Synthesis and Characterization of Nano Structured Zinc(II) Cysteine Complex Under Ultrasound Irradiation

Abstract

Cysteine and zinc oxides are important materials that have a wide range of applications especially in biomedical sciences. In this study, synthesis and characterization of nano structured Zn(II) complex of cysteine, 2-amino-3-mercuptonoic acid, has been investigated. The reaction of Zinc(II) acetate and KI with cysteine ligand under ultrasonic irradiation, leads to the formation of nano sized Zn(II) cysteine complex. The hexagonal micro crystalline zinc oxide, has been prepared using Zn(II) cysteine complex as precursor. Characterization of the Zn(II) complex, has been performed using elemental analysis, FTIR spectroscopy, energy dispersed X-ray analysis (EDAX), scanning electron microscopy (SEM) and thermal analysis (TG/DTA) and gel-permeation chromatography analysis (GPC). Based on the results chemical formula for the Zn(II) cysteine complex is proposed as $[ZnI_2(C_3H_5NO_2S)]_n$. Scanning electron microscopy (SEM) analysis has demonstrated hexagonal nano particles Zn(II) complex with average diameter of about 38-54 nm. Hexagonal ZnO micro structures were characterized by FTIR, X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray (EDAX) techniques.

Keywords: Zn(II) complex, zinc oxide, sonochemical method, cysteine ligand

Introduction

Cysteine is known to act as an active site in bio performance of the enzymes known as cysteine protease. Many cysteine containing natural products exhibit important biological activities [1]. It is used in some antibiotics for the treatment

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of skin damages and as a radio protective agent. It is also involved in the structure of vasopressin as anti diuretic hormone [2]. Cysteine synthesis in plants represents the final step of assimilatory sulfate reduction and the almost exclusive entry reaction sulfur into metabolism not only of plants, but also the human food chain in general. It is accomplished by the sequential reaction of two enzymes, serine acetyltransferase (SAT) and O-acetylserine (thiol) lyase (OAS-TL) [3]. Metal Complexes continue to find applications in the treatment of a wide variety of human ailments. For example, in medical imaging, gadolinium (III) complexes are used in MRI as contrast agents while ^{99}TC complexes are employed as cardiovascular imaging dyes [4,5]. Recently Mercury (II) complex with L-Cysteine in alkaline aqueous solutions have been structurally characterized by means of extended X-ray absorption fine structure spectroscopy [6]. Transition metal-cysteine complexes have considerable biological activities; some of their antitumor properties show promise in therapeutic applications.[7]. Mamdouh S. Masond et al. has been investigated the formation of the stable complexes with [S,O] coordination mode that has been characteristic for cobalt(II), zinc(II), and cadmium(II) ions [8].

In recent years, nano structured compounds have witnessed an increasing interest in both fundamental and technological applications [9,10]. Considerable efforts have been dedicated to the controlled synthesis of metal oxides, sulfides and ceramic materials with micron and nano scale dimensions. A review in the literature showed that among various methods for preparing nano scale materials, sonochemistry has attracted much attention [11-15]. A.Morsali's research team has succeeded in preparing different kinds of metal oxide such as PbO, Mn_3O_4, MgO, HgO, $BaCO_3$ under ultra sonic radiation and or using metal complexes, as precursors [16-19]. Recently, zinc oxide (ZnO) has attracted much attention within the scientific community as a future material. ZnO has been widely studied since 1935 [20]. The renewed interest in this material has arisen

out of the development of growth technologies for the fabrication of high quality single crystal and epitaxial layers, allowing for the realization of ZnO-based electronic and optoelectronic devices [21].

The aim of the present work is to synthesizes new Zn(II) cysteine complex in nanosized particle size, because of its potential important application in biomedical field. The present work also describes the synthesis of ZnO with predictable morphology from thermal decomposition of Zn(II) cysteine complex as precursor.

Experimental

All reagents and solvents for the synthesis and analysis were commercially available and were used as received. A multiwave ultrasonic generator (UP 400 Germany), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 24 kHz with a maximum power output of 400 W, was used for the ultrasonic irradiation. The ultrasonic generator automatically adjusts the power level. FTIR spectra (400-4000 cm^{-1}) were recorded on a Bruker tensor 27 spectrometer in a KBr matrix. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer and Atomic absorption, Py unican Philips, Ion Analyzer Jenway, for I^- measurement. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. X-ray powder diffraction (XRD) measurements were performed with monochromatized CuK_α radiation using a Philips diffractometer manufactured by X'pert. Crystallite sizes of selected samples were estimated using the Sherrer method. The samples were gold coated for characterization with a scanning electron microscope. Thermo gravimetric analysis was carried out using a pyres Diamond instrument. The Compound was heated in a static atmosphere of nitrogen from 10-600 $^\circ$C, with a heating rate of 10 $^\circ$C/min. Gel permeation chromatograms were measured on a

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Waters GPC system consisting of an isocratic pump, solvent degasser, column oven, 2996 photo diode array (PDA) detector, 2414, refractive index detector, 717plus autosampler and a Styragel HT 4 GPC column with precolumn installed. Linear PMMA standards were used for calibration. The solvent was DMF containing 5 mmol/L NH 4 PF 6 . The flow speed was 0.5 mL/min.

Synthesis of nano-structured Zn(II) cysteine complex

Zinc acetate (0.109gr, 0.5 mmol) and cysteine ligand (0.06gr, 0.5 mmol) were mixed in double distilled water (10ml) and the mixture was stirred at 80 °C for 5 min, and the solid KI (0.116 gr, 1mmol) was placed in an ultrasound vessel. Then the mixture after one hour yielded a white powder upon cooling to room temperature. This was then separated by centrifuging at 4000 rpm for 15 min and washed with double distilled water and acetone successively.

0.14 g of the product and 15 ml double distilled water was placed in 50 ml autoclave. After 48 h at 150˚C, the autoclave was immersed in 4˚C water. The suspension formed was centrifuged at 4000 rpm for 15 min. The precipitate was washed and dried at room temperature. The resulting white powder indicated a 77% yield of $[ZnI_2(C_3H_5NO_2S)]_n$, Dec.P: 230-232 ˚C. Anal. Calcd for (ZnI_2 $C_3H_5NO_2S$): Zn, 14.92; C, 8.21; H, 1.14; N, 3.19; I, 57.92. Found: Zn, 14.6; C, 8.14; H, 1.24; N, 3.17; I, 58.12. FTIR (KBr) 3247(b), 1596(s), 1401(w), 1304(w), 1110(w), 984(w), 643(w), 575(w). M_n (GPC) = 19400 $g.mol^{-1}$, PDI (GPC) = 1.15; Mw = 22500 $g.mol^{-1}$

Synthesis of ZnO micro particles

In order to prepare the ZnO micro particles, the white powders of the Zn(II) cysteine complex was calcinated at 600 °C for 2 hours, under ambient atmospheric condition. The product was separated by centrifuging at 4000 rpm for 15 min and was washed with double distilled water and acetone successively.

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The product was characterized with FTIR, UV-Vis spectroscopy, scanning electron microscopy (SEM), energy dispersive X-Ray (EDAX) and X-Ray powder diffraction (XRD*).*

Results and discussion

Reaction between cysteine ligand, 2-amino 3-mercuptonoic acid, with mixture of Zn(II) acetate and potassium iodide led to the formation of the new Zn(II) cysteine complex (Scheme I) in 77% yield. The resulting cysteine complex was insoluble in H_2O and DMSO. The first step to check the purity of the new cysteine complex was a melting point measurement, which was quite different from starting materials indicating a new product formation. Elemental analysis for Zn, I, C, N, H and O values and GPC results indicated that the chemical formula of the product can be $[ZnI_2(C_3H_5NO_2S)]_n$. A comparison between FTIR spectrum of free cysteine ligand and its Zn(II) complex, revealed that a distinct carbonyl peak υ(COOH) around 1608 cm^{-1} in free cysteine, has been shifted to 1595 cm^{-1} and the weak vibration mode due to υ(SH) at 2547 cm^{-1} disappeared. It is quite likely to be due to the coordination link of O and S atoms to Zn(II) metal ion. The peaks at 3417 cm^{-1} indicated the presence of free $\upsilon(NH_2)$. The IR spectra of ZnO showed characteristic bands in the region from 680 up to 434 cm^{-1} [13]. The morphology of the Zn(II) cysteine complex was examined by SEM . Typical SEM image is shown in Fig. 1 shows hexagonal nano crystals with about 54 nm. After hydrothermal treatment in autoclave the particle size reduced up to about 38 nm (Fig 2). Of substantial significance is the fact that the results show that the product is stable in aqueous solution under super critical condition. The energy dispersive X-ray analysis (EDAX) both of the Zn(II) cysteine complexes, confirm the existence of zinc and iodide (Fig 3) . Zinc oxide hexagonal particles has been prepared from the calcination of the polymeric Zinc(II) complex at 600 °C under ambient air atmosphere after 2 hours, Fig. 4 shows the SEM

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photograph of ZnO. The energy dispersive X-ray analysis (EDAX) indicated the yield of ZnO to be 100%, (Fig 5).

The X-ray powder diffraction (XRD) pattern of the as-prepared sample is shown in Fig. 6. The XRD pattern is consistent with the reflections of pure ZnO without any impurity, that can be indexed well to hexagonal wurtzite (hexagonal) ZnO diffraction can be indexed to wurtzite (hexagonal) structured ZnO (space group $P6_3mc$; JCPDS No. 36-1451) the sharp diffraction peaks are due to high crystallinity of ZnO obtained. Additionally, the EDAX image of the hexagonal micro crystals (Fig. 7) confirmed the XRD results.

Thermal gravimetric (TG) and differential thermal analysis (DTA) were carried out between 10 to 600 °C in a static atmosphere of nitrogen (Fig. 7). Decomposition of the compound starts from 79 °C. Between this temperature and 372 °C removal of the ligands occurs. At higher temperature more than 550 °C residue compound, probably Zn, was decomposed. Complex start to decompose at 231 °C. TG curve exhibits two distinct decomposition stages between 231 to 372 °C with a mass loss of about 55%.

Conclusion

A new Zn(II) cysteine and iodide complex, has been synthesized by sonochemical method and the complex has been found to be stable under hydrothermal treatment in autoclave. Based on the results the proposed chemical formula is $[ZnI_2(C_3H_5NO_2S)]_n$. The complex has been characterized by elemental analysis, FTIR, scanning electron microscopy (SEM) and EDAX and thermal analysis (TG/DTA). Calcination of the complex was produced hexagonal ZnO micro structures. The complex was shown to be nano sized and hexagonal in structure. This study demonstrates that the Zn(II) cysteine and iodide type of nano-sized polymeric complex may be a suitable precursor for preparation of

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zinc oxides with interesting morphologies. The importance of this method of synthesis is that it not only produces good yield but also it does not require high temperatures or high pressures. The products obtained by this synthetic method may turn out to be good candidates for specific industrial and biomedical applications.

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Caption of Scheme and Figures:

Scheme I. Materials produced and synthetic methods.

Fig. 1 SEM photograph of Zn(II) cysteine complex.

Fig. 2 SEM photograph of Zn(II) cysteine complex after hydrothermal treatment.

Fig. 3 Energy-dispersive X-ray analysis of Zn(II) cysteine complex.

Fig. 4 SEM photographof ZnO (produced by calcination of the Zn(II) cysteine complex in air atmosphere).

Fig. 5 Energy-dispersive X-ray analysis of hexagonal ZnO micro particles.

Fig. 6 XRD pattern of the ZnO.

Fig. 7 TG/DTA diagrams of Zn(II) cysteine complex.

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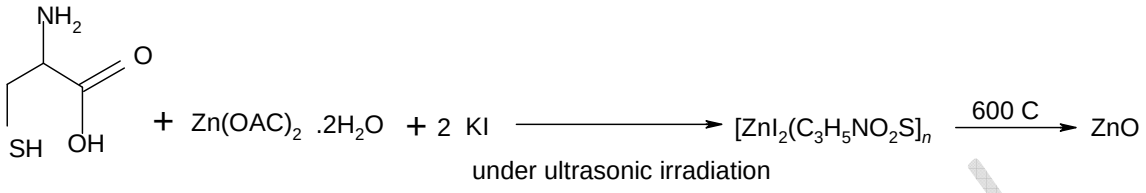

Scheme I

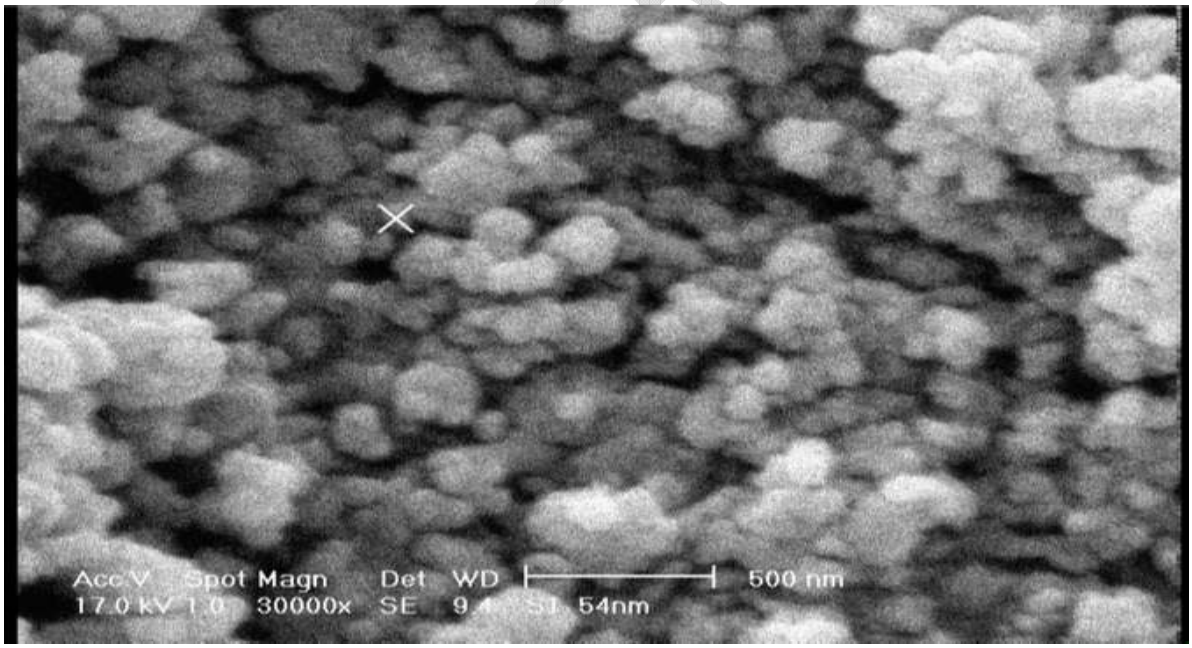

Fig. 1

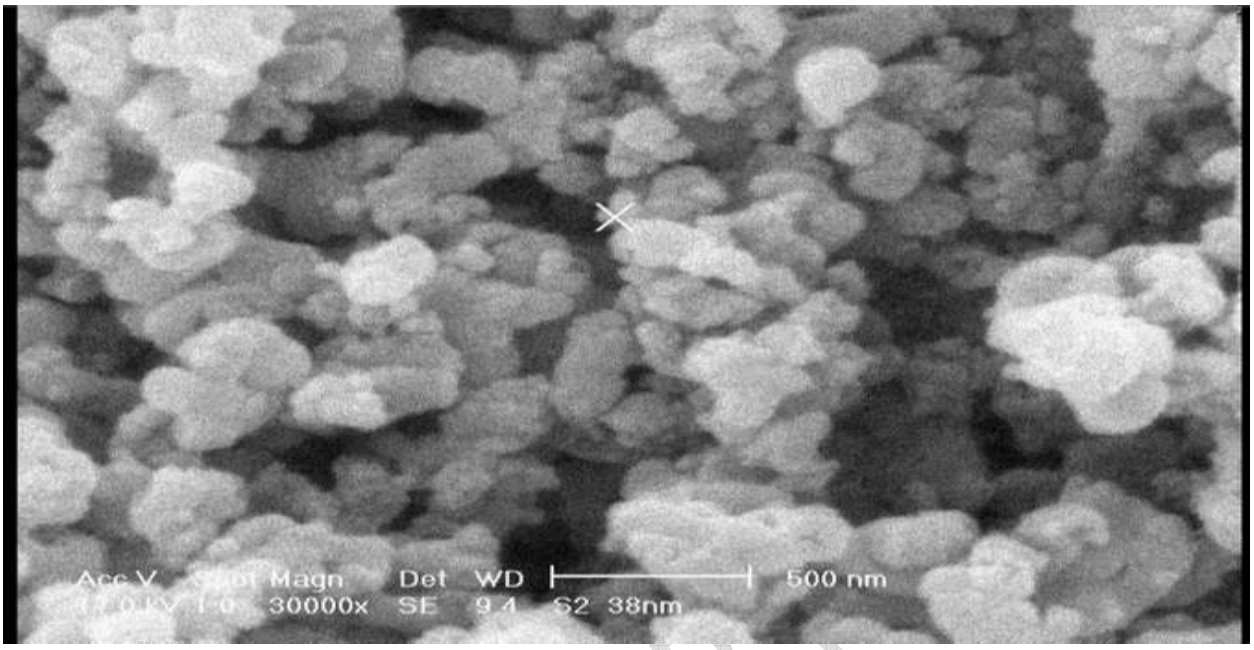

Fig. 2

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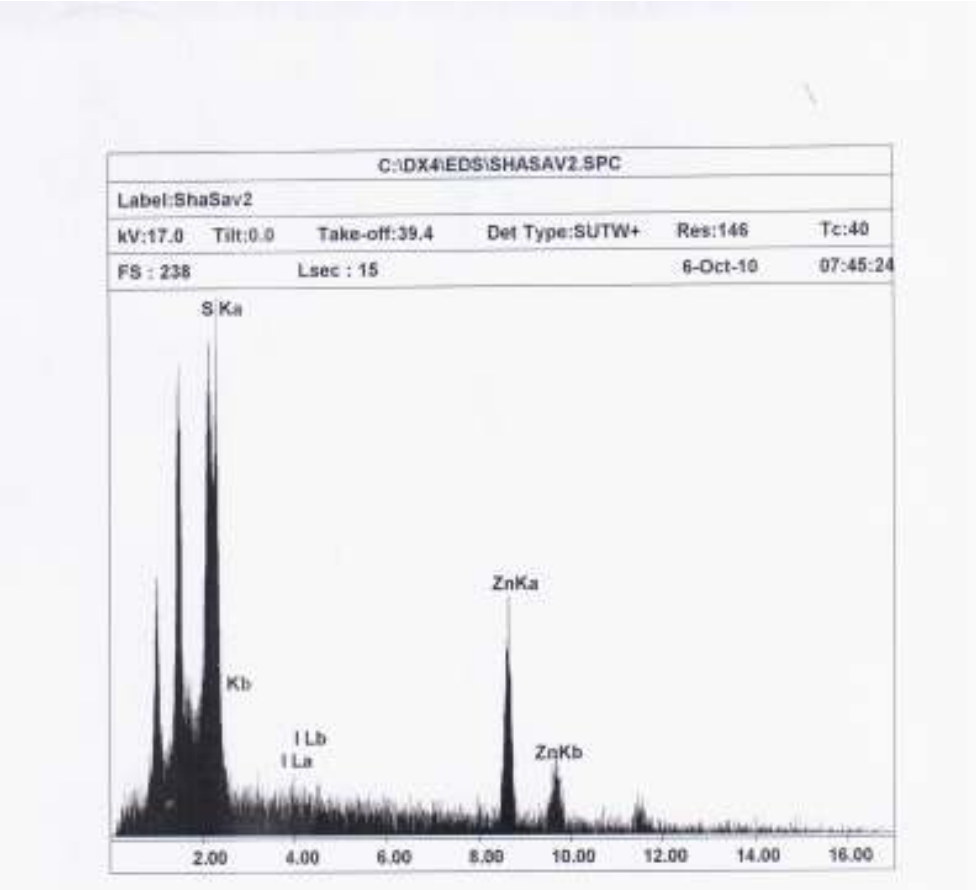

Fig. 3

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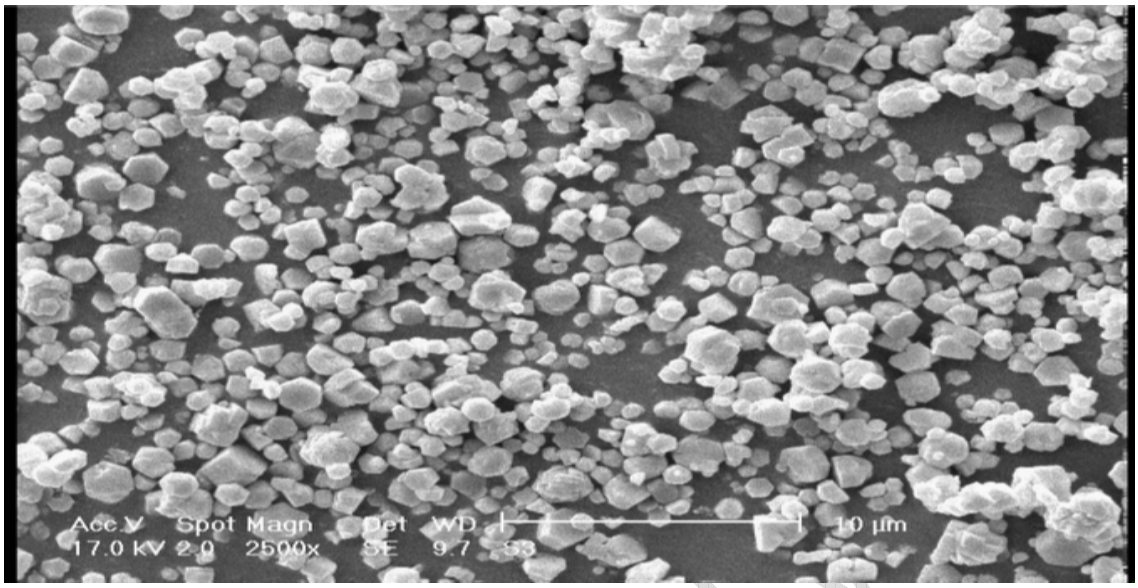

Fig. 4

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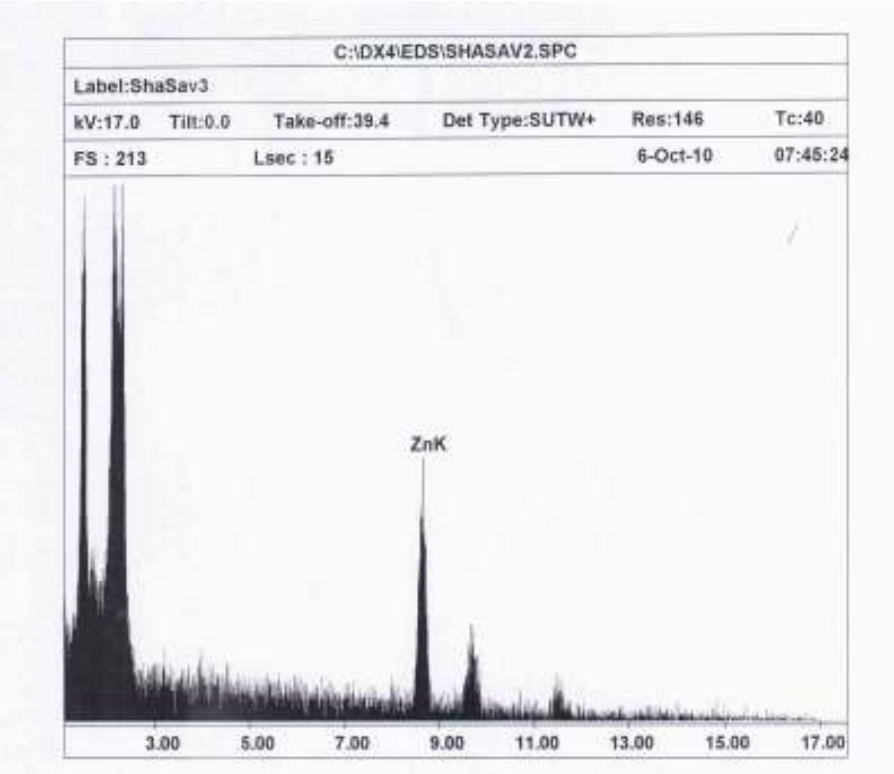

Fig. 5

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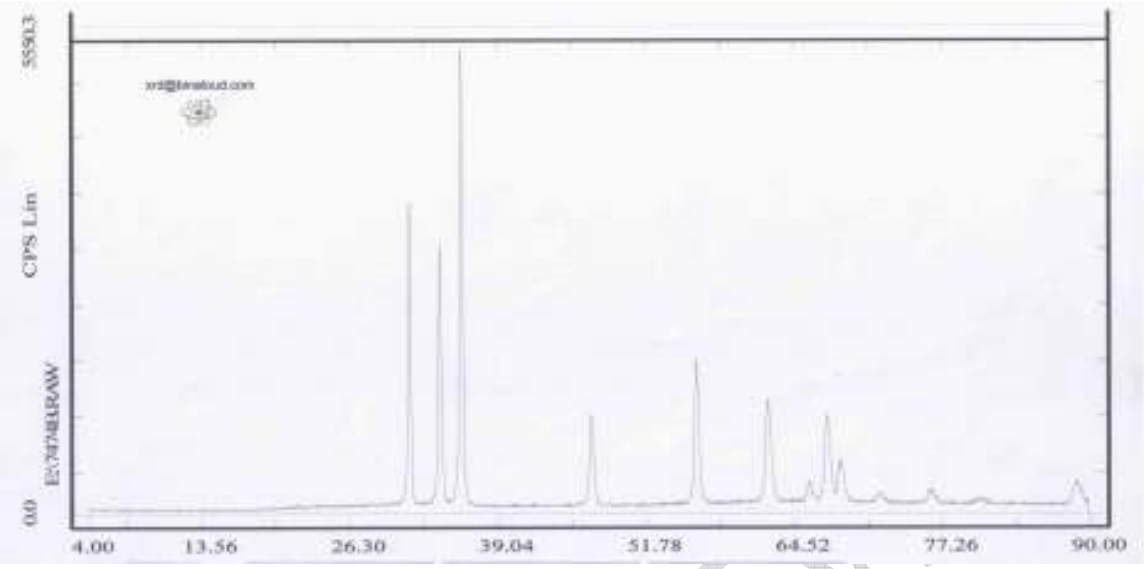

Fig. 6

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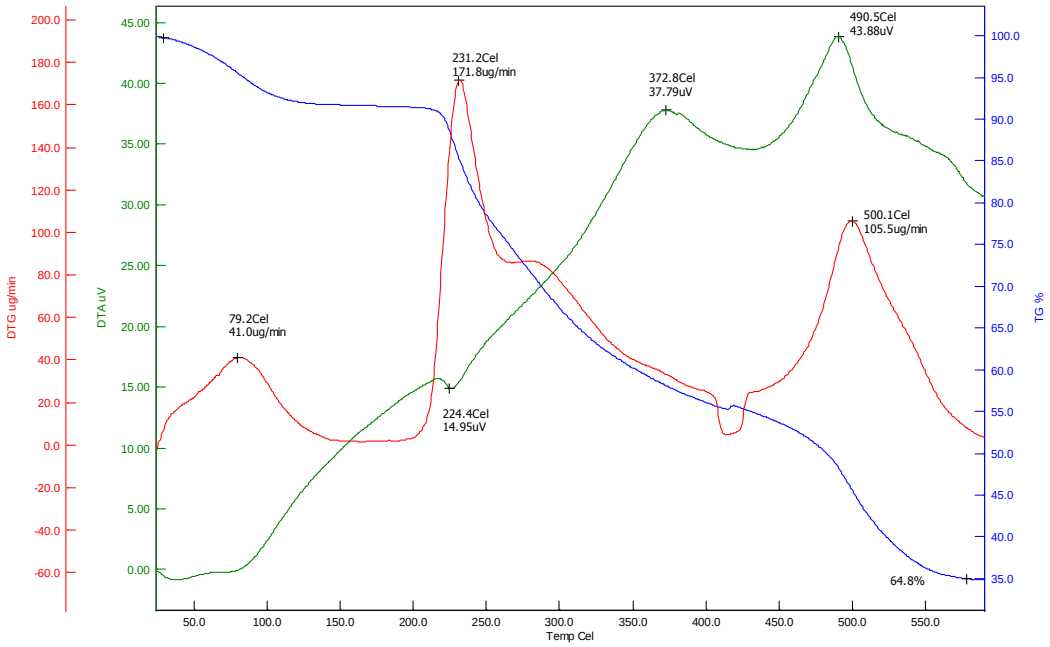

Fig. 7

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