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Influence of halogens on the growth aspects of Allylthiourea cadmium complex nonlinear optical single crystals

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ABSTRACT

Allylthiourea complex crystals is an organometallic complex, a new nonlinear optical materials with high second harmonic generation effect. Tri-allylthiourea cadmium chloride and Tri-allylthiourea cadmium bromide are the promising nonlinear optical crystals belonging to this family. Both the crystals have been grown from an aqueous solution by slow cooling technique. The solubility and growth optimization of the grown crystals in terms of pH were analyzed and the influence of the different halogen atoms on the properties of as grown single crystals was studied by conducting various characterization techniques. Powder X-ray diffraction studies revealed that both the crystals are trigonal crystal structure with R3C space group. The spectroscopic properties were investigated by recording the Fourier Transform Infra Red and UV-Visible-NIR spectroscopy. Spectrocopic study confirmed the coordination of metal and red shift of the grown crystal. Nonlinear behavior of the as grown crystals was identified by Kurtz powder technique. Thermal and electrical properties of the as grown crystals were also analyzed by thermogravimetric and dielectric studies. Influence of the halogens on the growth as well as the properties were studied.
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1. INTRODUCTION

Nonlinear frequency conversion materials have played more important role in many fields, such as laser technology, optical communication, optical data storage, etc., The rapid development of optical communications systems had led to the search for more efficient components for the processing of optical signals. Second order NLO materials plays key role to the future photonics technology. There has been an intense research effort in second-order NLO materials over the past two decades. The unsuitability of organic NLO materials for practical applications is primarily due to the requirement of non centrosymmertric arrangements because most of the organic mateials are being centrosymmetric arrangements in nature. The potential of organometallic materials for this purpose has recently come into prominence [1-3]. Studies on organometallic complexes have proved that the formation of a coordination bond can increase the interaction between molecules and thus improve their melting point and mechanical properties. Moreover, the structure radical of the complex is no longer planar as seen in benzyl ring; hence the anisotropy of the crystal is reduced when compared with the organic crystals [4].Based on the physical idea of double-radical structure model (i.e.,) combining inorganic distorted polyhedrons with organic conjugated molecular system, metal halides used as the inorganic part, and the allylthiourea serves as the organic counterpart when forming the organometallic complexes. A comparatively high optical nonlinearity in these complexes comes from the distortion of the tetrahedron, which is composed of three allylthiourea (AT) combining with Cd.The II (B) group metals (Cd) as these compounds usually have a high transparency in the UV region because of their closed d^{10} shell. These ligand and their M(IIB) complexes are always colorless. The ligands can be medium-sized π-electrom systems and the particular salts selected have the added advantage of containinig metals with filled 'd' shells which should also enhance the effective polarizability. A series of optically negative NLO crystals within the R3 space group have been identified. They have the general formula $M(CH_2=CHCH_2NHCSNH_2)X$, M= Cd or Hg, X=Cl,Br [5] and has possess several attractive properties like higher transparency range, more damage threshold, large conversion efficiency and good thermal stability. Their second harmonic generation effects are stronger than that of urea [3]. Among these series allylthiourea cadmium chloride(ATCC) and allylthiourea cadmium bromide(ATCB) are the cadmium complexes with different halogens. Effect of different metal ions on structural, thermal, spectroscopic and optical properties of ATCC and ATMC has been investigated by the

authors [6]. But how the things will be if the halogen atom changes to be Br?. So it is impossible to study the influences on crystal properties of different end atoms and summaries some regularity.

In the present work, attempts have been made to grow single crystals of ATCC and ATCB by isothermal solvent evaporation as well as by conventional temperature lowering methods. The material was synthesized aqueous soluion. The solubility was determined by gravimetric analysis. The growth conditions were analyzed and identified the optimal conditions to grow bulk size single crystals. Charactization studies such as powder XRD, FTIR, UV-Visible-NIR, TGA/DTA are carried out to determine the structural, spectral, optical, thermal and elelctrical properties. The nonlinear behaviour of the as grown sample has been confirmed by well-known Kurtz powder analysis. From the result of these analyses the influence of the different halogen atoms on structural, spectral, optical, thermal and elelctrical properties were reported.

2. EXPERIMENTAL PROCEDURE

The synthesis and growth process were carried out in solutions and the starting materials were of analytic reagent grade from Sigma Aldrich (98% purity). Solubility studies of the as grown crystals were carried out by gravimetric analysis. Growth procedure was optimized to get good quality bulk size single crystals especially pH parameter. Powder X-ray diffraction pattern of the grown fine crystalline powder samples were recorded on a Rich Seifert X-ray diffractometer using CuKα (λ= 1.5418 Å). The sample was scanned for a 2θ range of 10 and 65 and at a scan speed of 2θ/minute. FTIR spectra of the ligand and the as grown crystalline powders were recorded in the region 400 and 4000 cm^{-1} using a Bruker IFS 66V spectrophotometer by KBr pellet technique. The optical spectra of the as grown single crystals from the UV to NIR in the wavelength spectral range from 200 to 1100 nm were recorded by means of the Shimadzu UV-Visible spectrophotometer. The non-linear optical property of the as grown crystals was illustrated using spectra physics quanta Nd:YAG laser with first harmonics output of 1064 nm. Thermo gravimetric analysis (TGA) and Diferential thermal analysis (DTA) was carried out using a STA 409 PC Thermal analyzer at the room temperature. Both analyses was carried out in an inert nitrogen atmosphere. Fine powders of the crystals sample weighing 2 mg were used for these studies. Alumina (Al_2O_3) was used as a reference material for the samples. Dielectric properties of the as grown crystals (of size >3mm) have been studied by using HIOKI 3532 50 LCR HITESTER instrument for various frequency and temperature.

2.1.Material Synthesis

Allylthiourea complex crystals, Triallylthiourea cadmium chloride (ATCC) and Triallylthiourea cadmium bromide (ATCB) were synthesized by using allylthiourea(AT) and Cadimium Chloride ($CdCl_2$) and Cadimium Bromide ($CdBr_2$) as raw materials. The salts were mixed in the molar ratio of 3:1 (AT: $CdCl_2$ and $CdBr_2$) and were dissolved separately in deionised water (resistivity 18.2 Ω^{-1} cm^{-1}) with continuous stirring. Then they were mixed together at 58°C. This mixture was slowly heated for 60°C and stirred to remove the unwanted nuclei present in the supersaturated solution. The reaction during the synthesis process is

$$3(CH_2-CHCH_2NHCSNH_2)+CdCl_2 \rightarrow [CdCl(CH_2-CHCH_2NHCSNH_2)_3]+Cl^-$$

$$3(CH_2-CHCH_2NHCSNH_2)+CdBr_2 \rightarrow [CdBr(CH_2-CHCH_2NHCSNH_2)_3]+Br^-$$

Syntheses product was further purified by repeated recrystallization process.

2.2.Solubility Studies

Solubility is an essential pre-requisite for solution growth method. Solubility studies were carried out in an optically heated constant temperature bath with a control accuracy of ± 0.01°C with continuous stirring. The solubility of ATMX was determined by dissolving the solute in an aqueous solution (18.2 MW-cm) in an airtight container maintained at a constant temperature with continuous stirring. Solutions were stirred for six hours continuously to achieve the equilibrium condition.After attaining the saturation, the equilibrium concentration of the solute was analyzed gravimetrically. The solubility was estimated for seven different temperatures 30, 35, 40, 45, 50, 55°C. The solubility curve for different temperatures was plotted as shown in Figure 1. The solubility increase nonlinearly with increasing temperature. The solubility curve clearly depicts that the solubility is notably decreases, for the complexes forming with 'Br' then 'Cl' in the low temperature region. But in the higher temperature region the solubility is similar for both cases.

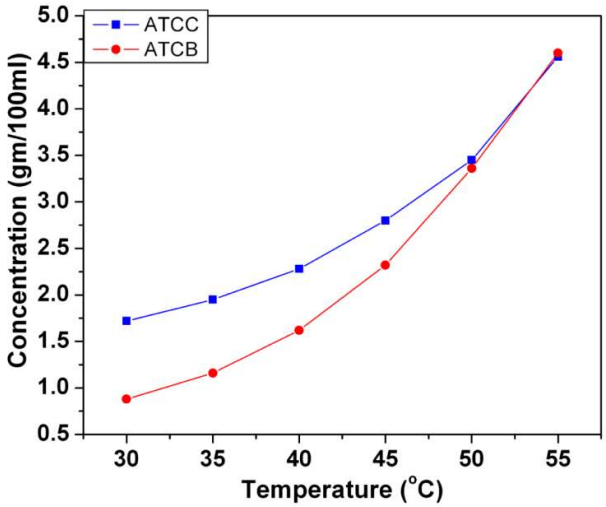

Figure 1. Solubility curve for ATCC and ATCB crstals at different temperature.

2.3 Single Crystal Growth

The solubility diagram of ATCC and ATCB in aqueous solution indicates that the solubility temperature co-efficient has positive values. Therefore, temperature-lowering method was used to grow bulk ATCC and ATCB single crystals. Seed crystals of ATCC and ATCB are formed by heterogeneous nucleation in a supersaturated solution by controlled solvent evaporation technique. The embryos crystals of perfect shape and free of macro defect were chosen by using microscope for carrying out regeneration. The growth temperature was varied in between 56 and 40°C. At the starting stage, the initial temperature-lowering rate should be slower i.e., 0.1 °C/day, as the surface of the seed is very small. After some

time the rate of temperature lowering can be gradually increased upto 0.5°C/day. Under these conditions good quality ATCC and ATCB crystals can be harvested within 100 days and shown in Figure 2a,b. The grown crystals are optically transparent and non-hygroscopic in nature. The influence of pH in the saturated solution of the both the crystals play the vital role. It affects the growth rate and also incorporates inclusions in the as grown crystals. So it plays the vital role during the growth of colourless crystals, the pH of the solution was carefully adjusted with dilute HCl. The optimized pH value is 2.5 Å, When the pH of the solution was not adjusted to the optimized pH value the crystal grows in the yellow colour may be the formation of the cadmium oxide which were shown in Figure 3a,b, this is due to the hydrolyzes reaction.

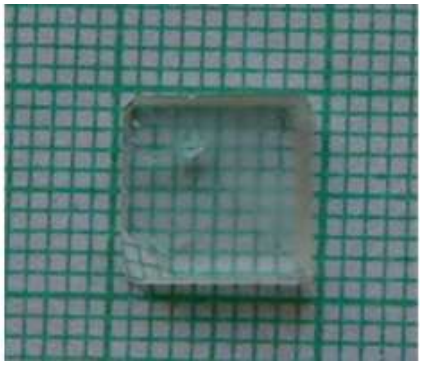

Figure 2a. ATCC crystal grown by slow cooling evaporation technique.

Figure 2b. ATCB crystal grown by slow cooling evaporation technique.

3. RESULTS AND DISCUSSION

3.1. Powder X-ray diffraction analysis

The X-ray powder diffractogram of the as grown crystals of ATCC and ATCB are as shown in Figure 3a,b. The revelation of well defined Bragg's peaks at specific 2θ angles and the crystasllogaphic planes were indexed, which shows the better crystallinity of the as grown materials. Both the crystals belong to trigonal system with space group R3C and the crystallographic parameters were determined as (a = b = 11.527 Å, c= 27.992 Å) for ATCC and (a = b = 11.6209 Å, c= 28.5692 Å) for ATCB crystals. The various halogens are not affected the crystal structure and the space group.

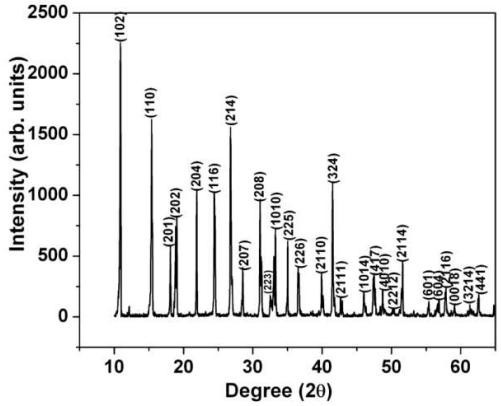

Figure 3a. X-ray diffractogram of the grown ATCC crystals

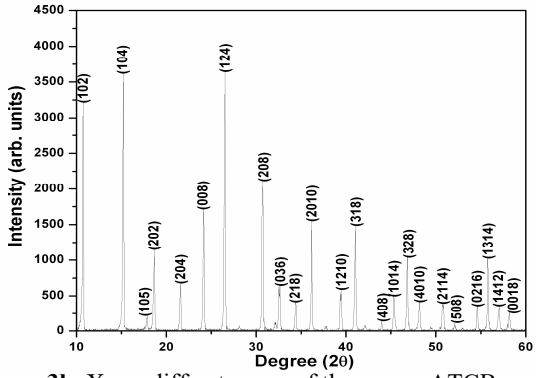

Figure 3b. X-ray diffractogram of the grown ATCB crystals

3.2. FT-IR spectral studies

The Fourier Transform Infrared absorption spectrum of ATCC and ATCB crystals were recorded. The resultant Fourier Transform infrared absorption spectrum of pure Allylthiourea, ATCC, and ATCB crystalline powders are given in Figure 4 respectively. Generally, the molecular structures of thiourea derivatives have characteristic resonance [7]. They highly favorable sulfur coordination to the metal when forming complexes with metal halides. The highly favorable sulfur coordination with the metal was confirmed through, two modes of frequencies have been used to demonstrate sulfur coordination C=S stretch and the C-N stretch in the FTIR spectra shifted to higher wavenumber (19 cm^{-1}) i.e. the corresponding frequency found in allylthiourea is 1543cm^{-1} and in ATCC and ATCB it is 1562cm^{-1} and that of ν(C=S) to lower wavenumber (9 cm^{-1} for ATCC and 8 cm^{-1} for ATCB) in allylthiourea was 775 cm^{-1} and in ATCC was 766 cm^{-1} and in ATCB was 765cm^{-1} observed, indicating that sulfur coordination to cadmium not with nitrogen. All the peaks of ATCB can find their counterparts in allylthiourea, which indicates the existence of allylthiourea ligand in the sample. Similar status can also be observed in some other allylthiourea coordination compounds.

3.3 Optical studies

The grown crystals were cut into rectangular plates along the crystallographic axes and polished to optical quality. The well-polished specimen across 5 mm thickness is subjected to transmittance and absorbance percentage structure.

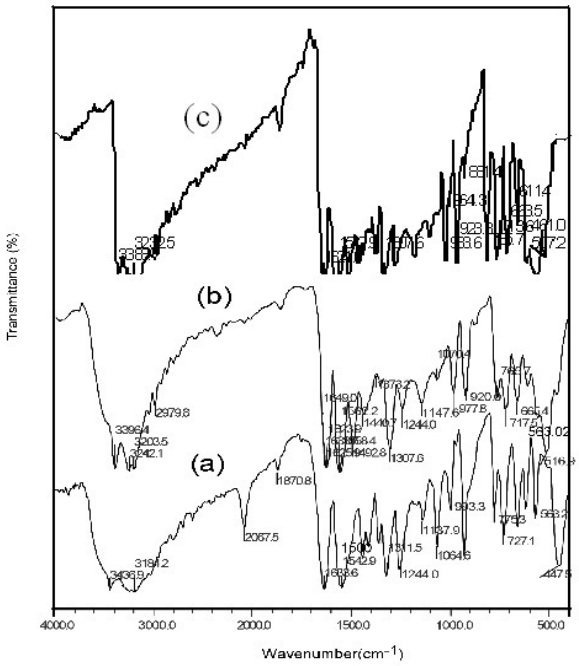

Figure 4. FTIR spectrum of (a) allylthiourea (b) ATCC (c) ATCC crystals

measurement with in the range of wavelength in between 350 and 1100 nm. Percentage of transmittance for ATCC and ATCB crystal is shown in Figure 5 indicate the transparent nature of the materials in the entire Ultra Violet Near Infrared spectrum. The value of lower cut off wavelength for ATCC and ATCB crystals were 285 and 295 nm, respectively. The variation in cut off wavelength of different metal ion was attributed due to the distortion of the tetrahedron The transparency is in the entire visible region for the crystals suggests that their suitability for second harmonic generation applications [8]. The observation of remarkable red shift was observed for different halogen may be due to the various value of electronegativity. Remarkable red-shift was observed for different halogen and metals due to their various electronegativity values.The nonlinearity of the as grown ATMX crystals was identified through Kurtz and Perry powder technique [9].

3.4. Thermal analysis

Thermogravimetric–analysis (TGA) and differential thermal anlaysis (DTA) have been carried out for grown crystals. Simultaneously recorded TG and DTA curves of ATCC and ATCB samples are shown in Figure 6a,b. ATCC is thermally stable upto 205°C, ATCB is 203°C. There is no phase transition till the material melts and this enhances the temperature range for the utility of the crystals for NLO application. Below the decomposition temperature, there is no detectable weight loss and hence the crystal rejects solvent molecules during crystallization.

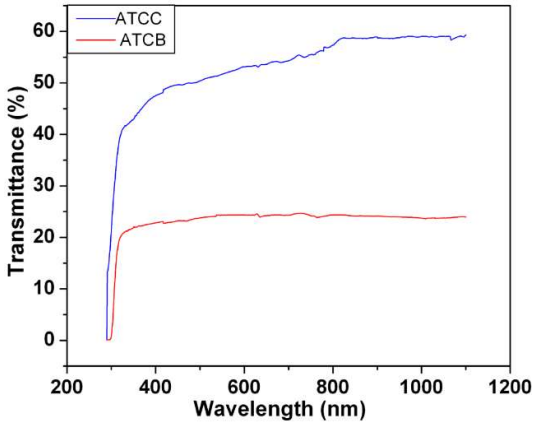

Figure 5 Optical spectra of ATMX single crystal

Compound degradation takes place above the decomposition temperature in the form of various volatile products.From the DTA curve it is confirmed that ATCC, ATCB undergoes an irreversible endothermic transition at 101°C, 97°C which are corresponds to their melting points of the as grown crystals respectively. From these results ATCC has more stable than ATCB. This is also due to the influence of various halogens in the complex formation. Generally both the grown crystals have the higher melting temperature comparing with it's double lignad allylthiourea [10]. A complex formed with Cadmium than Mercury possesses less melting temperature in comparing with the complexes formed with Mercury [6].

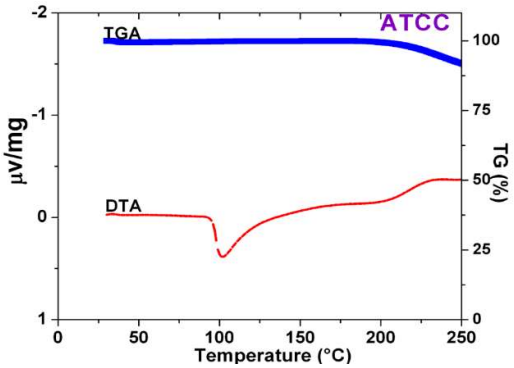

Figure 6a Characteristics thermal curves of ATCC single crystals

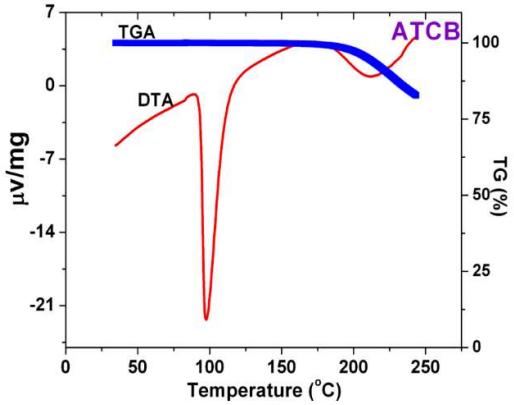

Figure 6b. Characteristic thermal curves of ATCB single crystals

3.5 Dielelctric studies

Electro-optic co-efficient have correspondence in the dielectric behaviors [11]. It was great interest for technical applications to know crystals electro-optic coefficient and dielectric properties [12]. Both dielectric constant and dielectric loss were measured, using parallel equivalent static capacitance (C_p) and loss coefficient (D) for various frequency and temperature as shown in Figure 7a,b. Crystals were carefully selected with high transparency and surface defect free (without any pit or crack or scratch on the surface). As the frequency increases, both the dielectric constant and dielectric loss values for both (ATCC and ATCB) crystals are found to be decrease exponentially. The dielectric constant (ε^l) at low frequencies depends on the exciation of bound electrons, lattice vibrations, dipole orientation, and space charge polarization (atomic or electronic).

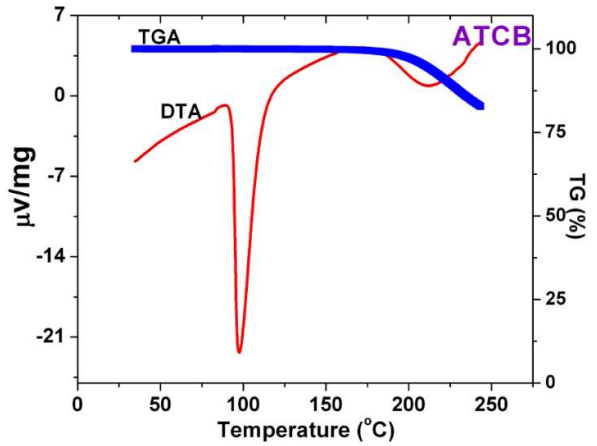

Figure 7a. Variation of dielectric constant of ATCC single crystal as a function of frequency at various temperatures

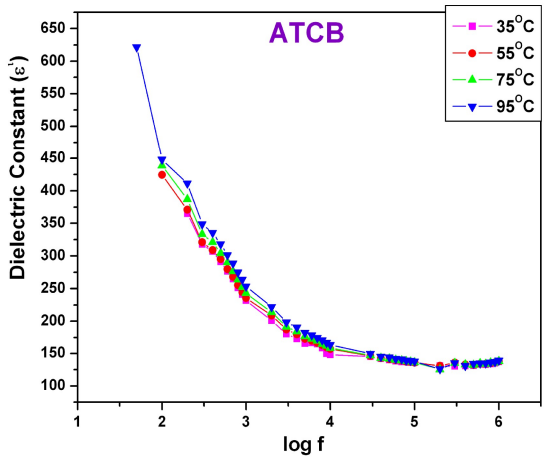

Figure 7b. Variation of dielectric constant of ATCB single crystal as a function of frequency at various temperatures

At very low frequencies all four contributions may be active so it has the high value. The lower value of the dielectric constant at higher frequencies explains the higher SHG conversion efficiency of the as grown crystal and this is agreement with the Miller rule [13]. The characteristic of low dielectric loss with higher frequencies for a measured sample suggests that the grown crystal have lesser number of electrically active defects [14]. So that, the grown crystals can be used for electro-optic applications in wide frequency regions.

4. CONCLUSION

Single crystals of allylthiourea cadmium chloride and allylthiourea cadmium bromide were grown from aqueous solution by temperature lowering method and the influence of the different halogens on complex formation were investigated. The solubility of the as grown crystals were estimated from gravimetric analysis and both the crystals have lower solubility and shows the similar behaviour in the higher temperature regions. The influence of the different halogens does not affect the crystal structure and the metal ligand coordination. Remarkable redshift was absorbed from the optical spectra and the significant variation in the melting as well as decomposion were observed from the thermal analysis. Similar dielelctric behaviour was observed for both crystals at different temperatures as well as frequencies and it reveals the grown crystals suitabilities for nonlinear optical applications. Results imply that the halogen modifies slightly the grown crystals optical, thermal and electrical behaviour and does not affect the crystal structure and metal ligand coordinations.

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