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Growth and Physical Properties of Pure and Potassium Iodide Doped Zinc Tris Thiourea Sulphate Single Crystals

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ABSTRACT
Nonlinear Optical Single crystals of undoped and potassium iodide doped zinc tris thiourea sulphate (ZTS) were grown from aqueous solutions by slow evaporation method at ambient conditions. The dielectric studies revealed that the dielectric constant is relatively higher in the low frequency region and lower (~ 226 and ~ 221) in the higher frequency region. The information on the quality of samples and smoothness of the crystal surface without having any defects are provided by the scanning electron microscopy results. The grown crystals act as window in the visible regions which is confirmed by PL studies. The estimated energy band gap of the pure and doped crystals is 2.67 eV and 2.69 eV. The values of elemental content of the grown crystals were measured by EDAX technique. The results suggest that the material is highly suitable for the fabrication of Photonic devices.
Keywords: Nonlinear optical single crystals; SEM; EDAX analysis; PL Studies; Dielectric studies

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I. INTRODUCTION

In the recent years, metal organic nonlinear optical materials have attracted much attention because of their potential applications in the fields of laser technology, data processing, optical storage technology, optical communication, colour displays, optical switching and optical computing [1-6]. The last four decades, researchers have been taken extensive effort to develop new organic, inorganic and semiorganic nonlinear optical (NLO) single crystals. The material selection not only depends upon the laser conditions but also on the physical properties of the crystals such as surface morphology, dielectric nature and optical transparency [7-10]. Zinc Tris thiourea sulphate (ZTS) is a good engineering material for second harmonic generation (SHG) device applications and laser tuned experiments was extensively investigated by Ushasree et al [11] and Rajasekaran et al [12]. Tapati et al [13] have reported the crystal growth kinetics and characterization of ZTS. Crystal growth, structural, spectral and mechanical studies of pure and KI doped ZTS single crystals have been reported recently in our earlier communication [2].The present investigation deals with the effect of potassium iodide addition on crystal growth and physical properties of zinc tris thiourea sulphate single crystals. The synthesis of pure and KI doped zinc tris thiourea single crystals, characterization of the grown single crystals by SEM, EDAX, PL and dielectric studies are reported in this paper.

II. EXPERIMENTAL DETAILS

Pure and potassium Iodide doped ZTS single crystals have been grown by low solvent evaporation method at ambient temperature according to reaction (1) [14]. The analar grade zinc sulphate ($ZnSO_4·7H_2O$) and thiourea ($CS[(NH_2)_2]$) were taken in the molar ratio 1:3 and were dissolved in de-ionized (DI) water. After three hours, the saturated homogeneous solution was prepared by using magnetic stirrer. The saturated solution was filtered with help of whatmann filter paper in order to increase the purity of the solution. This saturated homogeneous solution was kept in a glass vessel covered with perforated filter paper and kept unperturbed place for slow evaporation. The well defined transparent colourless ZTS crystals were harvested in a time period of about 15 days.

$$ZnSO_4·7\,H_2O + 3CS\,[(NH_2)_2] \rightarrow Zn\,[CS\,(NH_2)_2]_3·SO_4 \longrightarrow \quad (1)$$

KI doped ZTS crystals were also grown by adding 1 mol % of potassium iodide in ZTS solution according to the above reaction. Good quality and well transparent single crystals were harvested at the end of 20th day. Grown crystals were subjected to various characterisation viz., Scanning Electron Microscopy (SEM), Energy dispersive X-ray (EDAX) analysis, PL Studies and Dielectric studies. The as grown pure and KI doped ZTS single crystals are shown in Fig. 1(a) and 1(b) respectively.

III. RESULTS AND DISCUSSION

3.1Dielectric Studies

The rectangular single crystals of pure and KI doped ZTS with dimension of thickness 2.42 x 2.32 mm^2 and area of cross section 14.63 mm^2 and 17.53 mm^2 is subjected to dielectric studies by using HIOKI 3532-50 LCR HI Tester. The capacitance and dissipation factor are measured by forming parallel plate capacitor with copper disc electrodes and grown materials as dielectric medium in the frequency range from 10^3 Hz to 1 MHz. The dielectric constant of the materials was estimated by using the relation,

$$\varepsilon_r = cd/A\varepsilon_0 \longrightarrow (2)$$

where, d is the thickness of the sample, A is the area of cross section and ε_0 is the permittivity of free space (8.85 X 10^{-12} N m^2 C^{-2}). Frequency dependence of dielectric constant of pure and KI doped ZTS single crystals are shown in figures 2 and 3. The dielectric constant of pure and KI doped ZTS crystals are found to decrease exponentially with increasing frequency and attain the lower values at different temperatures. This decrease in dielectric constant at high frequencies may be attributed to the contribution of the electronic, ionic, orientational and space charge polarizations [15, 16]. The contribution of all the four kinds of polarizations is active at lower frequencies. The lower value of dielectric constant of the crystals at higher frequencies is considered to be important for the construction of photonic and nonlinear optical devices [17].

The graph plotted between the log frequency and dielectric loss is shown in figures 4 and 5. The dielectric loss of the grown materials is low at higher frequencies indicate that the frequency of the electric field is equal to the natural frequency of the bounded charge. This will lead to the oscillation of the molecules with higher energy. The dipole energy is quickly dissipated due to the presence of damping forces in solids. The measured dielectric loss of the grown materials is relatively low at higher frequencies because the frequency of the electric wave is not equal to that of the natural frequency of the bound charge. Due to dipole rotation, the grown materials possess low dielectric loss at higher frequencies. It is observed that both pure and KI doped ZTS single crystals possess the average low dielectric constant of ~ 226, 221and the average low dielectric loss of ~ 0.025, 0.0375 and hence found suitable for electro-optic applications.

3.2 Photoluminescence Studies

Photoluminescence (PL) measurements of pure and KI doped ZTS single crystals were measured at room temperature. He – Ne laser with 20 mW, 633 nm was used for the excitation energy during measurements. PL spectra of pure and KI doped ZTS single crystals are shown in figure 6. Strong emission peaks of as-grown pure and doped materials were observed from the spectra at ~ 424 nm and ~ 421 nm respectively. The observed wavelength revealed that the grown materials have a blue emission property. The calculated energy band gap of the pure and doped crystals is 2.67 eV and 2.69 eV which may be attributed to the recombination between donors and acceptors. The strong emission of blue radiation indicates that the presence of potassium ion in the forbidden band region of the pure zinc tris thiourea sulphate single crystal.

3.3 EDX Analysis

Elemental analysis of as-grown pure and 1 mol % of KI doped ZTS crystals were carried out by using Energy Dispersive X-ray analysis measurement which is attached with scanning electron microscope. Figure 7 and 8 shows the EDX spectrum of grown single crystals. Table-1 portrays the values of elemental content of the crystals as measured by EDX technical and theoretical calculation from molecular formula. Table-1 indicates the values of weight % and Atomic % of pure and 1 mol % of KI doped ZTS crystals measured by EDX. These are in line with the estimated values from molecular formula.

3.4 SEM Analysis

The surface features of pure and KI doped ZTS crystals were observed by a Scanning Electron Microscopy (SEM) using a Hitachi (Model No) scanning electron microscope. The SEM micrograph taken on the selected planes of pure and KI doped ZTS crystals are shown in Figure 9 and 10. This shows that the crystals surface as a whole appear smooth but there also observed few isolated islands and minute crystallites over the surface. Thus the SEM analysis indicates that pure and KI doped ZTS crystals possess relatively smooth surfaces and free from major defects.

IV. CONCLUSION

Semiorganic nonlinear optical single crystals of pure and potassium iodide doped Zinc tris thiourea sulphate have been grown by slow solvent evaporation technique from aqueous solution at ambient temperature. The observed peaks at 424 nm and 423 nm wavelengths from PL spectra revealed that the grown materials have blue emission property. The dielectric studies confirmed that the grown crystals posses the average dielectric constant of 226, 221 and average low dielectric loss of 0.025, 0.0375 at high frequency and hence the pure and KI doped ZTS will be a promising materials for electro optic applications. Elemental compositions of grown crystals were obtained by using Energy Dispersive X-ray analysis. Morphological observations through SEM analysis indicates that pure and KI doped ZTS crystals possess relatively smooth surfaces and free from major defects.

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Table Caption:

Table-1 EDX Quantitative results of Pure and 1 mol % KI doped ZTS

S.No.	Elements	Pure ZTS		1 mol % KI doped ZTS crystal	
		Weight %	Atomic %	Weight %	Atomic %
1	C	30.6	45.56	22.05	27.9
2	N	13.97	18.22	32.4	35.16
3	O	13.54	15.47	33.08	31.43
4	S	27.65	15.76	11.09	5.26
5	Zn	14.24	4.99	0.65	0.15
6	K	0	0	0.06	0.02
7	I	0	0	0.67	0.08

Figure Caption:
Figure 1(a) The as grown pure ZTS single crystal
Figure 1 (b) The as grown KI doped ZTS single crystal
Figure 2 Frequency dependence of dielectric constant of pure ZTS single crystal
Figure 3 Frequency dependence of dielectric constant of KI doped ZTS single crystal
Figure 4 Log frequency vs dielectric loss of pure ZTS crystal
Figure 5 Log frequency vs dielectric loss of KI doped ZTS crystal
Figure 6 PL spectra of pure and KI doped ZTS single crystals
Figure 7 EDAX spectrum of pure ZTS
Figure 8 EDAX spectrum of 1 mol % KI doped ZTS
Figure 9 SEM photograph of Pure ZTS
Figure 10 SEM photograph of 1 mol % KI doped ZTS

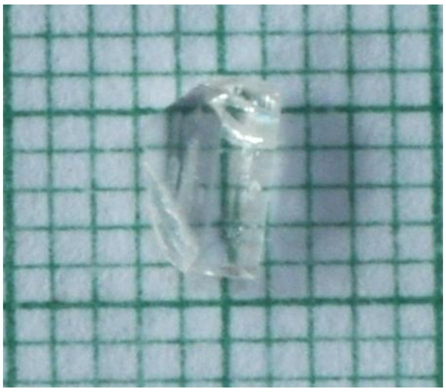

Figure 1(a) The as grown pure ZTS single crystal

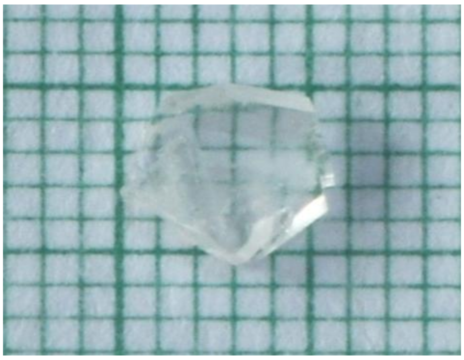

Figure 1 (b) The as grown KI doped ZTS single crystal

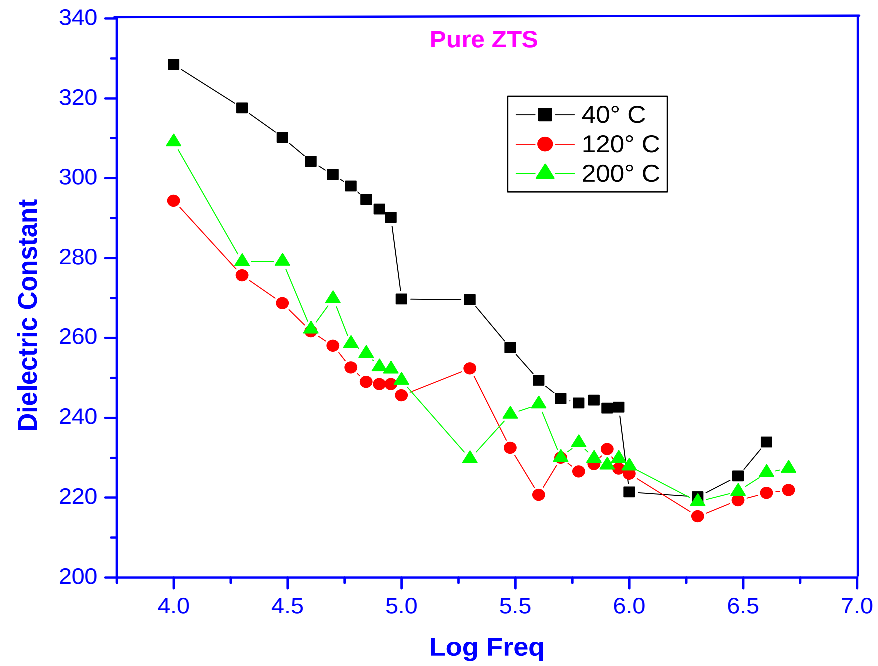

Figure 2 Frequency dependence of dielectric constant of pure ZTS single crystal

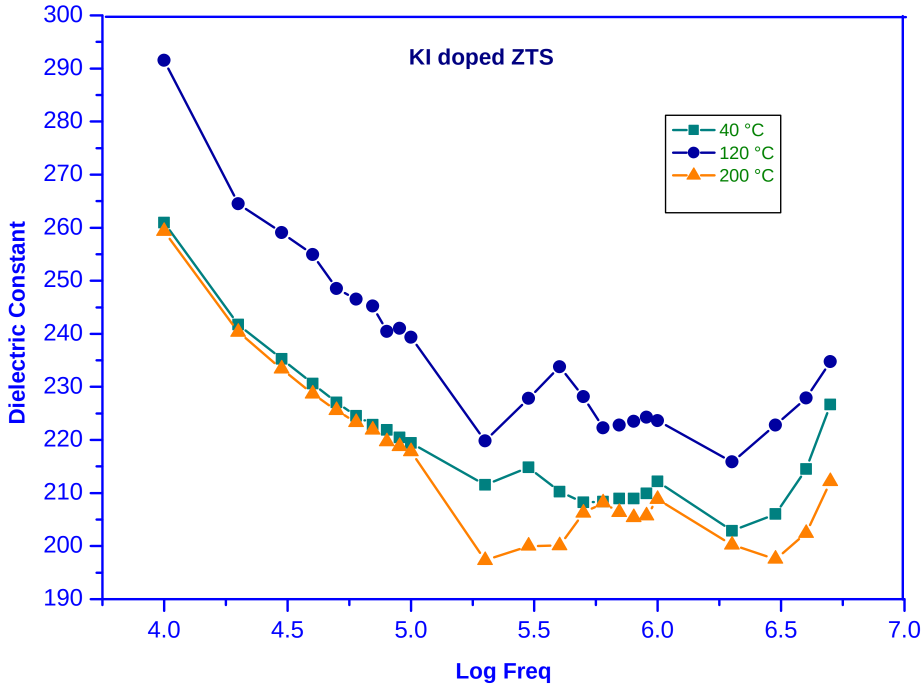

Figure 3 Frequency dependence of dielectric constant of KI doped ZTS single crystal

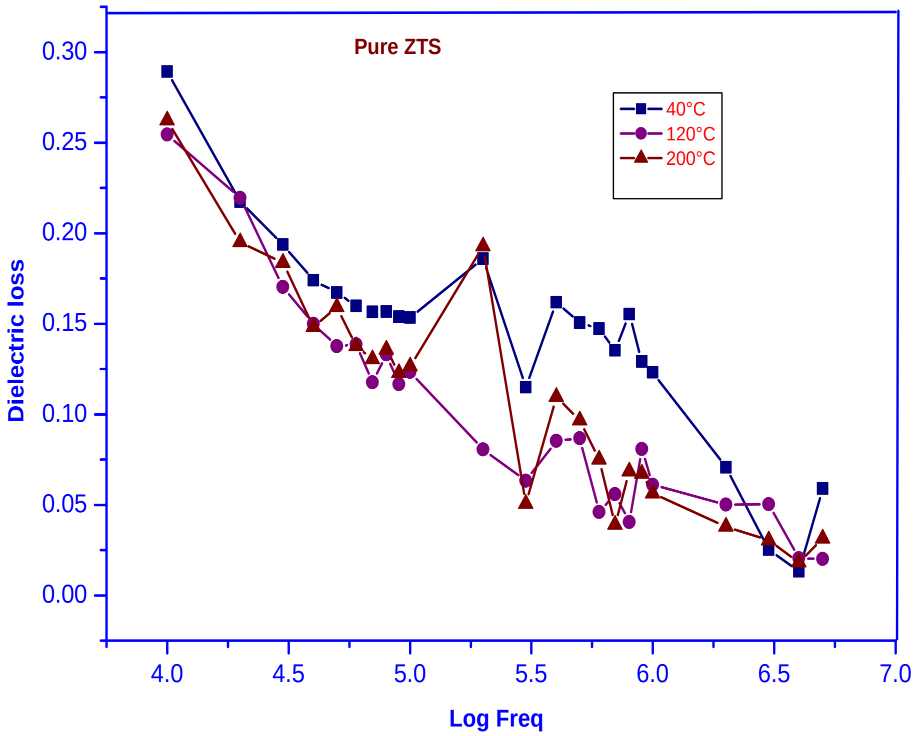

Figure 4 Log frequency vs dielectric loss of pure ZTS crystal

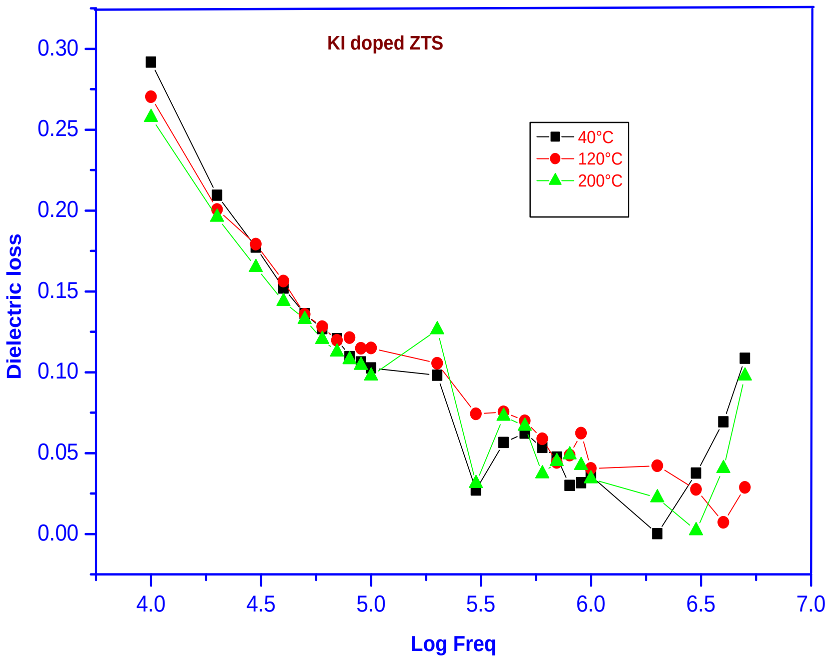

Figure 5 Log frequency vs dielectric loss of KI doped ZTS crystal

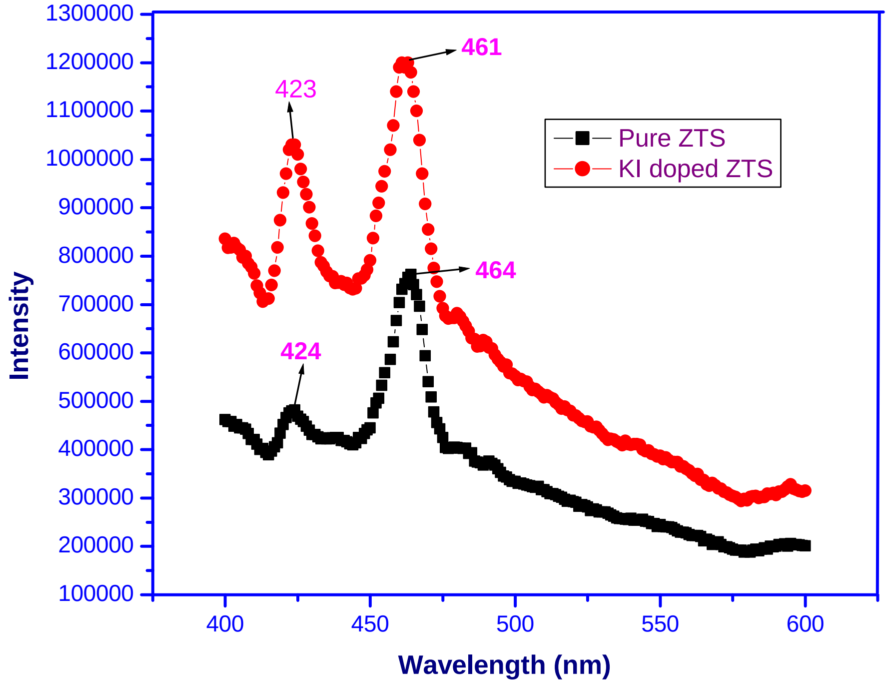

Figure 6 PL spectra of pure and KI doped ZTS single crystals

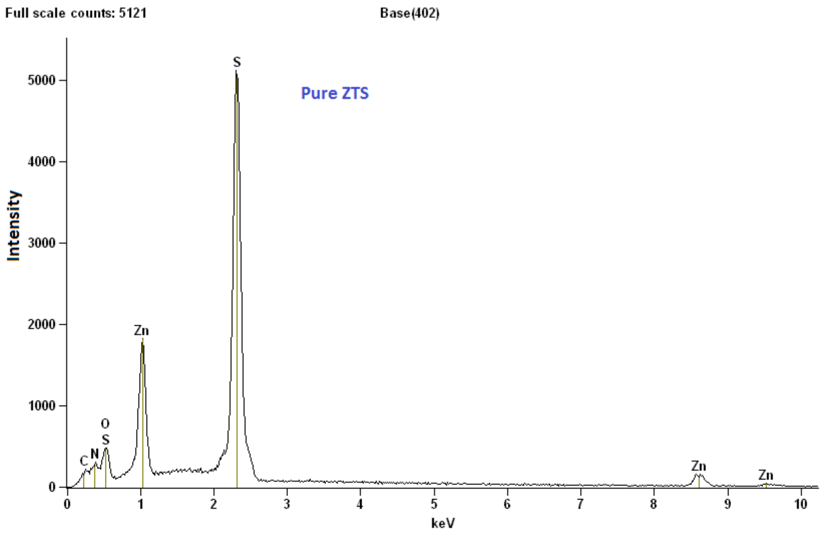

Figure 7 EDAX spectrum of pure ZTS

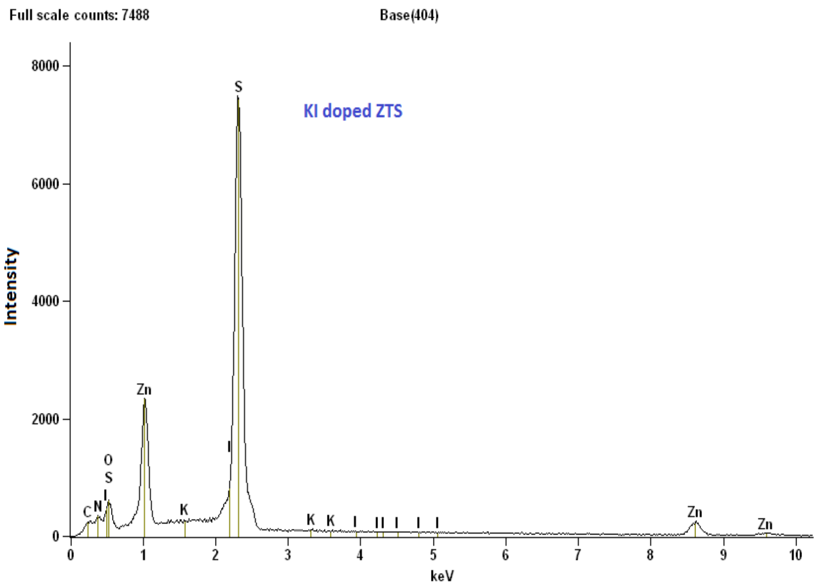

Figure 8 EDAX spectrum of 1 mol % KI doped ZTS

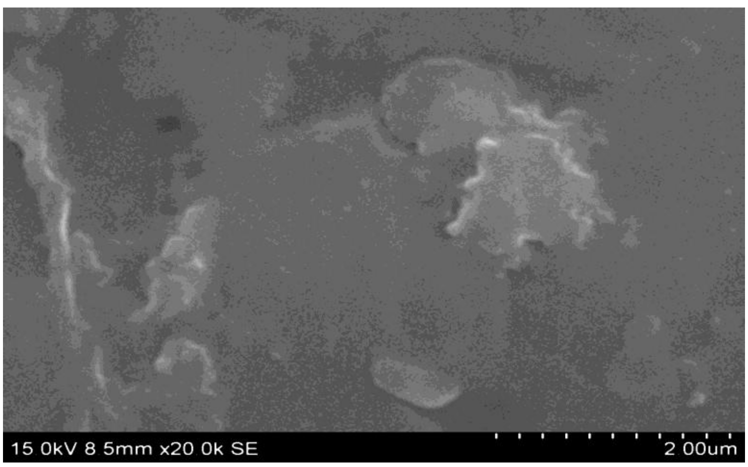

Figure 9 SEM photograph of Pure ZTS

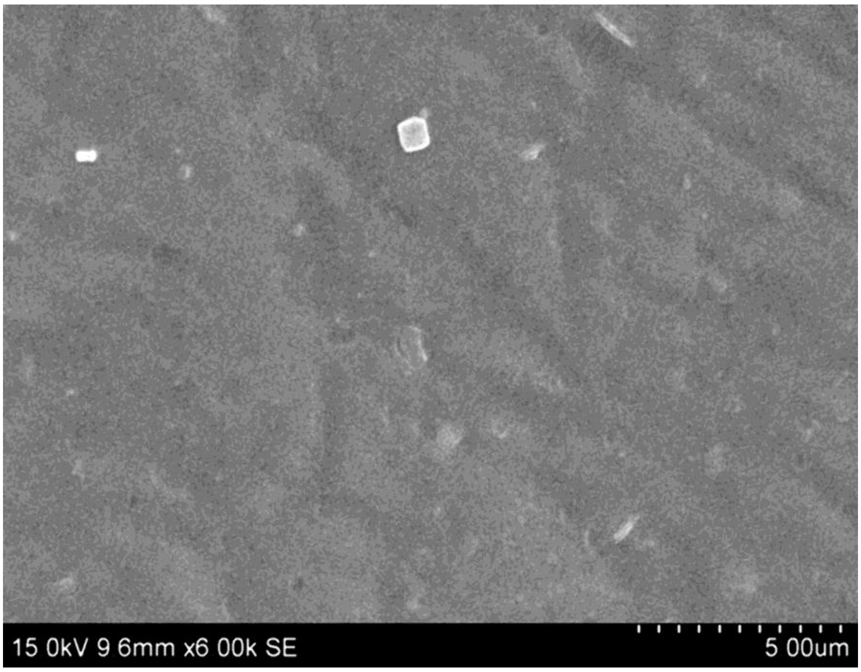

Figure 10 SEM photograph of 1 mol % KI doped ZTS

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