Effect of Alkali metal on the growth and properties of Zinc Mercury Thiocyanate crystals

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Potassium doped zinc mercury thiocyanate $ZnHg(SCN)_4$ crystals have been grown by gel technique by diffusion process in silica gel medium in various pH values ranging between 2.0 – 2.8. The grown crystal was characterized to explore its structural, molecular and nonlinear optical properties. Fourier transform infrared spectrum (FTIR) studies were performed and the strong absorption bands due to SCN were revealed. UV-visible-near infrared spectrum was recorded and the cut off wavelength was determined. SHG studies have shown an enhancement in the conversion efficiency with respect to Voltage (V) versus Time (s). Chemical analysis was carried out using EDAX and the actual composition of the crystal material was identified. The unit cell parameters and cell volume are obtained by single crystal X-ray diffraction analysis. Thermogravimetric and differential thermal analysis were performed and the thermal stability of the crystal was analysed.

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1. Introduction

Nonlinear materials find a wide application in the field of optoelectronics. Organic materials possess good nonlinear properties, but poor mechanical stability (laser damage threshold). On the other hand, inorganic materials are good in their mechanical and thermal stability but shows low nonlinear properties. Recently it was found that semiorganic materials show excellent nonlinear optical properties as well as good mechanical and thermal stability together. Thus, semiorganic materials find a greater attention in the research community. In particular, bimetallic thiocyanates of type $AB(SCN)_4$ show very good nonlinear properties [1,2]. Among the bimetallic thiocyanate crystals, zinc mercury thiocyanate (ZMTC) and cadmium mercury thiocyanate (CMTC) were found to have excellent nonlinear optical properties. They belong to noncentrosymmetric space group of $I\bar{4}$ and possess very high thermal stability and exhibit second harmonic generation [3-6]. Efficient phase-matchable optical second harmonic generation in crystal class 10 was realized in zinc mercury thiocyanate (ZMTC) and cadmium mercury thiocyanate (CMTC) by W. Sturmer et. al.[7]. Structural features, crystal parameters, growth habit and NLO properties of CMTC, MMTC were investigated by many researchers [8-10]. G.P. Joseph et. al. [11] have studied the influence of metallic substitution on the physical properties of manganese mercury thiocyanate (MMTC) crystals and also analysed the thermal stability owing to metal ion inclusion. In the present research work we have doped ZMTC by alkali metal (potassium) and studied the variations occurring in the properties of the crystal.

This paper reports the effect of potassium on the growth and properties of ZMTC single crystals grown from silica gel by diffusion. The grown crystal was characterized with X-ray diffractrometer, UV visible spectrometer, Fourier transform infrared spectroscopy (FTIR), Thermogravimetric and differential thermal analysis (TG/DTA), second harmonic generation test (SHG) and EDAX. All the results obtained are analysed and interpreted in comparison with pure ZMTC crystals.

2. Experimental

Analytical reagents of zinc chloride, mercuric (II) chloride and ammonium thiocyanate were used along with potassium chloride as dopant for the growth of potassium doped ZMTC crystals using gel diffusion technique.

Stock solution was prepared by adding 244 g of sodium meta silicate ($Na_2SiO_3.9H_2O$) to 500 ml of distilled water. Stock solution of 7.5 ml was diluted with equal amount of distilled water. ExcelaR grade glacial acetic acid was added to the stock solution and the pH was adjusted to 2.0, 2.4, and 2.8 in three different beakers. Aqueous solution of $HgCl_2$ (0.3M) was prepared and 32 ml each were added to the stock solution at different pH along with 16 ml of 4M aqueous solution of NH_4SCN and allowed for gelling in test tube of length 15 cm and diameter 1.5 cm. After gelation, it was left undisturbed for another 48 hours for ageing of the gel. Then $ZnCl_2$ (3M) and 10% aqueous solution KCl (3M) were mixed thoroughly and added on the top of the gel using a pipette carefully without disturbing the gel network.

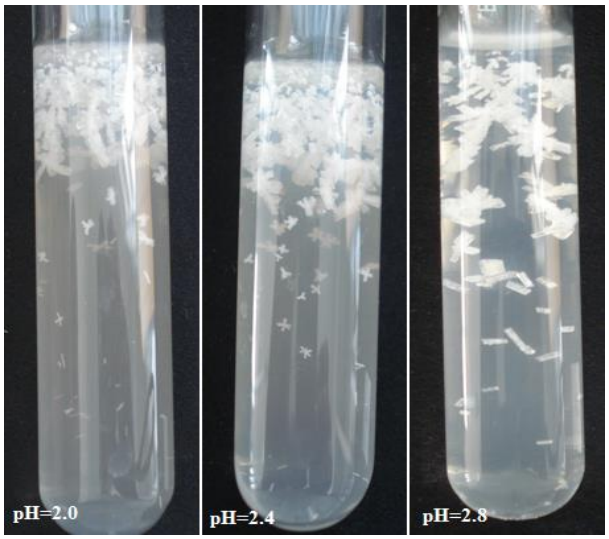
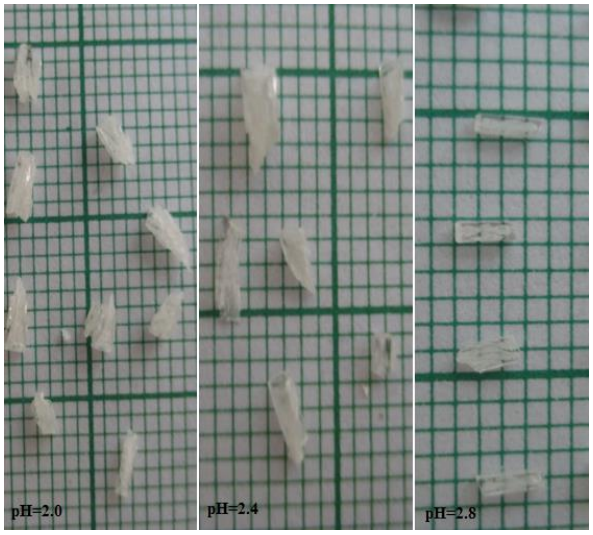


Fig. 1. (a) K doped ZMTC crystals in gel at different pH.



(b) Harvested crystal of K doped ZMTC at different pH.

After a period of 30 days, it was observed that fairly good crystals were obtained at a pH of 2.8. At the pH of 2.0 and 2.4, crystals obtained were like aggregate solid with very poor transparency. Comparison of crystals grown at different pH of the stock solution is given in Fig. 1a and 1b.

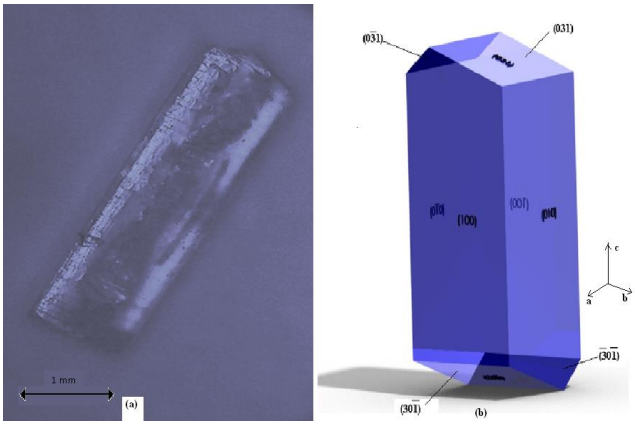


Fig. 2. (a) Optical microscope image (b)Solid morphology indexed of K doped ZMTC grown at pH 2.8.

The high resolution optical microscope image and the solid morphology of crystals with its faces indexed are shown in Fig. 2a and 2b.

3. Characterization

3.1 Single crystal X-ray diffraction analysis

The K doped ZMTC crystals were subjected to single crystal X-ray diffraction to obtain the unit cell parameters and to confirm the crystallinity of grown crystals, using single crystal diffractometer CAD 4/MACH 3 with MoK_{α} radiation in the wavelength 0.71073 Å.

The unit cell dimensions were determined as a = b = 11.095 Å, c = 4.439 Å, $\alpha = \beta = \gamma = 90°$, unit cell volume = 546.44 $A^{\circ 3}$ and belongs to tetragonal crystal system with space group of $I\bar{4}$. It is observed that the unit cell parameters are in good agreement with the crystallographic data reported by D. Xu. et. al. [12] and the cell volume shows an increase as a result of doping when compared to the pure ZMTC crystal.

3.2 Fourier transform infrared and optical transmission studies

The FTIR spectrum was recorded using a Perkin-Elmer FTIR spectrum RXI spectrometer by KBr pellet technique in the range 4000 – 400 cm^{-1} and is shown in Fig. 3.

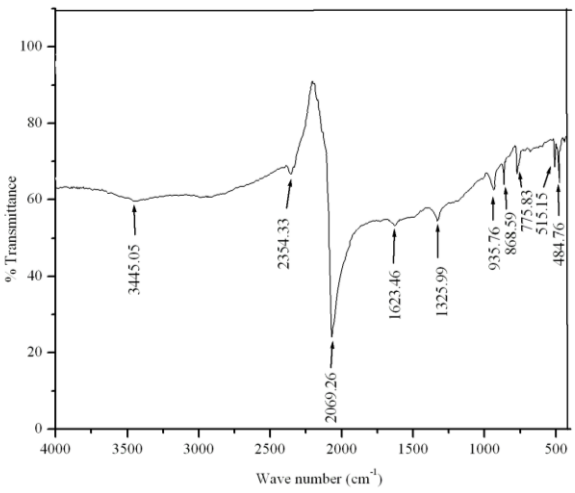


Fig. 3. FTIR spectrum of K doped ZMTC crystals.

The vibration peaks are in good agreement with the values reported by Wang et. al [3]. The sharp intense peak at 2069.26 cm^{-1} corresponds to CN stretching vibration (ν_{CN}) and the peak at 775.83 cm^{-1} corresponds to CS stretching vibration (ν_{CS}). SCN bending vibrations (δ_{NCS}) are observed at 484.75 cm^{-1}, whereas $2\delta_{NCS}$ bending vibrations are observed at 935.76 and 868.59 cm^{-1}. As reported by Wang et. al. [3] the increase in the CN and CS stretching vibrations and decrease in the SCN bending vibrations occurred as a result of electron transfer from nitrogen (N) to Zn^{2+} and sulphur (S) to Hg^{2+}. The slight distorsion in the wavenumbers compared to pure ZMTC is attributed to the effect of dopant alkali metal (K).

The UV-vis-NIR study of the single crystal was done using Lambda 35 UV spectrophotometer. The size of the crystal obtained was not sufficient to perform optical transmission studies in crystal form. So, the UV transmission spectra were taken for the solution of K doped ZMTC crystal prepared using the solvent of ethanol-water mixture in 1:1 ratio. As shown in the Fig. 3, the transparency cut off occurs at 260 nm.

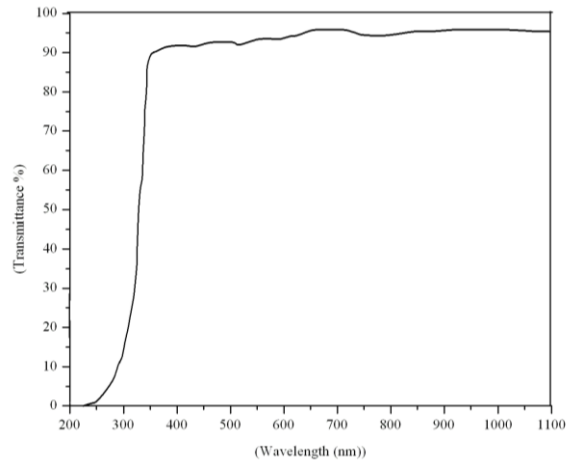


Fig. 4. UV Vis-NIR spectrum of K doped ZMTC crystals.

Second harmonic generation efficiency of the K doped ZMTC crystal was carried out by Kurtz and Perry powder technique [13] with reference to urea using Nd:YAG passively Q-switched laser of wavelength 1064 nm. The crystal was powdered using mortar and pestle, and packed tightly in a micro capillary tube and exposed to the laser beam of pulse energy 7.3 mJ. The green light emission confirmed the SHG property of the crystal. The second harmonic generation efficiency of K doped ZMTC was 14 times greater than urea. The optical transmission studies thus confirm the NLO property of the reported crystal. It is found that no significant change was observed compared to pure ZMTC [2, 3].

4. Thermogravimetric and Differential thermal analysis

Thermogravimetric and differential thermal analysis were performed in the atmosphere of nitrogen within the temperature range of 50-600°C (Fig. 4) and the thermal stability of the crystal was analysed.

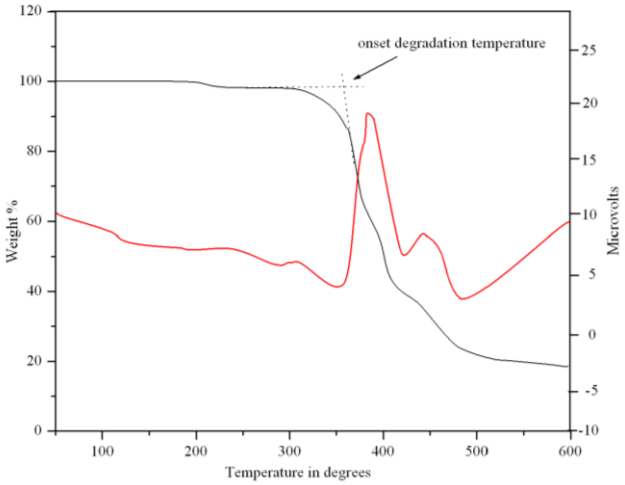


Fig. 5. TG/DTA curve of K doped ZMTC crystals.

The potassium doped ZMTC crystal is found to be stable upto 305 °C. Beyond this temperature it started to decompose. The TGA study shows that the thermal decomposition has followed two overlapping processes. One is the breakdown of three dimensional steric structure occur between 50 °C to 340 °C along with the corresponding mass loss and the other is evaluation of different components extending upto 600 °C.

In the first step between, 180 °C to 375 °C mass loss of 34.50% takes place. The second step extends upto 600 °C which accounts for a mass loss of 44.28% and the remaining mass 21.22% appeared as residue.

The first step involves breakdown of three dimensional steric structure and the loss of one CS_2 (carbon disulphide), half nitrogen gas (N_2) and 1 ½ dicyanogen $(CN)_2$. Mass loss occurred in the second step

is due to the sublimation of one HgS which is most possible at higher temperatures. DTA curve shows an endothermic curve corresponding to the mass loss in the decomposition process. Endothermic curve at 280 °C and 353 °C corresponds to the two overlapping process of step one. Curve at 423.5 °C and 480 °C are for the sublimation of HgS with reference to TGA curve. The TG/DTA analysis suggests that the high thermal stability is associated with the incorporation of the potassium into ZMTC compared to reported literature [2, 3].

5. EDAX analysis

Energy dispersive x-ray spectroscopy for potassium doped ZMTC crystal was carried out using JEOL: Model JSM6390 scanning electron microscope coupled to OXFORT INSTRUMENT energy dispersive analyzer. The operating parameters such as electron beam energy and focusing spot diameter were maintained at 20 KeV and 6 μm diameter respectively.

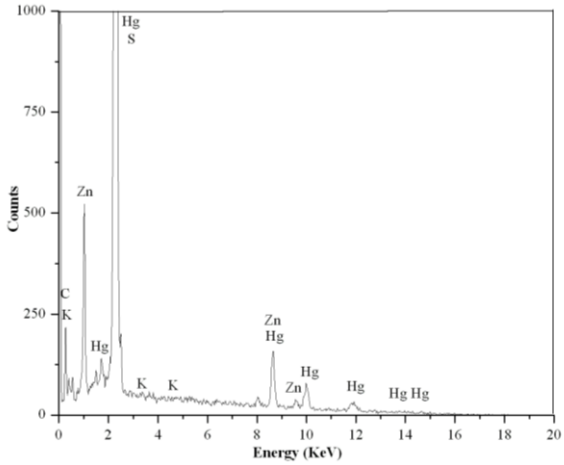


Fig. 6. EDAX spectra showing peaks corresponding to metal constituents in the K doped ZMTC crystal.

The relative elemental composition and weight percentage were directly computed with 'INCA' software. The analysis was repeated at 4 different location of the sample and the mean response of the each element detected in the sample was calculated. The peaks identified in the Fig. 6 are those of potassium (K), zinc (Zn), mercury (Hg), sulphur (S) and carbon (C). It confirms that the potassium has entered into the lattice of ZMTC crystals. The approximate concentration, weight percentage and atomic percentage of metals detected in the crystal sample are given in the Table 1.

Table 1. EDAX analysis data for K doped ZMTC crystals.

Elements	Approximate	Intensity	Weight %	Weight% Sigma (±)	Atomic %
C	9.46	0.2793	28.28	2.49	58.92
N	1.13	0.1118	8.44	2.16	15.92
S	26.23	0.9447	23.17	1.05	18.08
K	0.13	0.8859	0.12	0.12	0.08
Zn	11.68	0.8845	11.02	0.75	4.22
Hg	32.99	0.9498	28.98	1.48	3.62
		Total	**=**	**100.00**	

6. Conclusion

Single crystals of potassium doped ZMTC have been grown in silica gel medium at three different pH. The crystals grown at pH of 2.8 were found to be better in size and transparency. The tetragonal structure of the grown crystal was confirmed by single crystal X-ray diffraction. All the faces of the crystal are indexed in the solid morphology diagram. The presence of various functional groups was identified by FTIR analysis. The UV spectral studies show a high percentage of transmittance with a cut off of 260 nm. Kurtz powder test have shown a high efficiency and therefore the grown crystal is found suitable for nonlinear optical applications. The TG/DTA analysis have shown that the thermal decomposition of the grown crystal is a multi-step process, which involves breakdown of the three dimensional steric structure and the formation of mixed metal sulfides and oxides, owing to high thermal

stability of the crystal. EDAX analysis was performed and the relative elemental composition and weight percentage present in the crystal confirms the dopant concentration.

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