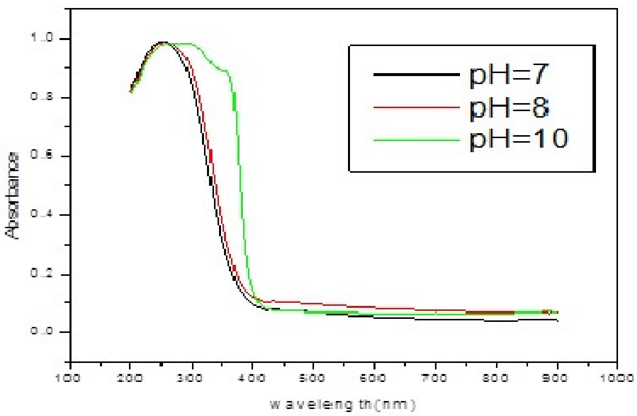

Figure-7
Comparison of UV absorption spectra of samples with pH7,8 and 10

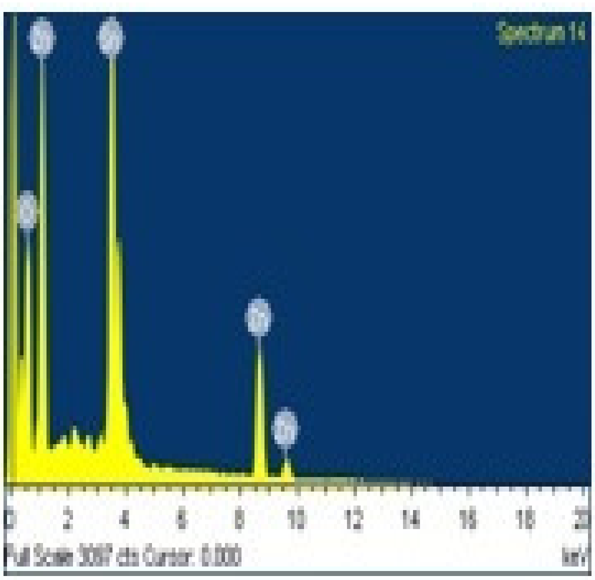

Figure-8
EDS Spectrum of sample with pH7

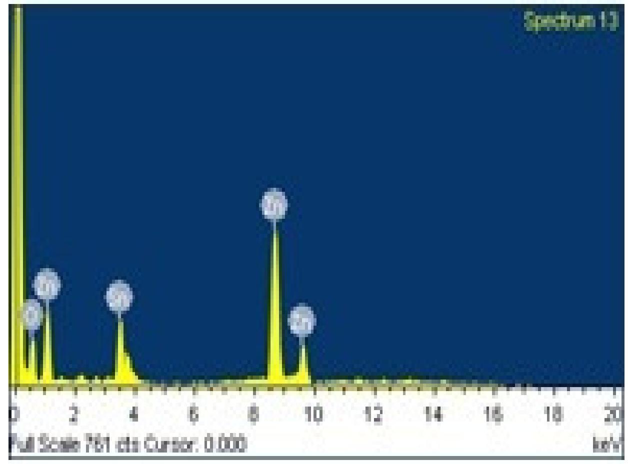

Figure-9
EDS Spectrum of sample with pH8

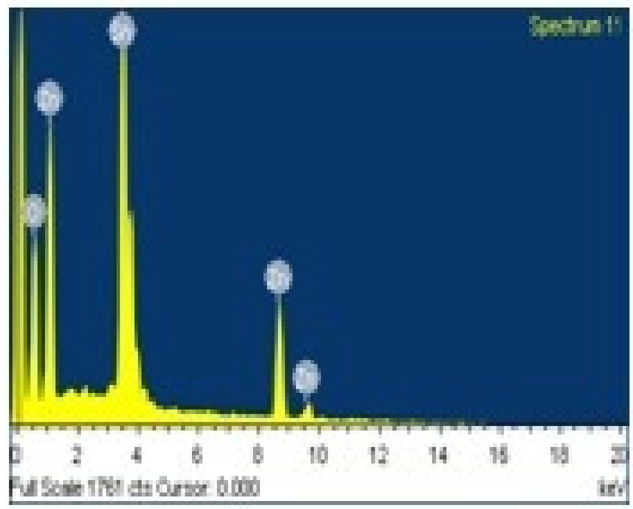

Figure-10
EDS Spectrum of sample with pH10

Conclusion

In this work, we have synthesized zinc stannate ceramics via low temperature hydrothermal method in the precursor pH range 7-10. The XRD result shows that the crystalline nature of products is well influenced by the pH of precursors. The SEM results are also in agreement with the XRD results. The morphology of the samples get improved with increase in pH of the medium. Uniform arrangement of cubic shaped particles was observed at pH 10. The chemical composition is confirmed by the EDS. The UV absorption characteristics of the sample are found to increase with the basicity of the precursor medium. It is obvious from this study that a pH of 10 is appropriate for the synthesis of highly crystalline uniform cubic shaped zinc stannate particles with high UV absorbance. This work can be extended for further applications such as gas sensing and photo catalysis.

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