INVESTIGATIONS ON THE PHYSICO-CHEMICAL PROPERTIES OF ALLYLTHIOUREA COMPLEX NLO CRYSTALS

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Single crystals of allylthiourea complex crystals have been successfully grown by slow evaporation technique. The grown samples were confirmed by CHN analysis. The band gap of ATCC, ATCB and ATMC were found to be 3.93 eV, 3.58 eV and 3.18 eV respectively. Thermal parameters such as thermal diffusivity ($\alpha$) and effusivity ($e$), the thermal conductivity ($k$) and heat capacity ($C_p$) of the grown samples were studied using photorpyroelectric technique. The frequency response of dielectric constant and dielectric loss were also studied.

1. Introduction

The introduction of the theory of Double-radical Model, popularly known as double ligand theory, has kindled the interest of scientists working in the field of NLO materials. A series of novel metal organic compounds has developed on the basis of the above model [1-3]. These materials have considerable high NLO coefficient (contrast to inorganic material), stable physicochemical properties and better mechanical intention (contrast to organic materials). Studies on organ metallic complexes have proved that the
formation of a co-ordination 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 the benzyl ring, so that the anisotropy of the crystal is reduced as compared with the organic crystals [1]. Organo-metallic allylthiourea crystals of type ATMX₂ (AT=allylthiourea, M=Cd or Hg, X=Cl or Br) is one type of metal-organic coordination material in which AT acts as the ligand. A comparatively high optical nonlinearity in these complexes comes from the distortion of the tetrahedron, which is composed of three allylthiourea (AT) and one Cl (or Br) combining with Cd (or Hg) [4]. The present investigation is a continuation of our ongoing research work on allylthiourea complexes and it deals with the growth aspects of promising allylthiourea complex crystals such as Allylthiourea Cadmium Chloride (ATCC), Allylthiourea Cadmium Bromide (ATCB), Allylthiourea Mercury Chloride (ATMC), grown from aqueous solution. The structural and optical properties of the crystals have been reported earlier. The electrical and thermal properties of ATCC, ATCB and ATMC have been studied and reported in this paper.

2. Synthesis and growth

Organo-metallic allylthiourea crystals of type ATMX₂ (AT=allylthiourea, M=Cd or Hg, X=Cl or Br) is one type of metal-organic coordination material in which AT acts as the ligand. The molecular structure contains distorted MX₃S tetrahedron and the crystals show powder SHG efficiency higher than urea. All the starting materials were highly pure (Aldrich). The crystals were synthesized using slow evaporation technique. Allylthiourea complex crystals were synthesized according to the reaction formula:

\[ \text{MX}_2 + 3\text{CH}_2=\text{CHCH}_2\text{NHCSNH}_2 \rightarrow \text{MX}_2 (\text{CH}_2=\text{CHCH}_2\text{NHCSNH}_2)_3 \]

To ensure high purity, the material was purified by successive crystallization twice or thrice, using deionised water. Recrystallized salt was taken and dissolved in deionised water according to the solubility data. The solution was constantly stirred for 24 hours using magnetic stirrer to overcome the concentration gradient in the crystallizer. The saturated solution was taken in a crystallizing vessel and covered with a perforated sheet to facilitate slow evaporation of the solvent at room temperature. The solution gradually attained supersaturation due to evaporation which resulted in nucleation followed by the growth of crystals. Tiny crystals of type ATMX₂ were formed by spontaneous nucleation within 7-10 days. Single crystals with perfect external shape were obtained by spontaneous nucleation. Good quality crystals, free from macro defects were chosen as seeds to carry out the further growth experiments. The period of growth for growing good-sized quality crystals ranged between 30 to 40 days. The photographs of as grown single crystals of allylthiourea are shown in Fig.1-3. The grown crystals are stable, do not decompose in air and non-hygroscopic in nature.
3. Results and discussion

3.1. CHN Analysis

In order to confirm the grown samples, CHN analysis was carried out using Elementar Vario EL 111 Elemental analyzer. The theoretical and experimental atomic weight percentages of C, H and N are summarized in the Table1. The result indicates the absence of water in the salt. Thus the chemical composition of allylthiourea complex crystals is established as ATMX₂.

3.2. Optical absorption studies.

The optical absorption spectra of allylthiourea complex crystals recorded in the range 200–2000 nm using Varian Cary 5E spectrophotometer. The cut off wavelength of ATCC, ATCB and ATMC occurs at 290, 295 and 335 nm respectively [5]. The efficient NLO crystals has an optical transparency at lower cut-off wavelength between 200 and 400 nm. Band gap has been calculated from the UV-Vis absorbance data. A graph (Fig. 3).
4) has been plotted between \( h\nu \) and \((\alpha h\nu)^2\) to determine the band gap value, where \( \alpha \) is absorption coefficient and \( h\nu \) is the energy of the incident photon. The band gap of ATCC, ATCB and ATMC was found to be 3.93 eV, 3.58 eV and 3.18 eV respectively. The band gap of ATCC single crystal is slightly more than that of organic crystal of L-alanine acetate [6] and semi organic crystals of bis (thiourea) cadmium zinc chloride [7]. Also the band gap of ATCC and ATCB is higher than that of bis thiourea zinc bromide (BTZB) while that of ATMC is lesser [8]. The higher energy band gap shows that the defect concentration in the grown crystals is very low.

| Samples | Weight Composition % |  |
|---------|----------------------|---|
|         | Carbon | Hydrogen | Nitrogen |  |
|         | Theoretical | Experimental | Theoretical | Experimental | Theoretical | Experimental |  |
| ATCC    | 27.09 | 27.08 | 4.55 | 4.48 | 15.89 | 15.87 |  |
| ATCB    | 23.2 | 24.21 | 3.9 | 4.03 | 13.5 | 14.17 |  |
| ATMC    | 23.3 | 23.3 | 3.8 | 3.52 | 13.55 | 13.66 |  |

**Figure 4.** Band gap plot of Allyl Thiourea complexes
3.3. Photopyroelectric (PPE) Studies

The thermal parameters such as thermal diffusivity ($\alpha$) and effusivity ($e$), the thermal conductivity ($k$) and heat capacity ($C_p$) of allyltioure complex crystals have been measured by using improved photopyroelectric electric technique [9]. The samples were carefully polished initially with water and finally with alumina powder to ensure good surface finish. In this measurement, a thermally thick pyroelectric detector was attached to one side of the sample, which was also thermally thick and the combination was mounted on a thermally thick backing medium. Intensity modulated light from a 120 mW He-Cd laser (KIMMON) of wavelength $\lambda=442$nm has been used as the optical heating source. The pyroelectric detector used in this measurement was polyvinylidene difluoride (PVDF) film of thickness 28 $\mu$m, with both sides coated with Ni-Cr film, and its pyroelectric coefficient is $p = 0.25 \times 10^{-8}$ Vcm$^{-1}$ K$^{-1}$. The sample-detector-backing assembly was enclosed in a chamber, which was maintained at room temperature. Measurement of the PPE signal phase and amplitude enable one to determine the thermal diffusivity ($\alpha=K/\rho C_p$, $\rho$ being the sample density) and thermal effusivity ($e=(KC_p\rho)^{1/2}$) respectively. From the measured values of $\alpha$ and $e$, the thermal conductivity ($k$) and heat capacity ($C_p$) of allyltioure complex crystals were calculated, and are presented in Table 2. for a frequency of 40 Hz.

Table 1. Thermal Parameters of ATMC, ATCC and ATCB crystals at 40Hz

| Sample Code | Thermal effusivity. $e$ (Ws$^{1/2}$/m²K) | Thermal diffusivity. $\alpha$ ($\times 10^{-6}$m²/s) | Thermal conductivity. $k$ (W/m K) | Sp. Heat capacity. $C_p$ (J/kg K) |
|-------------|----------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|
| ATMC        | 3167 ± 70                              | 6.36 ± 0.39                            | 7.97 ± 0.37                            | 577 ± 15                               |
| ATCC        | 1196±65                                | 5.27±0.28                              | 8.86±0.40                              | 101±18                                 |
| ATCB        | 3122 ± 62                              | 6.47 ± 0.39                            | 7.93 ± 0.37                            | 776±20                                 |

3.4. Dielectric studies

In the present work, dielectric measurements on allyltioure complex single crystals were carried out at room temperature using multi frequency LCR meter (Agilent E 4980 A) for a frequency range from 1KHz to 2 MHz. A rectangular sample with dimension 6 x 4 x 3 mm$^3$ were cut and polished using fine grade alumina powder in order to obtain smooth surface. Further, the sample was coated with silver paint and placed between the copper electrodes of the sample holder. Both dielectric constant and loss were calculated and graphs were plotted. Fig. 5 shows the plot of dielectric constant versus applied frequency. The dielectric constant has high values in the lower frequency region and
then it decreases with the applied frequency. Fig.6 shows the variation of dielectric loss with frequency. The curve shows that the dielectric loss decreases with increase in frequency, and at high frequency, it remains almost a constant. The high value of dielectric constant at low frequencies may be due to the presence of all the four polarizations namely, space charge, orientational, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually. The dielectric nature of allylthiourea complexes is in good agreement with the reported work [5]. The low dielectric constant favours high SHG efficiency in accordance with Miller’s rule [10].
4. Conclusion

Single crystals of ATCC, ATCB and ATMC were conveniently grown by employing slow evaporation technique. The optical absorption study confirmed that the crystals has a low absorption, with UV cut-off wavelength starting around 290 nm, which is an essential consideration for the NLO crystals. The thermal parameters such as thermal diffusivity (α) and thermal effusivity (e), thermal conductivity (k) and heat capacity (Cp) of single crystals is also determined. The dielectric studies reveal that the dielectric constant is relatively higher in the low frequency region and lower in the high frequency region.

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