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# Growth and physicochemical characterization of calcium cadmium thiocyanate CaCd(SCN)$_4$ single crystals

C. LATHA[1], C.K. MAHADEVAN[2,*]

[1]Department of Chemistry, TDMNS College, T. Kallikulam, Tamil Nadu 627113, India
[2]Center for Scientific and Applied Research, PSN College of Engineering and Technology, Tirunelveli,
Tamil Nadu 627152, India

It is important to grow and characterize new bimetallic thiocyanate single crystals as they are expected to exhibit useful optical and electrical properties. In the present study, calcium cadmium thiocyanate CaCd(SCN)$_4$ single crystals were grown by slow evaporation of solvent and were characterized chemically, structurally, thermally, optically and electrically. X-ray diffraction analysis indicates that the grown crystal belongs to the tetragonal crystal system with lattice parameters: a = b = 12.2491(7) Å and c = 15.1012(5) Å. EDAX spectral analysis confirms the expected chemical composition. Thermogravimetric (TG/DTA) measurement implies good thermal stability. Optical (UV-Vis-NIR absorption spectral and SHG efficiency) measurements suggest good optical absorption in the UV and blue regions and the SHG efficiency of 6.13 (in urea unit). The dielectric measurements carried out in the temperature range of 40 °C to 150 °C at five different frequencies, viz. 100 Hz, 1 kHz, 10 kHz, 100 kHz and 1 MHz indicate a normal dielectric behavior.

Keywords: *bimetallic thiocyanates; dielectric materials; NLO materials; single crystal growth; growth from solution; characterization*

## 1. Introduction

Research on various metalorganic crystals formed with organic ligands, such as urea, thiourea, allylthiourea, thiosemicarbozide and thiocyanate, confirm NLO activity in these materials. Crystals formed with thiocyanate (SCN) ligand show a relatively higher second harmonic generation (SHG) effect than the crystals formed with the other organic ligands. Bimetallic thiocyanate complexes with AB(SCN)$_4$ structure (where A and B are bivalent metal atoms), in particular, possess favorable properties to become candidate materials for SHG devices [1, 2]. In these complexes, thiocyanate (SCN) plays a crucial role in combining the versatile ambidentate ligand with two donor atoms. The modes of metal coordination with thiocyanates can be understood in terms of the hard-soft acid-base (HSAB) concept developed by Pearson [3] and Balarew et al. [4].

Single crystals of several bimetallic thiocyanates have already been grown and studied. However, it is important to grow and characterize new bimetallic thiocyanate single crystals because of their importance. Recently, we have reported [5] the growth and physicochemical properties of undoped and K$^+$, Ca$^{2+}$, Mn$^{2+}$, Mg$^{2+}$, Cu$^{2+}$ doped (with 1 mol% concentration) ZnCd(SCN)$_4$ and Zn$_x$Cd$_{2-x}$SCN$_4$ (with x = 0.0, 0.4, 0.8, 1.2, 1.6 and 2.0) single crystals. Single crystals could be grown with x = 0.0 (leading to Cd(SCN)$_2$) but not when x = 2.0 (leading to Zn(SCN)$_2$). The above study indicated not only the formation of the mentioned hybrid crystals but also an increase in dielectric constant and SHG efficiency when ZnCd(SCN)$_4$ crystal is doped with a metallic impurity and a decrease of dielectric constant and SHG efficiency when quasi mixing is done.

It is expected that the physicochemical properties of ZnCd(SCN)$_4$ may change significantly if zinc is replaced by calcium (an alkaline earth metal). Thus, in the present study, we have made an attempt to grow (by slow evaporation of solvent

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*E-mail: mahadevan58@yahoo.co.in

method) and characterize (chemically, structurally, thermally, optically and electrically) the single crystals of calcium cadmium thiocyante (CCTC), $CaCd(SCN)_4$. The details are presented herein.

## 2. Experimental

### 2.1. Growth of single crystals

Analytical reagent (AR) grade chemicals (precursors), viz. calcium chloride, cadmium chloride and ammonium thiocyanate were mixed together in deionized water to synthesize the calcium cadmium thiocyanate (CCTC) salt according to the following reaction:

$$4NH_4(SCN) + CaCl_2 + CdCl_2 \rightarrow$$
$$\rightarrow CaCd(SCN)_4 + 4NH_4Cl \quad (1)$$
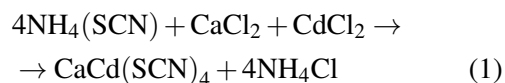
The synthesized salt was further purified by repeated crystallization process until optically clear tiny crystals were obtained. The aqueous solution of CCTC was adjusted to the pH value of 3 to 4. The solution was continuously stirred for few hours and the condition of supersaturation was achieved. After attaining the supersaturation, the solution was filtered twice and then allowed to evaporate at a temperature of ca. 30 °C. Well-defined and optically good quality crystals of considerable size were obtained in a period of about two weeks. Solution with pH value ~3.5 gave only one sufficiently large crystal in each crystal growth cell considered in the present study. Similar result was obtained in all the five crystal growth cells containing the solution with the same pH value, indicating repeatability of the process of crystal growth. Fig. 1 shows the photograph of a sample of a grown CCTC crystal.

### 2.2. Characterization

The grown CCTC crystal was subjected to single crystal X-ray diffraction (SXRD) analysis using an ENRAF NONIUS CAD4-F single crystal X-ray diffractometer with graphite monochromatic MoK$\alpha$ radiation. From the measurements, crystal lattice parameters were determined. Energy dispersive X-ray absorption (EDAX) spectrum was obtained with a SEM-EDAX apparatus (Hitachi
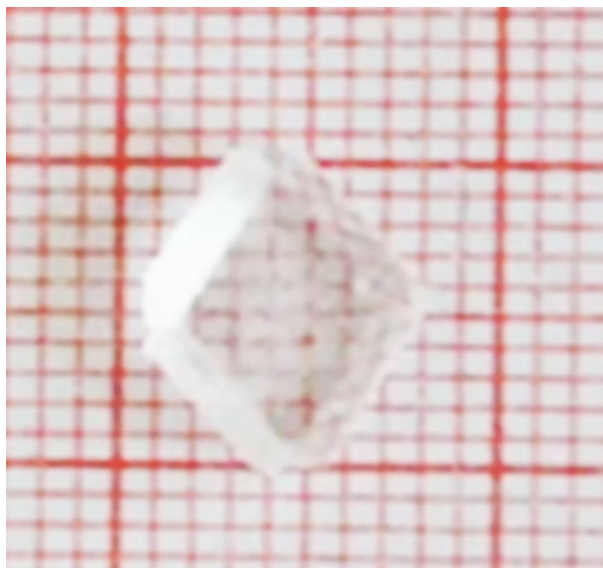


Fig. 1. Photograph of a sample of a grown CCTC crystal.

scanning electron microscope, model S-4200). Thermogravimetric (TG/DTA) analysis was carried out in the temperature range of 28 °C to 900 °C at a heating rate of 20 °C/min using a NETSZCH STA 409C thermal analyzer.

Optical (UV-Vis-NIR) absorption spectrum was recorded in the wavelength range of 200 nm to 900 nm using a Shimadzu UV-2400PC spectrophotometer. SHG efficiency of the powdered sample was estimated within an accuracy of ±10 % by Kurtz et al. technique [6] using a Nd:YAG Q-switched laser with a fundamental laser beam of a wavelength of 1060 nm and 8 ns laser pulses with a spot radius of 1 mm. Urea crystal powder was used as a reference material for comparing the SHG efficiency of the CCTC crystal powder.

Capacitance $C_{crys}$ and dielectric loss factor tan$\delta$ measurements were carried out within an accuracy of ±2 % using an LCR meter (Agilent 4284A) by the parallel plate capacitor method along the direction normal to the large surface area of the crystal at various temperatures in the range of 40 °C to 150 °C at five different frequencies, viz. 100 Hz, 1 kHz, 10 kHz, 100 kHz and 1 MHz in a way similar to that followed by Mahadevan et al. [7–9].

The dielectric constant of the crystal $\epsilon_r$ was calculated using Mahadevan relation (as the area of the crystal was smaller than the plate area of the cell) [5, 10, 11]:

$$\varepsilon_r = [A_{air}/A_{crys}]$$
$$[(C_{crys} - C_{air}(1 - (A_{crys}/A_{air})))/C_{air}] \quad (2)$$

where $A_{crys}$ is the area of crystal touching the electrode and $A_{air}$ is the area of the electrode. The AC electrical conductivity $\sigma_{AC}$ was calculated using the relation [12]:

$$\sigma_{AC} = \varepsilon_0 \varepsilon_r \omega (\tan \delta) \quad (3)$$

where $\epsilon_0$ is the permittivity of free space $(8.85 \times 10^{-12}$ $C^2 \cdot N^{-1} \cdot m^{-2})$ and $\omega$ is the angular frequency (equal to $2\pi f$, where f is the frequency) of the applied field.

A crystal with high transparency and large defect-free surface (free of pits, cracks or scratches, tested with a traveling microscope) of a size >3 mm was selected and used for the measurement. The opposite faces were polished and coated with good quality graphite to obtain a good conductive surface layer. The dimensions of the crystal were measured using a traveling microscope (LC = 0.001 cm). The temperature was controlled within an accuracy of $\pm 1$ °C and the observations were made while cooling the sample.

## 3. Results and discussion

### 3.1. Crystal nature and lattice parameters

The CCTC crystal grown is found to be quite stable without being hygroscopic and losing its optical transparency for several months (as observed visually) in the normal atmospheric conditions. The SXRD data obtained indicate that the CCTC crystal belongs to the tetragonal crystal system with lattice parameters a = b = 12.2491(7) Å and c = 15.1012(5) Å.

### 3.2. Chemical composition and thermal stability

The EDAX spectrum of the CCTC crystal is shown in Fig. 2. The experimentally observed

(by considering the X-ray absorption peak intensities corresponding to the existing elements) and expected (estimated theoretically assuming the chemical formula as $CaCd(SCN)_4$) chemical composition are given in Table 1. The experimentally observed and expected chemical compositions are found to be nearly the same which confirms that the grown CCTC crystal has the chemical formula $CaCd(SCN)_4$.
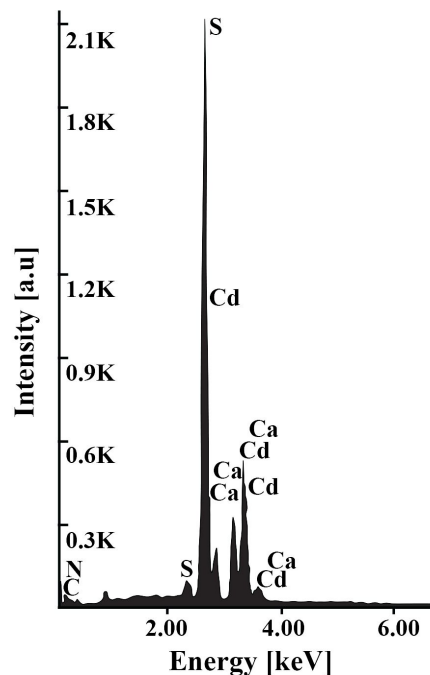
Fig. 2. EDAX spectrum of the grown CCTC crystal.

The observed TG/DTA pattern is shown in Fig. 3. The grown CCTC crystal can be considered to be thermally stable at least up to 200 °C. The thermal decomposition takes place in two steps (one at around 300 °C and the other one at around 600 °C) with two major weight losses. The DTA curve confirms this by showing two significant exothermic peaks at around 300 °C and 600 °C. This can be considered as resulting from the evolution of volatile gases in two stages.

### 3.3. Optical properties

Optical transmittance in a given range of optical spectrum is dependent on several factors, such
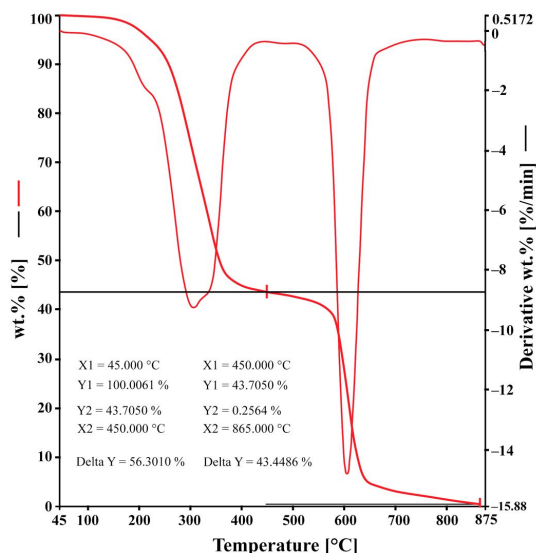
Fig. 3. TG/DTA pattern of the grown CCTC crystal.

Table 1. Experimentally observed and expected chemical compositions.

| Element | Experimental [wt.%] | Expected [wt.%] |
|---------|---------------------|-----------------|
| Ca | 10.89 | 10.42 |
| Cd | 28.98 | 29.21 |
| S | 34.16 | 33.33 |
| C | 12.41 | 12.48 |
| N | 13.56 | 14.56 |

as material composition, electronic transition and defects (structural/crystalline) associated with the material [13–15]. The defects control internal scattering/absorption of a signal in crystal medium which tunes the limit of optical transmittance in the spectrum [16, 17]. The measured UV-Vis-NIR absorption spectrum is shown in Fig. 4. The grown CCTC crystal is found to exhibit good absorption in the UV and blue regions and has higher cut-off (absorption edge) wavelength. The transparency is good on the higher side of visible wavelength range covering the green, yellow, orange and red regions. This optical properties indicate that this crystal can be used in sunscreen devices to filter the lower wavelength region of the sun light [5, 18].

The result obtained in the SHG efficiency measurement indicates that, for a laser input pulse of 6.2 mJ, the second harmonic signals (532 nm) of 145 mV and 889 mV have been obtained for urea and CCTC, respectively. Therefore, the SHG efficiency of CCTC is found to be 6.13 (in urea unit). This is a quite high value which makes the CCTC crystal a very interesting NLO material to be used in SHG devices.

Manganese(II)-mercury(II) thiocyanate bis(dimethyl sulfoxide) has been reported [19] to have the maximum SHG efficiency 23 times of that of urea. Xinqiang et al. [20] reported an SHG efficiency of 18 (in urea unit) for $MnHg(SCN)_4$. Recently, we have found that SHG efficiency of $MnHg(SCN)_4$ has increased from 18 to 20.3 (in urea unit) on doping with $Ca^{2+}$ [21]. The SHG efficiencies reported in the literature [5] for undoped and $Ca^{2+}$ (1 mol%) doped $ZnCd(SCN)_4$ are 12 and 13 (in urea unit), respectively. From the above considerations, it can be inferred that $Ca^{2+}$ (as a dopant) increases the SHG efficiency of $MnHg(SCN)_4$ and $ZnCd(SCN)_4$. The present study indicates a decrease of SHG efficiency from 12 to 6.13 (in urea unit) when $Zn^{2+}$ in $ZnCd(SCN)_4$ is replaced fully by $Ca^{2+}$ to become $CaCd(SCN)_4$. This change can be considered similar to that observed for the doped and quasi mixed crystals based on $ZnCd(SCN)_4$ [5].



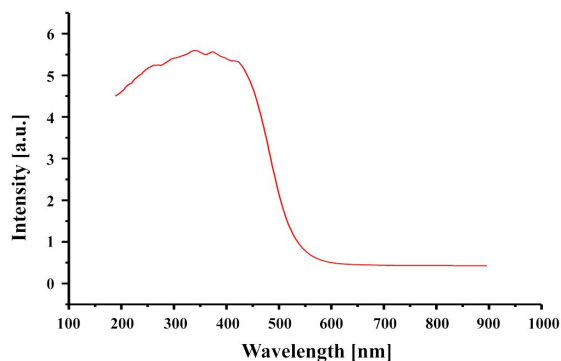Fig. 4. UV-Vis-NIR absorption spectrum of the grown CCTC crystal.

## 3.4. Electrical properties

The dielectric parameters, viz. $\epsilon_r$, $\tan\delta$ and $\sigma_{AC}$ observed for the grown CCTC crystal are shown

in Fig. 5. All the three considered parameters were found to increase with the increase in temperature. Further, the $\epsilon_r$ and $\tan\delta$ values decrease, while the $\sigma_{AC}$ value increases with the increase in frequency of the applied field. As this is a normal dielectric behavior, it can be stated that the grown CCTC crystal behaves as a normal dielectric material.
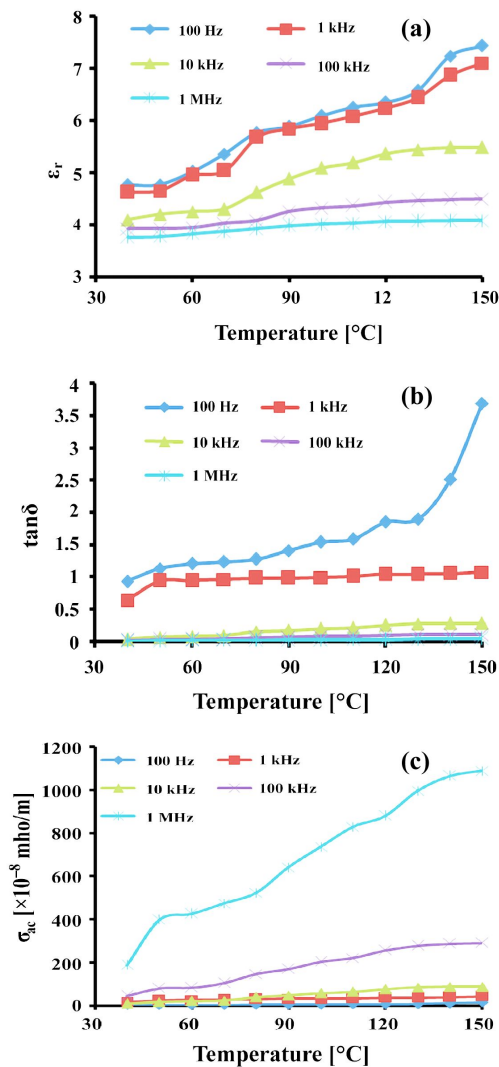


Fig. 5. Dielectric parameters: (a) dielectric constant; (b) dielectric loss factor; (c) AC electrical conductivity.

The nature of variations of dielectric constant with frequency of applied AC field and temperature indicates the type of phenomena occurring in the material. The major contributions to dielectric constant of the crystal considered in the present

study may come from electronic and ionic polarizations. An increase in the ionic distance due to an increase in temperature of the crystal influences the ionic and electronic polarizations. The increase in $\epsilon_r$ with temperature is generally attributed to crystal expansion and electronic and ionic polarizations. At higher temperatures, it is mainly attributed to thermally generated charge carriers and impurity dipoles. Varotsos [22], with simple arguments, has shown that the electronic polarizability practically remains constant and temperature independent for the ionic crystals. In these crystals, an increase in dielectric constant with temperature is essentially due to the temperature variation of ionic polarizability. The CCTC crystal considered in the present study is mainly of ionic nature and the $\epsilon_r$ values observed in the present study vary from 3.759 (at 40 °C and frequency of 1 MHz) to 7.440 (at 150 °C and frequency of 100 Hz). Thus, this variation of dielectric constant with temperature observed in the CCTC crystal can be understood as resulting from the temperature dependence of the ionic polarizability.

Displacement of an ion from an equilibrium position is equivalent to placing a fictitious dipole at the state of equilibrium with an ion. Although positive and negative ions are displaced in opposite direction in an electric field, all the induced moments have the same sign. Since ionic (vibrational/displacement) polarization is related to the oscillation of ions, the proper field frequencies are much lower than those of electrons due to large difference in their masses [23]. In normal dielectric behavior, $\epsilon_r$ value decreases with increasing frequency and reaches a constant value, because of the fact that beyond a certain frequency of the electric field, the dipole does not follow the alternating field.

The dielectric constants observed for the grown CCTC crystal can be considered as small. The $\epsilon_r$ values observed at 1 kHz frequency (normally considered to be the maximum limit of static field) at low temperatures are only 4.618 and 4.647 at 40 °C and 50 °C, respectively. The material having lower dielectric constant has less number of dipoles per unit volume and, as a result, it will have minimum

losses as compared to the material having higher dielectric constant [24]. The observed low dielectric constant at higher frequency indicates that the CCTC crystal may offer less power consumption and reduced RC delay [25] which is a prerequisite demand for designing microelectronic, THz wave generators, electro-optic modulators and field detector devices [26–28]. Also, a low dielectric constant is a parameter suitable for the enhancement of SHG coefficient which is in accordance with the Miller rule [29]. This explains the observation of higher SHG coefficient for the grown CCTC crystal.

The variation of dielectric constant observed within the temperature and frequency ranges considered in the present study may be treated as small (the variation increases from 1.001 to 3.363 only when the temperature increases from 40 °C to 150 °C and from 0.318 to 2.680 only when the frequency decreases from 1 MHz to 100 Hz). This indicates that the crystal may be useful for high speed electro-optic modulations. Moreover, the observed low tanδ values indicate that the grown CCTC crystal is well-ordered and possesses less electrically active defects [13].

The electrical conduction in dielectrics is mainly a defect controlled process. The Gibbs free energy of a crystal, at any particular temperature, is minimum when certain fraction of ions leave the normal lattice. As the temperature rises more and more, defects are produced which, in turn, increases the conductivity. Motion of ions and not motion of electrons is usually the mechanism of electrical conductivity in alkali and silver halide crystals which has been established by comparing the transport of charge with the transport of mass as measured for the material plated on electrodes in contact with a crystal [30]. The conduction mechanism considered in the present study seems to be connected with mobility of vacancies. Moreover, in the CCTC crystal, simultaneous presence of positive and negative ions has been revealed. Thus, the movement of ions and related vacancies is a possible mechanism of conductivity of CCTC crystal. This can be understood by the small temperature dependence of AC electrical

conductivity observed at lower frequencies. The variations of $\sigma_{AC}$ observed at frequencies of 100 Hz, 1 kHz and 10 kHz in the considered temperature range (40 °C to 150 °C) are only $12.80 \times 10^{-8}$ mho/m, $25.97 \times 10^{-8}$ mho/m and $79.37 \times 10^{-8}$ mho/m, respectively.

## 4.   Conclusions

Calcium cadmium thiocyanate (CCTC) single crystals have been successfully grown by slow evaporation of solvent at room temperature and characterized by different methods. X-ray diffraction analysis indicates that the grown crystal belongs to the tetragonal crystal system. EDAX spectral analysis confirms the chemical composition of the grown crystal. The TG/DTA pattern indicates that the CCTC crystal is thermally stable at least up to 200 ° C and shows two major weight losses along with significant exothermic peaks at around 300 °C and 600 °C corresponding to the evolution of volatile gases in two stages. Results of optical measurements indicate a good optical absorption in the UV and blue regions and SHG efficiency of 6.13 (in urea unit) making the grown crystal useful in sun-screen and SHG devices. Results of dielectric measurements indicate a normal dielectric behavior of the compound. The temperature dependence of dielectric constant could be understood as resulting from temperature dependence of ionic polarizability. Also, the AC electrical conduction could be understood as caused by the movement of ions and related vacancies. Variations of dielectric constant with temperature and frequency of applied field are considered to be small which makes the crystal useful for high speed electro-optic modulations.

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