

Influence of pH on the growth of tris-allylthiourea cadmium chloride single crystals

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ABSTRACT

Single crystal growth of non-linear optical material tris-allylthiourea cadmium chloride (ATCC) single crystals has been investigated. The crystals were grown from aqueous solution by slow evaporation as well as by slow cooling technique. The influence of pH of the solution on the morphological and optical properties of the grown crystals was investigated. At pH 5-6, the crystals are elongated along a-axis. Bulk crystals have been grown from the optimized pH value of 3-4. The powder XRD analysis carried out on the grown crystals indicate no variation in lattice parameter values for different pH values of the growth solution. The FTIR analysis confirms the presence of sulfur to cadmium bonds in the complex for the crystals grown at different pH values of the solution. The functional groups present in the crystals were confirmed by Raman spectral studies. The mechanical property of the crystal grown at optimized pH was studied using Vicker's microhardness method. The change in the crystal morphology at pH values 3-4, 4-5 and 5-6 was attributed to the growth rate variations of prismatic planes at different pH values of the growth solution. Crystals grown at an optimized pH value (3-4) possess higher optical transmittance. The second harmonic generation conversion efficiency was measured qualitatively using Nd:YAG laser.

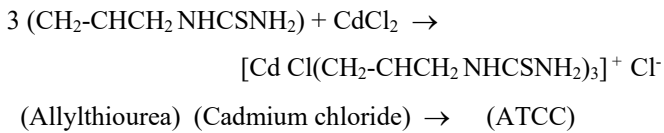
1. INTRODUCTION

Recently, a variety of hybrid Second-order nonlinear optical (SONLO) materials have attracted much attention because of their extraordinary potential applications in emerging photonic and optoelectronic technologies [1,2]. Materials with short transparency cut-off wavelength and stable physiochemical, good thermal stability and high laser damage threshold are needed in order to realize many of the NLO applications. The search for new frequency conversion materials over the past decade has concentrated on organo-metallic complexes. Organic crystals have very large nonlinear susceptibilities compared with inorganic crystals, but their low optical transparencies, poor mechanical properties, low laser damage thresholds and difficulties in the growth of large crystals impede their use. Pure inorganic NLO materials typically have excellent mechanical and thermal properties but possess relatively modest optical nonlinearities because of the lack of extended π -electron delocalization. In organometallic complexes, polarizable organic molecules are stoichiometrically bound within an organic host [3]. During the past several years, according to the idea of combining the inorganic distorted polyhedron with asymmetric conjugate organic molecule, organometallic materials have been attracting a great deal of attention in the nonlinear optical field. These materials have the potential for combining the high optical nonlinearity and chemical

flexibility of organics with temporal, thermal stability and excellent transmittance of inorganic [4]. The influence of pH plays a vital role on the formation of single-phase and its study is very important to obtain device quality single crystal NLO crystals [5]. ATMX [where AT=(allylthiourea)= $C_4H_8N_2S$, M=Cd or Hg, X=Cl or Br] Allylthiourea cadmium chloride (ATCC), Allyl thiourea cadmium bromide (ATCB), Allylthiourea mercury chloride (ATMC) and Allylthiourea mercury bromide (ATMB) are a series of novel organo-metallic complex crystals in which AT acts as ligand and M acts as a central atom [6]. The high optical nonlinearity comes from the distortion of the tetrahedron. The second harmonic generation (SHG) efficiency of each of these materials is three times higher than that of well known organic NLO crystal Urea [7]. In the present investigation, the influence of pH of the growth solution on the structural, morphological, spectroscopic and optical property of the ATCC crystals is studied.

2. SYNTHESIS OF ATCC

Growth solution for ATCC was prepared by dissolving allylthiourea and cadmium chloride in stoichiometric ratio (3:1) in Millipore water of resistivity $18.2 \text{ M}\Omega \text{ cm}^{-1}$. The polycrystalline starting material was synthesized by evaporating the solution to almost dryness at room temperature according to the reaction



The purity of synthesized salt was further improved by successive recrystallization process. The solution pH was varied by the addition of dilute HCl into the saturated solution [6]. The mixture was slowly heated with stirring and held at 65°C for 6 hours to remove unwanted nuclei [8]. Care was taken to avoid any decomposition during heating of saturated solution.

3. CRYSTAL GROWTH BY SLOW EVAPORATION

The synthesized salt was dissolved in Millipore water of resistivity 18.2 MΩ cm⁻¹. The solution was held in slightly undersaturated condition and was constantly stirred for 6 hours using magnetic stirrer. The pH of the solution was varied with addition of dilute Hcl. Growth solution at different pH was prepared in a similar process then the solution was filtered and was poured in different petri dishes, and covered with porous papers. Different seed crystals from growth solution of different pH values were prepared in the same procedure. Seed crystals prepared at different pH values 3 , 4 and 5 were shown in Figure1a,b,c respectively. Good quality seed crystals, free from macro defects were collected from the petri dishes and were used for growing large size crystals by slow cooling technique

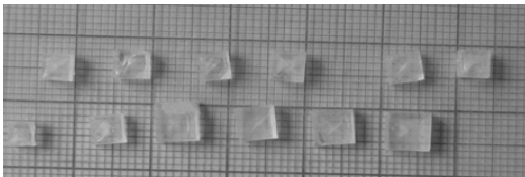


Figure 1^a. pH : (3 – 4) ± 0.1



Figure 1b: pH : (4 – 5) ± 0.1



Figure 1c: pH : (5 – 6) ± 0.1

Figure 1, b, c. As Grown Crystals of ATCC by slow evaporation method

4. CRYSTAL GROWTH BY SLOW COOLING

ATCC crystals were grown by low temperature solution growth technique by slow cooling in a constant temperature bath controlled to an accuracy of 0.01°C. Crystal growth was

initiated on the seeds suspended in the growth solution saturated at 56 °C by the temperature lowering from 56 °C to room temperature at a rate of 0.1-0.3 °C/day. The period of growth ranged from 90-120 days. The crystals grown by slow cooling method at pH values 3-4, 4-5 and 5-6 are as shown in figs.2(a), 2(b) and 2 (c) respectively. Crystals grown at pH value 5-6 have more inclusions

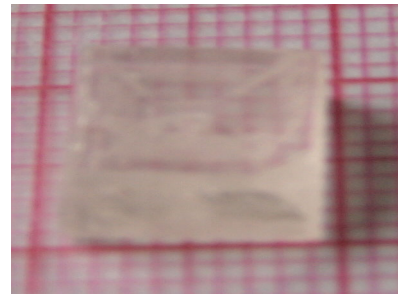


Figure 2a: pH : (3 – 4) ± 0.1

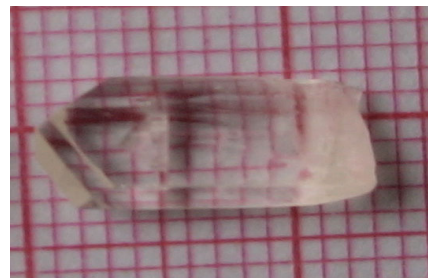


Figure 2b: pH : (4 – 5) ± 0.1



Figure 2c: pH : (5 – 6) ± 0.1

Figure 2. As Grown Crystals of ATCC by temperature lowering method

4.1. Influence of pH on growth rate and morphology

The principal requirement of the crystals to be used for device application is that they should be of large size and free from strain and imperfection [9]. The major problem with ATCC crystal was its non-availability in the bulk form. Hence, it was necessary to increase the growth rate of the crystal along all direction. The growth rate of a crystal plane is a function of a set of crystal growth parameters like temperature, degree of supersaturation of the solution, pH of the solution, concentration of impurities in the solution and other physio-chemical properties [10]. In general, the following equation can be used to express the function relation:

$$R = F(t, S, \text{pH}, C)$$

Where, R expresses the growth rate of the crystals; t, S, pH and C express the temperature, supersaturation, pH of the

solution and concentration of the impurity in the solution respectively. In the present study, all the growth parameters, t , S and C were kept constant during the growth runs, to study the influence of pH on the growth rate. The influence of pH on the morphology and growth rate of ATCC crystals was investigated through growth of ATCC from aqueous solution with pH values ranging from 3 to 6.

ATCC under normal conditions, grow faster along a-direction compared to the other directions. Hence it was necessary to increase the growth rate of the crystal along the other crystallographic directions (b and c directions), for the growth of bulk crystals. Crystal growth with solution pH of 5-6 elongates the a-axis in the growing crystal. When the pH is reduced to 4-5 the crystal growth starts along b and c directions and also the growth along a-direction was suppressed. Further reducing the pH (i.e., pH value to 3-4) the growth along all the crystallographic directions are almost equal. At pH 5-6, a-axis exhibits a rapid growth indicating an adequate transport of Cd^{2+} , Cl^- and allylthiourea to this plane. The decrease in the growth along a-axis and gradual increase in the growth along b-axis with decrease in pH clearly indicates different ways of supplying the ingredients to the crystal growth. At lower pH values, obtained by the addition of HCl, there should be lower concentration of free Cd^{2+} , as much of these ions would be in the form of $CdCl_4^{2-}$ complex and most of the allylthiourea might be in the protonated form. This helps rapid transport of such protonated allylthiourea towards the crystal surface. The $2Cl^-$ bonded to Cd^{2+} also provides the necessary driving force for such transport through hydrogen bonding. This transport enhances the growth along b and c-axis rather than along the a-axis. The crystallographic theory of Hartman and Perdok aims to predict the morphology of growing crystal [11-12]. Hartman-Perdok theory does not take into account possible relaxation or reconstructions at the crystal surface, nor the influence of the solution on the interface. The surface termination is possible and is controlled by adjusting the crystal growth parameters. Among the other parameters pH causes the harmful effects for the growing crystals in aqueous solution. The atomic structure at the solid-liquid interface, including relaxations or even reconstructions, is important for controlling the distribution and concentration of the molecules in the mother solution. A charge-compensating layer of solution adjacent to the surface and this must strongly affect the adsorption kinetics for the solute ions.

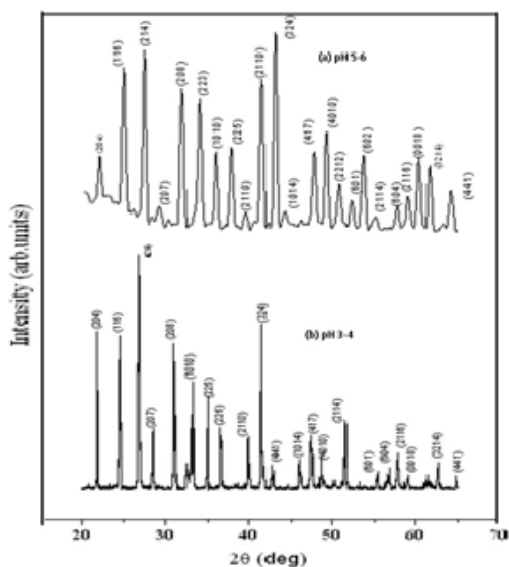


Figure 3 a,b The X-ray powder diffraction pattern of ATCC crystals of different pH

5. RESULTS AND DISCUSSION

X-ray powder diffraction pattern of the as grown crystals were recorded on a Rich Seifert X-ray diffractometer using $CuK\alpha$ (mean wavelength $\lambda = 1.5418 \text{ \AA}$) by crushing the ATCC crystals into very fine powder. The sample was scanned for a 2θ range of $10-65^\circ$ and at a scan speed of $2^\circ/\text{minute}$. Figures 3 shows the X-ray powder diffractogram of ATCC crystal. The high crystalline nature was confirmed by the recorded well defined Bragg's peaks at specific 2θ angles with high intensity of the grown crystalline specimen. The crystal belongs to trigonal system and the crystallographic parameters are $a = b = 11.527 \text{ \AA}$ and $c = 27.992 \text{ \AA}$. Figs.3 (a) and 3(b) show the XRD pattern of crystals grown at different pH values. Variation in the pH value of the solution does not show any considerable effects on the XRD pattern of the grown crystals.

FTIR absorption spectrum for the as grown crystals was recorded with BRUKER IFS 66V model spectrophotometer using KBr pellet method. The FTIR spectra of pure Allylthiourea and ATCC crystals grown at different pH values 3-4 and 5-6 are as shown in figs. 4a, b and 4 (c) respectively. The following inference are made from the observed FTIR results, The band at 775 cm^{-1} found for pure Allylthiourea is assigned to the $C=S$ stretching frequency. This band is slightly shifted to lower value of 766 cm^{-1} in ATCC due to the coordinate interaction of allylthiourea with the metal cation (Cd^{2+}) in ATCC. The shift in the strong band $N-C-N$ stretch at 1543 cm^{-1} of pure allylthiourea to higher value of 1563 cm^{-1} in ATCC provide additional confirmation to the co-ordinate interaction of allylthiourea with the metal ion.

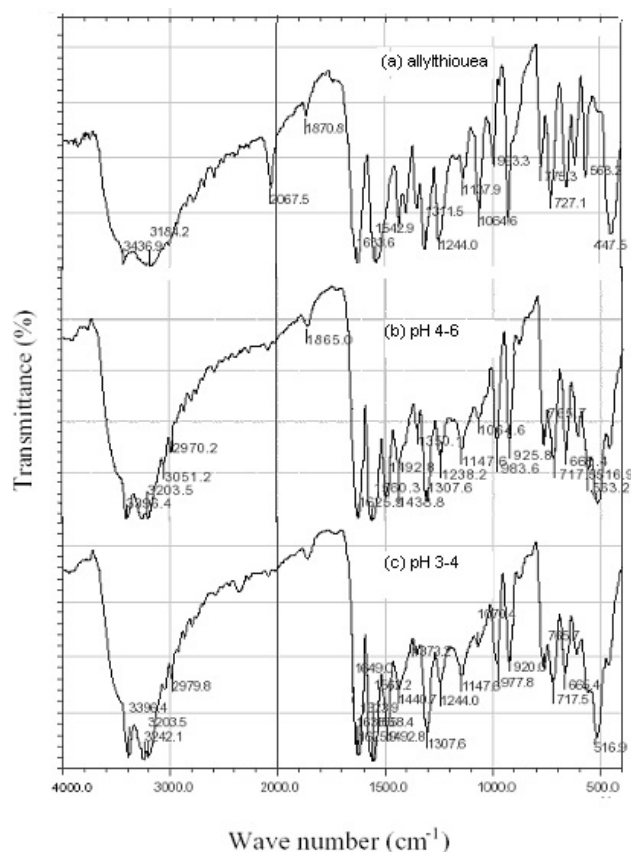


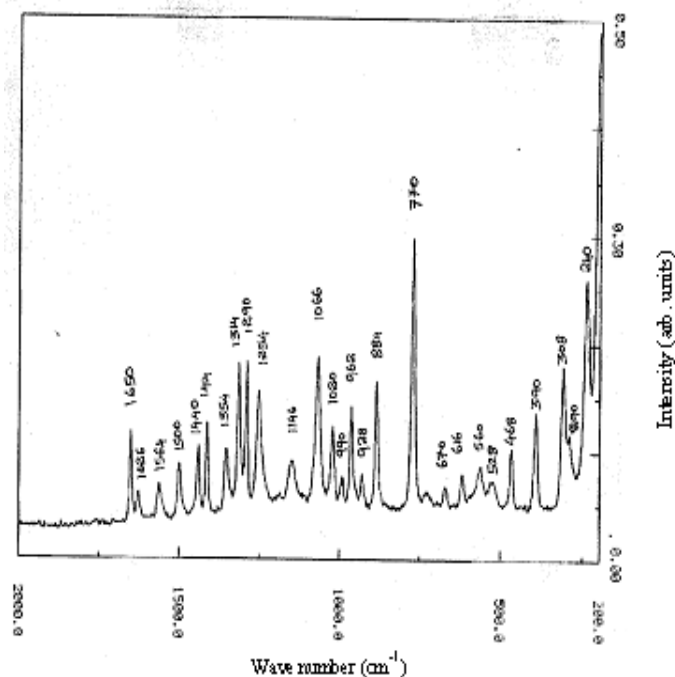
Figure 4. FTIR spectra of Allylthiourea and ATCC crystals at different pH values

From the above results, it is clearly evident that the sulphur atoms in the allylthiourea coordinate with metal ion (Cd) and forms the organometallic complex. This coordination has modified the double bond character of C=S stretching to single bond species and the single bond N-C-N stretching to double bond species and the other vibrational data of ATCC are listed in the Table 1.

The FT-Raman spectrum of ATCC crystalline powder was recorded on a JASCO NR-1100 Raman spectrophotometer that has the precision of 2 cm^{-1} . The spectrum was recorded in the region $2000\text{-}200 \text{ cm}^{-1}$ using the 488 nm line of an argon ion laser for the excitation operating at 200 mW power was shown in fig.5 further to confirm the functional groups present in the as grown crystal. The region above 300 cm^{-1} contains predominantly the bands due to allylthiourea. The stretching band $\nu(\text{C}=\text{S})$ at 770 cm^{-1} has occurred in the Raman spectrum, probably as a consequence of the coordination environments of bridging and terminal ligands in the $[\text{Cd}(\text{ATU})_3]^+$ unit. The presence of the peak at 240 cm^{-1} is mainly due to cadmium bonded sulphur stretching frequency. The predominant Raman spectral data of ATCC are listed in the Table 2. The FTIR and Raman spectroscopic analysis provide the conclusion that sulphur atoms present in allylthiourea reacts with cadmium (metal) ion in this coordination. Mechanical property of the crystal grown at an optimized pH value 3-4 was studied using Vicker's microhardness method. The smooth surface was selected for microhardness test. Indentations were carried out using Vicker's indenter for varying loads ($P = 5\text{-}35 \text{ g}$). For each load, several indentations were made and the average value of the diagonal length (d) was used to calculate the microhardness.

Table 1. Assignments of the main infrared (IR) bands (cm^{-1}) of ATCC and AT

AT	ATCC	ASSIGNMENT
3440 (s)	3396 (s)	$\nu_{\text{as}}(\text{NH}_2)$
3231 (s)	3203 (s)	$\nu(\text{NH})$
1629 (s)	1625 (s)	$\delta(\text{NH}_2)$
1542 (s)	1562 (s)	$\nu(\text{CN}), \delta(\text{NCN}),$ $\nu(\text{C}=\text{S})$
1500 (s)	1493 (m)	$\nu_{\text{as}}(\text{CN})$
1316 (s)	1308 (m)	$\nu_{\text{as}}(\text{CN})$
998 (vs), 928 (s)	978 (m), 920 (m)	$\pi(=\text{CH})$
778 (s)	766 (m)	$\nu(\text{C}=\text{S})$
570 (s)	568 (s)	$\tau(\text{CN}) \pi(\text{NH})$

**Figure 5.** Raman spectrum of ATCC crystal grown at pH 3-4**Table 2.** Main observed Raman vibrational spectra data (cm^{-1}) and their assignments of ATCC

ATCC	ASSIGNMENT
1626	$\delta(\text{NH}_2)$
1564	$\nu(\text{CN}), \delta(\text{NCN}),$ $\nu(\text{C}=\text{S})$
1500	$\nu(\text{CN})$
1414	$\nu_{\text{as}}(\text{C}=\text{S})$
1314	$\delta(\text{NH})$
1066	$\nu(\text{CN})$
990	$\pi(=\text{CH})$
770	$\nu(\text{C}=\text{S})$
560	$\delta(\text{NH})$
528	$\delta(\text{NH}_2)$
468	$\delta(\text{NCN})$
240	$\nu(\text{Cd}-\text{S})$

The hardness number was found to increase with the load. A plot drawn for the hardness value for various loads is shown in fig. 5. These single crystals are mainly used in optical applications, the optical transmittance range and transparency cutoff are the important parameters. The UV-Vis transmittance spectral studies were carried out in the range 200-800 nm using a Shimadzu UV-VIS spectrophotometer. The optical transmission spectrum of the as grown ATCC single crystals grown from solution of different pH values are as shown in Figure . 6.

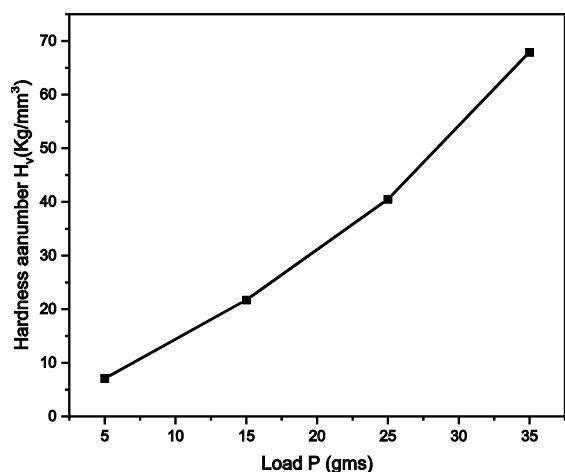


Figure 6. The load dependence of the hardness value of ATCC crystal grown at pH 3-4

The ATCC has a wide transparency window and good transmittance in the entire visible region. The lower cut-off wavelength for the ATCC crystal was determined at 290 nm. The crystals grown from solution of lower pH value (3-4) has the high transmittance performance due to the formation of $[CdCl_4]^{2-}$ complex and has no considerable absorbance in the working frequency region. These studies suggest its suitability for second harmonic generation [13]. The non-linear optical property of the grown crystals was studied using spectra physics quanta Nd:YAG laser with first harmonics output of 1064 nm, pulse width of 8 ns and pulse energy of up to 300 mJ. The second harmonic signal generated in the crystal was confirmed from the emission of green radiation of wavelength 532 nm by the crystal. A bright green light emission is observed from the crystal grown at lower pH compared with the weak signals observed from the other crystals. It reveals that ATCC crystals grown from more acidic medium (pH value of 3-4) has a better performance and is a potential material for frequency conversion.

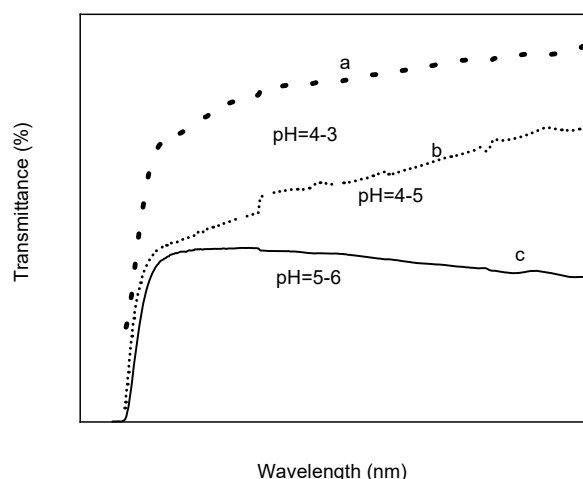


Figure 7. Transmittance spectrum of ATCC crystal for various ATCC crystal grown at various pH values.

Chemical etching is a simple and very powerful tool to analyze the defects present in the growing crystal surfaces. Dislocations easily appear in crystals, especially in the initial stages of their growth [14]. The cut and polished samples

were subjected to etching studies under identical conditions. Etching was carried out using deionised water (resistivity 18.2 M Ω) as etchant at room temperature. Once the damaged surface layer was removed by means of etching, a fresh surface appeared which in turn gave clear etch pits. The etched samples were immediately examined and their microstructure was analyzed using an optical microscope (Leitz metallux-II) in the reflection mode. Some well defined and crystallographically aligned etch pits were observed on the as grown surface. Growth spirals was observed on $\langle 10\bar{1}1 \rangle$ plane. Spirals are formed on the surface of crystals grown at low supersaturation. The “giant” spiral cannot correspond to one dislocation, such a spiral in fact corresponds to a group of dislocations, each having a unit burger vector, and the visible layers orientating from each screw dislocation. Figure 8a illustrates the spirals originating from a group of dislocations. In some cases etching produces etch hillocks rather than etch pits. They have been observed on $\langle 0\bar{1}\bar{1} \rangle$ faces. The well defined pyramidal etch hillock observed on ATCC crystals are shown in Fig.8(b). The hillock has been observed at the sites of dislocations. Hillock observed on crystal surfaces is either as a result of some sort of overgrowth in the etching media or due to the protection of the surface against etching.

6. CONCLUSIONS

ATCC single crystals have been grown by low temperature solution growth method. Influence of pH on the growth and properties of bulk ATCC single crystals has been investigated. The role of solution pH values on the growth mechanism of ATCC single crystal was investigated. Bulk single crystals of ATCC were grown with the reasonable growth rates along the three crystallographic directions at an optimized pH value of 3-4. The mechanical property of the crystal grown at an optimized pH is studied. The morphology of the crystals varies significantly with different pH value of the growth solution. FTIR analysis confirms similar nature of interactions among the groups and ions for all the crystals grown with different pH values. Further the functional groups and vibrational modes were assigned with Raman spectroscopic studies. Optical studies show crystals grown from the optimized pH value of 3-4 has good transmittance and has no considerable absorbance in the working frequency range and provide strong SHG signal among the crystals grown from solution with different pH values.

REFERENCES

- [1] Fafa Wu, Qingyin Wei, Xiaoqi Li, Yi Liu, Weiqi Huang, Qin Chen, Bingxuan Li, Junhua Luo, and Xitao (2022) Cooperative Enhancement of Second Harmonic Generation in an Organic-Inorganic Hybrid Antimony Halide Liu, Cryst. Growth Des. 6 3875-3881 <https://doi.org/10.1021/acs.cgd.2c00257>
- [2] MingYaoGangXu, MingtaoZhang, Linghang Wang, Binbin Zhang, Jinneng Zhu, Growth, (2022) Structure and optical properties of organic-inorganic hybrid $CH_3NH_3HgI_3$ crystal J. Cryst. Growth 594, 126782. <https://doi.org/10.1016/j.jcrysgro.2022.126782>
- [3] Y.J. Ding, X.Mu, and X.Gu, (2000) Efficient Generation Of Coherent Blue And Green Light Based On Frequency

- Conversion In Ktiopo4 Crystals J. Nonlinear Optical Physics and Materials 9, 21.
<https://doi.org/10.1142/S0218863502000857>
- [4].H.O. Marcy, M.J. Rosker, L.F. Warren, P.H. Cunningham, C.A. Thomas, L.A. Deloach, S.P. Velsko, C.A. Ebberts, J.H. Liao, and M.G. Kanatzidis, (1995) l-Histidine tetrafluoroborate: A solution-grown semiorganic crystal for nonlinear frequency conversion Optics. Lett. 20 252-254.
<https://doi.org/10.1364/OL.20.000252>
- [5].Mitsuaki Kogo, Tetsuo Umegaki, Yoshiyuki Kojima (2019) Effect of pH on formation of single-phase vaterite J. Cryst. Growth 517, 35 - 38.
<https://doi.org/10.1016/j.jcrysgro.2019.04.005>
- [6].H.Q. Sun, D.R. Yuan, X.Q. Wang, Y.Q. Lu, Z.H. Sun, X.C. Wei, X.L. Duan, C.N. Luan, M.K. Lu and D.Xu, (2003) Growth And Thermal Properties of TriAllylthiourea Cadmium Chloride (ATCC)Crystal J. Crystal Growth 256,183-187.
[https://doi.org/10.1016/S0022-0248\(03\)01344-7](https://doi.org/10.1016/S0022-0248(03)01344-7)
- [7].N. Zhang, M.H. jiang, D.R. Yuan, D. Xu and X.T. Tao,(1989) A new nonlinear optical material-organometallic complex tri-allylthiourea cadmium chloride Chinese Phys.Letters 6, 280-284.
<https://doi.org/10.1088/0256-307X/6/6/011>
- [8].N.Zhang, M.H.Jiang, D.R.Yuan, D.Xu, X.T. Tao, and Z.S.Shao, (1990) The quality and performance of the organometallic complex nonlinear optical material tri-allylthiourea cadmium chloride (ATCC) J. Crystal Growth 102,581.
[https://doi.org/10.1016/0022-0248\(90\)90417-J](https://doi.org/10.1016/0022-0248(90)90417-J)
- [9].P.Kerkoc,V.Venkataraman,S.Loehran,R.T.Bailey, F.R.Cruickshank, D. Pugh, J.N. Sherwood (1996) Thermal properties of the nonlinear optical crystal zinc tris (thiourea) sulphate J. Appl. Phys. 80, 6666.
<https://doi.org/10.1063/1.363791>
- [10]. P.M. Ushasree, R. Jayavel, C. Subramanian, and P.Ramasamy, (1999) Growth of zinc thiourea sulfate (ZTS) singlecrystals:: a potential semiorganic NLO material J. Crystal Growth 197 216.
[https://doi.org/10.1016/S0022-0248\(98\)00906-3](https://doi.org/10.1016/S0022-0248(98)00906-3)
- [11].P.Hartman, in Crystal Growth: An Introduction, edited by P.Hartman (North – Holland, Amsterdam, (1973), Chap. 14, 367.
- [12]. P. Bennema, in Handbook of Crystal Growth, edited by D.T.J. Hurlle (Elsevier Science Publishers Amsterdam (1993), Vol.1.(a), Chap. 7, p.477.
- [13].V.Venkataramanan, S.Maheswaran, J.N. Sherwood, and H.L. Bhat, J. Cryst. Growth (1997) Crystal growth and physical characterization of the semiorganic bis(thiourea) cadmium chloride 179, 605.
[https://doi.org/10.1016/S0022-0248\(97\)00137-1](https://doi.org/10.1016/S0022-0248(97)00137-1)
- [14]. A.A.Chernov, Contemp. Phys. (1989) Article Formation of crystals in solutions 30, 251.