Synthesis, growth and characterization of a new non-linear-optical crystal: Copper cobalt thiocyanate

C Ramachandra Raja* & B Vijayabhaskaranb

*aDepartment of Physics, Govt. Arts College (Autonomous), Kumbakonam 612 001
bDepartment of Physics, A A M Engineering College, Kovilvenni 614 403

*E-mail: crraja_phy@yahoo.com

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The synthesis and growth of non-linear optical crystal, copper cobalt thiocyanate, CuCo(SCN)₄ (CCTC) single crystals have been successfully carried out by slow evaporation technique using de-ionized water as solvent. The grown crystal is characterized by single crystal X-ray diffraction analysis, FTIR analysis, optical transmission spectral analysis and thermal analysis. The lower cut off wavelength of CCTC crystal occurs at 380 nm. The CCTC crystal exhibits good physicochemical stability up to 199.5°C. Test for second harmonic generation by the crystals of CCTC, using the method of Kurtz and Perry shows positive results.

Keywords: Characterization, Slow evaporation technique, Non-linear optical materials, Second harmonic generation

1 Introduction

Organic non-linear optical crystals have attracted much attention due to their superior properties such as large NLO coefficient, structural flexibility, faster response and larger susceptibility but low mechanical strength, poor physicochemical stability, lack of quality and size of the crystals limit their applications. Compared to organic crystals, the inorganic crystals have good physicochemical stabilities, short UV cut-off wavelength and large second order nonlinearities. Due to these reasons the inorganic crystals are gaining popularity in the field of nonlinear optics. Inorganic complex crystals have wide range of application in the field of optical computing, optical information processing, optical disk data storage, laser remote sensing, laser driven fusion, colour display and medical diagnostics. This analysis focuses on pure inorganic crystal materials, which are important in the emerging field of opto-electronic applications.

In the present study, cyanide group of materials are considered due to its good second order nonlinearity. The general formula of bimetallic thiocyanate family crystal is AB (SCN)₄, where A and B represents hard and soft metals, respectively. Various A and B group of metals are suitably selected for the study. The metal complexes produce a large variety of structures, higher environmental stability and much greater diversity of tunable electronic properties. These compounds have good architectural flexibility, easy of fabrication and charge transfer capability associated with charge transfer transitions either from metal to ligand or ligand to metal. In this paper, copper cobalt thiocyanate(CCTC) was successfully synthesized and single crystals were grown by slow evaporation method.

2 Experimental Details

All the basic starting materials were AR grade and used as purchased. All the synthesis and growth processes were carried out in aqueous solutions. The CCTC crystal was prepared by taking the raw materials in the proper molar ratios, according to the following reaction and dissolved in de-ionized water. Then, the solution was filtered twice to remove any insoluble impurities.

CuCl₂ + CoCl₂ + 4KSCN → CuCo(SCN)₄ + 4KCl

By using the slow evaporation method single crystals of CCTC were successfully grown from supersaturated solution at room temperature. Further, the purity of the synthesized material was increased by successive recrystallization processes. The grown single crystals have been harvested over a period of five weeks. The grown crystals are shown in the Fig. 1.

3 Results and Discussion

3.1 Single crystal XRD

The lattice parameters of the crystal were determined using a single crystal X-ray diffractometer (Model: ENRAF NONIUS CAD4). The observed
results indicate that the crystal belongs to orthorhombic crystal system. The determined unit cell parameters are $a=5.80$ Å, $b=7.52$ Å, $c=10.12$ Å, $\alpha=\beta=\gamma=90^\circ$ and $V=441$ Å$^3$.

3.2 Fourier transform infra-red (FT-IR) analysis

The Fourier transform infra-red analysis is a technique in which almost all functional groups in a molecule absorb characteristic frequencies. The FT-IR spectrum of CCTC crystals has been recorded in the KBr phase in the frequency region of 400-4000 cm$^{-1}$ using Perkin-Elmer 783 spectrometer and is shown in Fig. 2. The recorded spectrum has been compared with the available literature.$^9$-$^{12}$ The FT-IR absorption peaks appear at 3435, 2076, 750 and 598 cm$^{-1}$. The symmetric stretching of OH gives rise to the absorption band at 3435 cm$^{-1}$. The peak at 2076 cm$^{-1}$ corresponds to CN stretching vibration. The peak at 750 cm$^{-1}$ corresponds to CS stretching vibration and the peak at 598 cm$^{-1}$ corresponds to SCN stretching vibration. The SCN group present in the CuCo(SCN)$_4$ crystal is a good electron supplier and Cu$^{2+}$ and Co$^{2+}$ are strong electron acceptors. So, the electron transformation from SCN$^-$ to Cu$^{2+}$ and Co$^{2+}$ ions will increase the wavenumbers of CN and CS stretching vibrations for better non-linear optical applications.$^{13}$

3.3 Optical transmission spectral analysis

The optical transmission range and transparency cut off wavelength of CCTC crystals have been recorded by using Varian Cary 500 spectrophotometer. In the present study, the transmission spectrum of CCTC crystal was recorded in the range of 300-2000 nm. The recorded spectrum is shown in Fig. 3. The transparent wave band of CCTC crystal lies in the range of wavelength 380-1200 nm. The observed spectrum shows that the UV transparency cutoff wavelength of CCTC crystal occurs at 380 nm. The infra-red absorption peaks occur at 799 and 974 nm. CCTC crystal is transparent with a wide range of the spectrum from violet to IR light and reveals that the material has good optical transparency in the entire visible region.
3.4 Thermal analysis

The combined thermogravimetric (TG) and differential thermal analysis (DTA) of CCTC crystal was recorded in the temperature range of room temperature to 1000°C using NETZSCH STA 409 C/CD under nitrogen atmosphere with a heating rate of 20°C/min. The recorded TG/DTA curves of CCTC crystal are shown in Fig. 4.

The material exhibits single stage weight loss starting at 225°C. This initial weight loss is due to the evaporation of water molecules present in the crystal due to solvent inclusion and absorbed water molecules from the atmosphere. The observed results are better than zinc mercury thiocyanate (ZMTC) and cadmium mercury thiocyanate (CMTC). But below this temperature no weight loss is observed. The TGA analysis reveals that the thermal decomposition of CCTC is multistep process, namely breakdown of the three dimensional steric structure and the formation of metal sulfides, carbon bisulfide, nitrogen gas and dicyanogen\(^{14}\). In DTA analysis, there is a sharp endothermic peak at around 199.5°C, which is assigned for melting point of the specimen followed by a broad exothermic peak at around 768.6°C corresponds to decomposition of the CCTC compound.

3.5 Kurtz powder technique

The second harmonic generation efficiency has been studied using the powder technique of Kurtz and Perry\(^{15}\). A Q-switched Nd:YAG laser beam of wavelength 1064 nm, with an input power of 6.5 mJ/pulse, and pulse width of 8 ns with a repetition rate of 10 Hz was used. The grown crystals were crushed into a fine powder and then packed in a micro capillary of uniform bore and exposed to laser radiations. The 532 nm radiation was collected by a monochromater after separating the 1064 nm pump beam with an infra-red blocking filter. Second harmonic radiation generated by the randomly oriented micro crystals was focused by a lens and detected by a photo multiplier tube (Hamamatsu R2059). The emission of green light confirms the second harmonic generation property of the crystal.

4 Conclusions

The compound CCTC has been synthesized and the single crystals were grown successfully using the slow evaporation method. The cell parameters were determined using single crystal X-ray diffraction method. Functional groups were analyzed using FTIR analysis, which revealed the characteristic vibration modes of CCTC crystal. The optical property of the grown crystal was studied by UV-Vis-NIR spectroscopy and the UV cut off wavelength of the grown crystal was 380 nm. The crystal possesses good optical transparency in the entire visible region. The TGA and DTA analysis under nitrogen atmosphere reveals that CCTC crystal was stable up to 199.5°C (which is the melting point). The experiment for second harmonic generation efficiency using the Kurtz-Perry powder technique confirmed the second harmonic generation property of the crystal, which was found to be less than that of the standard potassium dihydrogen phosphate (KDP).

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