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Crystal Growth, Optical and Dielectric Properties of CMTC – Grown by Gel Technique

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Abstract: Many of the bimetallic thiocyanate complexes have been found to exhibit excellent nonlinear optical properties. Single crystals of one such material Cadmium mercury thiocyanate $CdHg(SCN)_4$ have been grown in silica gel using gel technique by the process of diffusion. The grown crystals subjected to single crystal X-ray diffraction study confirms that the crystals belong to tetragonal system. Dielectric studies reveal that the dielectric constant decreases with increase in frequency. Polarizability calculated by Penn analysis is compared with the traditional methods and tabulated. The Second harmonic generation efficiency of the gel grown CMTC crystal has been determined in comparison with Urea.
Keywords: Crystal Growth, Optical, Dielectric Properties, CMTC,Gel Technique.

1. Introduction and Experimental

The Bimetallic thiocyanate complexes are semi-organic compound of type $AB(SCN)_4$. Most of the bimetallic complexes of thiocyanate crystallize into noncentrosymmetric space group which confirms the second harmonic generation. They have excellent nonlinear optical properties. Nonlinear optical material finds application in optical computing, optical, switching, optical memories etc [1]. Cadmium Mercury Thiocyanate, Manganese Mercury Thiocyanate, Zinc Cadmium Thiocyanate are found to exhibit Second harmonic generation efficiency at short wavelength [2]. This paper discusses the growth of CMTC single crystal in silica gel.

1.1 Material synthesis

Stock solution of specific gravity $1.04g/cm^3$ was prepared by dissolving sodium Meta silicate in deionized water.10 ml of the Stock solution was taken and the pH was adjusted to 4 using glacial acetic acid. To this solution 35 ml of 0.3 M Mercury chloride and 15 ml of 4 M ammonium thiocyanate was added and stirred using a magnetic stirrer for 4 hrs. Then the solution was allowed to gel in a test tube of length 15cm and diameter 1.5 cm. The solution gelled within 48 hrs .The outer reagent, an aqueous sol of 5M cadmium chloride was added along the side the tube using a pipette. CMTC crystal as in fig 1 was obtained within 30 days.

Figure 1 CMTC Crystal

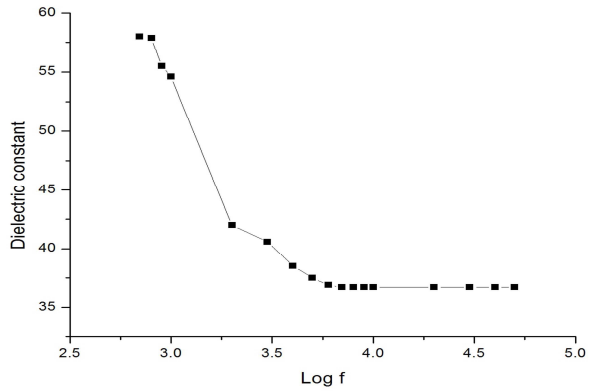

Figure 2a Log f vs Dielectric constant

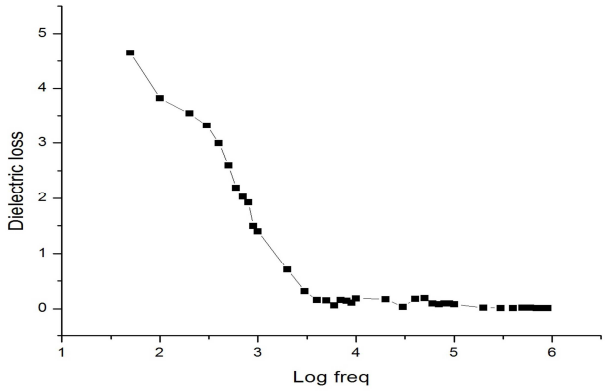

Figure 2b Log f vs Dielectric loss

1.2 X-ray diffraction study and Density measurements

Single crystal X-ray diffraction study was performed using ENRAF NONIUS FR590 diffractometer with Mo Kα radiation of wavelength 0.7170 A° to confirm the crystallographic system. The crystal structure is found to be tetragonal with the lattice parameters as a=b=11.473 A° , c=4.250 A°, α=β=γ = 90° and V=549A° [3]. The density of gel grown CMTC crystal was calculated using the following equation.

$$\rho = M Z / N_A a b c \quad (1)$$

The theoretical value of density calculated using the above equation is 3.234 g/cm^3. The density of the crystal was also determined experimentally by the floatation method at room temperature (32^o C), using the following equation:

$$\rho = m \rho_{solvent} / m - m' \quad (2)$$

The experimentally measured value of density by floatation technique is 3.234 g/cm^3 which is found to be in agreement with the theoretical value.

Determination of some characteristic data.

The molecular weight of the grown crystal is M=544.72 g/mol, density ρ = 3.254 g/cm^3 and dielectric constant at 5 MHz is ε = 252.1. The Plasma energy in terms of Penn gap and Fermi energy in eV is given as

$$E_p = \frac{\hbar \omega_p}{(\varepsilon_\infty - 1)^{1/2}} \quad (3)$$

And

$$E_F = 0.2948 \left(\hbar \omega_p\right)^{4/3} \quad (4)$$

Polarizability , α is obtained using the relation

$$\alpha = \left[\frac{(\hbar\omega_p)^2 S_0}{(\hbar\omega_p)^2 S_0 + 3E_p^2} \right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} \; cm^{-1} \tag{5}$$

The value of α so obtained agrees well with that of Clausius-Mossotti equation

$$\alpha = \frac{3M}{4\pi N_a \rho} \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} \tag{6}$$

The calculated values of the above parameters are shown in Table1.

Table 1 Theoretical data for gel grown CMTC crystal

Parameters	Values
Plasma energy (eV)	12.592
Penn Gap (eV)	0.7946
Fermi Gap (eV)	8.636
Polarizability (cm3) Penn analysis	6.55×10^{-23}
Polarizability Clausius-Mossotti Equation	6.56×10^{-23}

Refractive Index analysis

Refractive index of CMTC single crystal was measured using Abbe refractometer model (ATAGO, NAR-4T, Japan) connected to a digital thermometer using thermistor cable connector jack. The refractive index of CMTC is found to be 1.657 at an ambient temperature of 30.5^o c.

Dielectric Studies and Second harmonic generation test (SHG)

The dielectric constant and the dielectric loss of the CMTC crystals were studied at room temperature using HIOKI3532 LCR HITESTER in the frequency region 50Hz-5MHz. Figure 2a shows the variation of dielectric constant with log f. It is observed that the dielectric constant is relatively higher in the low frequency region and decreases with increase in frequency. The presence of electronic, ionic, dipolar and space charge polarizations may be the reason for the high value of dielectric constant at low frequencies. The variation of dielectric loss with frequency is shown in fig 2b. The low dielectric loss with high frequencies for the grown crystal suggests that the crystal possess enhanced optical quality which is necessary for playing a vital role for the fabrication of nonlinear optical devices [4].

A preliminary study on the second harmonic generation (SHG) efficiency of the crystal was carried out by Powder Kurtz method using Q-switched Nd-YAG laser. The second harmonic generation efficiency is found to be 6.2 times greater than that of urea [3].

Conclusion

CMTC single crystals can be obtained from silica gel using gel technique by the process of diffusion in an acidic medium. Theoretical and experimental values of density of the grown crystal are found to be in good agreement. Polarizability has been calculated using Penn analysis and Clausius Mossotti equation and tabulated. The low dielectric loss at high frequencies reveals the enhanced optical property of the crystal which is necessary for fabrication of nonlinear optical devices. The second harmonic generation efficiency is found to be greater than that of urea.

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