Optik 125 (2014) 1071–1074

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Synthesis, growth and physicochemical properties of an organometallic nonlinear optical crystal: Mercury cadmium chloride thiocyanate

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ARTICLE INFO

Article history:
Received 23 March 2013
Accepted 28 July 2013

Keywords:
Solution growth
NLO materials
X-ray diffraction
Dielectric
Photoconductivity

ABSTRACT

SCN^- ligand based organometallic non-linear optical mercury cadmium chloride thiocyanate (MCCTC) crystals are grown from water plus methanol mixed solvent by slow evaporation technique. The grown crystals are confirmed by single crystal X-ray diffraction analysis. MCCTC exhibits a SHG efficiency which is nearly 17 times more than that of KDP. The dielectric constant, dielectric loss and *ac* conductivity measurements of the sample have been carried out for different frequencies (100 Hz to 5 MHz) and, temperatures (308–388 K) and the results are discussed. Photoconductivity study confirms that the title compound possesses negative photoconducting nature. The surface morphology of MCCTC was also investigated.

1. Introduction

Nonlinear optics (NLO) has emerged as one of the most attractive fields of current research in view of its vital applications in areas like optical modulation, optical switching, optical logic, frequency shifting and optical data storage for developing technologies in telecommunications and signal processing. Materials with large SONLO properties, short transparency cut off wavelengths and stable physicochemical performance are needed to realize many of these applications [1,2]. Among the materials producing NLO effects, in particular the second harmonic generation (SHG), the first choice given is for those materials which possess high nonlinearity, shorter UV cut-off wavelength, large optical transparency window, ability to grow easily in large dimension, high laser damage threshold and good physicochemical stability. In this connection, attempts have been made by researchers to develop new organometallic compounds (which contain at least one direct M—C bond between metal and organic ligands) and coordination compounds (in which the metal and the ligands are connected through M—O, M—N, M—S or M—P bonds), these compounds combine the features of both inorganic and organic compounds. Organometallic and coordination compounds offer a variety of molecular structures by changing the metals, ligands, coordination numbers and so on. This diversity of molecular structure gives an opportunity to tune the electronic properties of the molecules, and hence to exploit the linear and nonlinear optical properties. In metal thiocyanate complexes, the thiocyanate (SCN) plays a crucial role in combining the versatile ambidentate ligand with two donor atoms. Being a ligand with potential S and N donors, thiocyanate (SCN) ion is of interest not only due to the structural chemistry of its multifunction coordination modes, but also because of the formation of complexes with NLO activities [3–7]. Metallic thiocyanates and their derivates are such potentially useful candidates among the organometallic systems because all of them contain —S=C=N— bridges, which connect with metal atoms, forming infinite two dimensional or three dimensional networks. The infinite networks confer a relatively large polarization, which induces relatively large macroscopic nonlinearities in these materials and the same has been proved recently by few research groups [8–10].

Mercury cadmium chloride thiocyanate (MCCTC) is one such potentially useful SONLO crystals with an empirical formula $Hg_3CdCl_2(SCN)_6$. In the earlier works, MCCTC was grown from methanol by slow evaporation; unfortunately, the reported size of the crystal was very small. Hence, attempts had been made to improve the crystal size from a mixed solvent (methanol plus water) by slow evaporation technique. The dimensions of the crystal size 10 mm × 4 mm × 2 mm were achieved and its various physical properties were measured and published already [11]. The present work is the continuous of the previous work and in this

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http://dx.doi.org/10.1016/j.ijleo.2013.09.001

dielectric, ac conductivity and photoconductivity studies and surface morphology studies are investigated and reported for the first time. The nonlinear optical property of the single crystal has been confirmed by SHG test.

2. Experimental procedure

2.1. Synthesis

The starting materials were analytical reagent grade (purity > 98.0%) and used as purchased. Appropriate amounts of mercury thiocyanate and cadmium chloride taken in the molar ratio of 3:1 were dissolved in methanol solvent to synthesis MCCTC. The chemical equation is as follows.

$$3(Hg(SCN)_2) + CdCl_2 \rightarrow Hg_3CdCl_2(SCN)_6$$

The synthesized salt was further purified by repeating the crystallization experiment twice or thrice.

2.2. Crystal growth

The saturated solution of MCCTC was prepared in methanol plus water mixed solvent at room temperature and stirred well to enable homogenization of the solution. The seed crystals were prepared by the conventional isothermal evaporation method. Good quality seed was chosen and then kept suspended into the supersaturated solution. MCCTC crystal was grown by slow evaporation method at 303 K. Crystal having dimensions up to 10 mm × 4 mm × 2 mm was harvested in a period of 35–40 days.

2.3. Characterization

Single crystal X-ray diffraction analysis of MCCTC crystal was carried out using Enraf Nonius CAD-4 X-ray diffractometer with MoK_{α} radiation (λ = 0.7170 Å). The structure was solved by direct method and refined by the full matrix least square technique using the SHELXL program. The second harmonic generation efficiency of the powdered sample was studied using Nd:YAG Q-switched laser with first harmonic output of 1064 nm. The dielectric constant, dielectric loss and *ac* conductivity measurements were carried out using HIOKI 3532-50 LCR HITESTER in the frequency region 100 Hz to 5 MHz. The electric and dielectric response of the sample was studied at different temperatures (308–388 K). Photoconductivity of the crystal was studied using Keithley 485 picoammeter. The surface morphology of MCCTC was investigated by using a JEOL JSM-6360 scanning electron microscope (SEM).

3. Results and discussion

3.1. X-ray diffraction (XRD) analysis

The lattice parameter values of MCCTC from single crystal XRD are determined as a = 11.184 Å, b = 11.191 Å and c = 59.908 Å. The values of unit cell volume (V) and density (D) are 6493.2 $Å^3$ and 3.47 g/cm^3 respectively. The XRD data is in good agreement with reported value [12], and thus confirm the grown crystal.

3.2. Nonlinear optical (NLO) study

The nonlinear optical property of MCCTC was evaluated by the Kurtz and Perry powder technique [13] and microcrystalline powder of KDP was taken as the reference material. For a laser input pulse of 5.6 mJ, the second harmonic signal of 160 mV and 2.7 V were obtained through KDP and MCCTC respectively and thus confirming its second harmonic efficiency to be 17 times that of KDP.

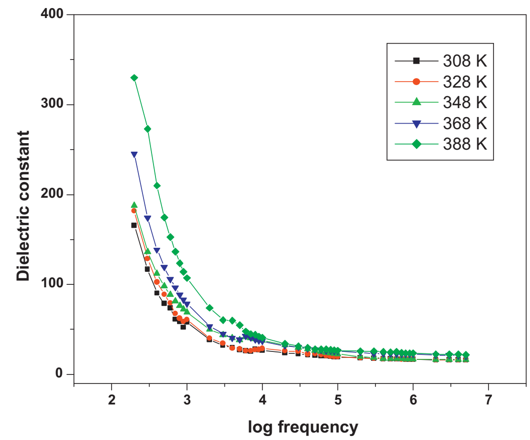

Fig. 1. Variation of dielectric constant with frequency for MCCTC at different temperatures.

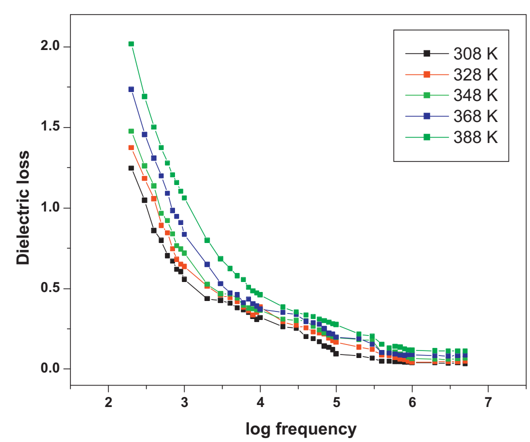

Fig. 2. Variation of dielectric loss with frequency for MCCTC at different temperatures.

3.3. Dielectric constant and dielectric loss measurements

Dielectric constant and dielectric loss of the sample have been measured for different frequencies (100 Hz to 5 MHz) at different temperatures (308–388 K). Figs. 1 and 2 show the variations of dielectric constant and dielectric loss as a function of frequency at different temperatures respectively. It is observed from Fig. 1 that the dielectric constant (at 308 K) decreases with increase in frequency from 100 Hz to 10 kHz and then attains a constant value of 28.61. The same trend is observed for other temperatures too. It is also observed that the value of dielectric constant increases with temperature. Such variations at higher temperature may be attributed to the blocking of charge carriers at the electrodes [14]. The decrease of dielectric constant at low frequency region may be due to space charge polarization. Fig. 2 indicates that as the frequency increases, the dielectric loss decrease exponentially and then attains a lower value of 0.049 at 308 K. The low value of dielectric loss confirms the lesser level of defects present in the grown sample.

3.4. AC conductivity

The ac conductivity measurements were made in the frequency range of 100 Hz to 5 MHz. It is well known that in the high temperature (intrinsic) region, the effect of impurity on electrical conduction will not make any appreciable change, whereas in the low temperature (extrinsic) region, the presence of impurity in the