Research Paper

Growth and characterization of bis(thiourea) potassium chloride crystals for NLO applications

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ABSTRACT

Growth of Bis(Thiourea) KCl doped with NaCl single crystals from aqueous solution by slow evaporation technique was reported. The solubility of the grown samples was found at various temperatures. Structural characterization of the grown crystals was determined by the single crystal X-ray diffraction (XRD). EDAX studies indicate the presence of thiourea in the doped L-alanine crystals. The functional groups were identified by FTIR spectroscopy. The UV-Vis-NIR spectral studies were carried out to analyze the optical absorption of the grown crystals and found that the absorption is very low in the wavelength region 290 to 1000 nm for both the samples. Improvement in the SHG efficiency was studied by the Kurtz and Perry method. Thermal analysis was carried out on the grown crystal.

Keywords: NLO, XRD, EDAX, FT-IR, UV-Vis-NIR, SHG, TGA.

INTRODUCTION

The demand for non-linear optical crystals with superior perfection is rising day by day due to quantum jump in the design of non-linear optical materials and investigations into them have become most indispensable and efficacious disciplines in the field of Materials Science and Engineering. Consequently, there have been extensive efforts to develop new kinds of non-linear optical crystals for number of applications such as second harmonic generation, frequency mixing and electro-optic modulation etc. Non-linear optical (NLO) organometallic complexes are given much attention due to their ability to combine the flexibility of organic materials with the thermal stability and mechanical strength of inorganic material.

Thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment and ability to form extensive network for hydrogen bond. Thiourea, in combination with metal complexes forms semi-organic compounds having low cut off wavelength and applications for high power frequency conversion (Angeli and Dhanuskodi, 2001; Lydia and Vasudevan, 2009; Manonmani et al., 2008). In the present study, Bis(Thiourea) KCl doped with sodium chloride semi-organic NLO crystal was grown from aqueous solution by slow evaporation method at room temperature. The grown crystal was subjected to various characterization studies such as XRD, FTIR, UV-VIS and NLO studies discussed in detail. Properties of thiourea possess large dipole moment
and forms number of NLO active metal co-ordination compounds like bis(thiourea) cadmium chloride (BTCC) and bis(thiourea) cadmium.

**Solubility**

The solubility of the solute can be determined by dissolving the solute in the solvent maintained at a constant temperature with continuous stirring. The solubility curve can be plotted from the amount of solute dissolved and temperature by repeating the measurements for different temperatures. Figure 1 shows the solubility curve of Bis(Thiourea) KCl doped with sodium chloride crystal. The solution of Bis(Thiourea) KCl doped with sodium chloride was prepared in water and maintained at 30°C with continuous stirring to ensure homogeneous temperature and concentration. On reaching saturation, the content of the solution was gravimetrically analyzed. This process was repeated for every 5°C in water from 30 to 50°C, respectively.

**MATERIALS AND METHODS**

The Bis(Thiourea) KCl doped with sodium chloride crystal was synthesized using thiourea, potassium chloride and sodium chloride as the starting material using double distilled water. The whole solution was continuously stirred for 3 h using magnetic stirrer to obtain a homogeneous mixture. The completely dissolved solution was filtered using Whatman filter paper to remove the suspended impurities and allowed to crystallize by slow evaporation method at room temperature for about 45 days. Finally, well-defined single seed crystals were obtained. Figure 2 shows the photographs of the grown crystals. The saturated solution of Bis(Thiourea) KCl doped with NaCl solution was prepared in accordance with the solubility data by dissolving potassium chloride, sodium chloride and thiourea in the stochiometric ratio of 1:1:2 in distilled water. The solution was constantly stirred for one day to avoid co-precipitation of multiple phases. The stirred solution was filtered and then allowed to evaporate at room temperature. In the period of 30 to 45 days, seed crystals of Bis(Thiourea) KCl doped with sodium chloride were formed due to spontaneous crystallization. Well defined single crystals were selected as seeds to grow bulk size crystals. Crystals having dimension up to $8 \times 5 \times 2$ mm$^3$ were harvested in a period of 50 to 60 days.

**RESULTS AND DISCUSSION**

**Single crystal XRD Analysis**

The Bis(Thiourea) KCl doped with NaCl were subjected to single crystal X-ray diffraction analysis using Bruker Smart

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**Figure 1:** Solubility curve of Bis(Thiourea) KCl doped with sodium chloride.
Figure 2: Grown crystals of Bis(Thiourea) KCl doped with sodium chloride.

Apex single crystal X-ray diffractometer to determine the lattice parameters and space group. X-ray diffraction (XRD) is a powerful non-destructive technique for characterizing crystalline materials (Moritra and Kar, 2008; Arriponnammal et al., 2005). It provides information on structures, phases, preferred crystal orientations (texture) and other structural parameters, such as average gain size, crystallinity, strain and crystal defects (Ushasree and Jayavel, 2002; Pricilla et al., 2004).

X-ray diffraction peaks are produced by constructive interference of a monochromatic beam of x-rays scattered at specific angles from each set of lattice planes in sample. The oldest and most precise method of X-ray crystallography is single-crystal X-ray diffraction, in which a beam of X-rays strikes a single crystal producing scattered beams. When they land on a piece of film or other detectors, these beams make a diffraction pattern of spots. From single crystal XRD it is observed that Bis(Thiourea) KCl doped with sodium chloride belongs to triclinic crystallographic system with cell parameters $a = 12.58 \, \text{Å}$, $b = 8.91 \, \text{Å}$, $c = 5.94 \, \text{Å}$, and cell volume $V = 665.8015 \, \text{Å}^3$.

Energy dispersive X-ray analysis

Energy dispersive X-ray analysis (EDAX) is a micro analytical technique that uses the characteristics spectrum of X-rays emitted by the sample after excitation by high-energy electrons. This analysis is used to obtain information about the elemental composition of the grown crystals. In the present study, the EDAX analysis was carried out for Bis(Thiourea) KCl doped with sodium chloride crystals using FEI QUANTA 200F energy dispersive X-ray micro analyzer. Figure 3 shows the results observed in the elemental analysis of the grown crystals. The EDAX spectrum confirms the presence of carbon, nitrogen, oxygen and chlorine. In addition to the aforementioned elements, sulphur was also present.

Fourier transform of infrared spectral analysis

Infrared spectroscopy is effectively used to determine the molecular structure and the identification of the functional groups in the synthesized compound (Yang and Luo, 2013; Venkattaramanan et al., 1997).

The FTIR spectrum was recorded using Bruker IFS 66V spectrophotometer by KBr pellet technique in the region 4000 to 400 cm$^{-1}$. The symmetric and asymmetric C=N stretching vibration at 740 and 1417 cm$^{-1}$ of thiourea are shifted to 730 and 1411 cm$^{-1}$ respectively. The N-H absorption bands in the high frequency region 3000 to 2000 cm$^{-1}$ in the thiourea were not shifted to lower frequencies on the formation of metal-thiourea complex indicating that nitrogen to hydrogen bonds are not present and bonding must be between potassium and sodium chloride atoms. Figure 4 shows the FTIR spectrum of Bis(Thiourea) KCl doped with sodium chloride.

UV-Visible spectral study

Figure 4 shows the the UV-Vis–NIR absorption spectra observed in the present study. All the grown crystals exhibit wide transmission window in the visible and NIR regions. This enables them to be potential candidates for opto-electronic application (Dhunane et al., 2008). The
lower cut off wavelengths lies within 290 nm. The low absorption in the visible and NIR regions along with low cut off wavelengths confirm the suitability of the grown crystals for NLO applications. The optical absorbance of Bis (Thiourea) KCl doped with sodium chloride crystal was recorded using VARIAN CARY 5E model spectrophotometer in the wavelength range 200 to 2000 nm. The Figure 5 shows the optical absorption spectrum of
Bis (Thiourea) KCl doped with sodium chloride. The cut-off wavelength as observed from the absorption spectrum is 290 nm. The crystal has very low absorption in the entire visible and NIR regions. The large transmittance window in the visible and NIR region enable a good optical transmission for the second harmonic frequencies. Single crystals are mainly used in optical applications and hence, optical transmittance window and the transparency lower cut off (200 to 400 nm) is very important for the realization of SHG output in this range using diode lasers.

Kurtz and Perry SHG test

The SHG efficiency of grown samples was measured by using the Kurtz powder technique. In this technique, the grown crystals were grounded into fine micro crystalline powder and densely packed between two transparent glass slides. The fundamental beam 1064 nm from Q-switched Nd: YAG laser (Prolab 170 Quanta ray, pulse width 8 ns and repetition rate 10 Hz) was made to fall normally on the crystalline powder densely packed in a micro-capillary tube. The bright emission of green light from Bis (Thiourea) KCl doped with sodium chloride crystals ($\lambda$=532 nm) confirms the second harmonic generation behavior of crystals.

Thermal analysis

The thermal stability of Bis (Thiourea) KCl doped with sodium chloride single crystal was estimated by TGA and DTA techniques. The TGA curve indicates that the sample is stable from ambient up to 250°C with a weight loss of 38.52%. A systematic weight loss was observed as the temperature further increased above the melting point. The total weight loss of the sample is 97.6% at 400°C. The DTA curve indicates that the material has an exothermic peak at 245°C which represents the melting point respectively. It is observed that there is no phase transition or decomposition up to the melting point (245°C) and also there is no mass reduction or decomposition up to 200°C indicating that one can crystallize this material by slow evaporation solution growth technique. Figure 6 shows the TG-DTG traces of Bis (Thiourea) KCl doped with sodium chloride.

Conclusion

Organometallic NLO crystals of Bis (Thiourea) KCl doped with sodium chloride were successfully grown by slow evaporation solution growth method. The grown crystal was confirmed by single crystal XRD. The EDAX spectrum confirms the presence of carbon, nitrogen, oxygen, sulphur and chlorine. The FTIR spectra and the corresponding band assignment clearly indicate that the symmetric and asymmetric C=N stretching vibration at 740 and 1417 cm$^{-1}$ of thiourea are shifted to 730 and 1411 cm$^{-1}$ respectively. The UV-Vis –NIR spectrum indicates that the grown crystals have minimum absorption in the entire visible region which is an important requirement for NLO
Temperatures (°C)  
Concentration (%/ min)  
Weight (%) 

Figure 6: TG-DTA traces of Bis(Thiourea) KCl doped with sodium chloride.

materials having non-linear optical applications. The TG trace of these crystals shows the decomposition temperature at 245°C.

REFERENCES


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