www.sphinxsai.com

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.14, pp 5692-5697, Nov-Dec 2014

Growth and Physio-Chemical Investigation on Cobalt Sulfamate Single Crystal

N. Senthilvelan[1]*, G. Rajarajan[2,3] and S. Sivakumar[4]

[1]Department of Physics, Arignar Anna Govt. Arts College, Attur – 636 121, India
[2]Department Physics, Selvam College of Technology, Namakkal – 637 003, India
[3]Selvam Centre for Materials Research, Selvam Educational Institutions,
Namakkal - 637 003, India
[4]Department of Physics, Government Arts College, Salem – 636 007, India

*Corres.author : nsenthilvelan2013@gmail.com

Abstract: Single crystal of Cobalt sulfamate (CSM) has been grown successfully by slow evaporation method. XRD, FTIR and SEM analysis were done to characterize the grown sample structurally. Optical property of the sample was studied by recording UV –Vis spectra and optical band gap was determined. Thermal stability of the CSM crystal was analyzed by TG/DSA analysis. Electrical measurements were done on the grown sample for various frequencies ranging from50-5MHz within three different temperatures. The optical and electrical properties of the crystal indicate the suitability of this crystal for photonic device fabrication. The results are reported herein.

1. Introduction

Development of Nonlinear optical (NLO) crystals with better linear optical and NLO properties, wider spectral transmission and phase matching range is obviously essential for further widening the application field of Laser. That is why still today many scientist working in search of new NLO materials with better efficiency. [1]. Amino acids find an important place in NLO applications because of its peculiar physical and chemical properties due to the presence of proton donor carboxyl acid (-coo) group, and the proton acceptor amino (-NH2) group. In solid state, amino acid exists as dipolar ion in which carboxyl group is present as carboxylate ion and this dipolar nature make them ideal candidates for NLO applications[2].Also, complexes of amino acid with inorganic salts have proved to be a better NLO materials [3-5].

Since the theory of double-radical model (organic conjugated molecular groups are included in the distorted polyhedron of coordination complex) was introduced in 1987 [6], metal-organic coordination compounds have attracted much more attention due to their considerable high NLO coefficients (contrast to inorganic materials), stable physico-chemical properties and better mechanical intension (contrast to organic materials).

With the guidance of this theory, many metal organic coordination materials with good NLO effect have been designed and synthesized[7-14]. The metal-organic coordination complexes can also provide the following advantages: i) an enhancement of the physico-chemical stability. ii) the breaking up of the centro-symmetry of the ligand in the crystal, and iii) an increase in NLO intensity, via metal-ligand bridging interactions. The central metal ion (together with its hybrid electronic orbital) not only offers a certain anisotropic field to keep the NLO active chromopher ligands in a favorable acentric arrangement but also involved in the NLO processes.

Sulfamic acid which also known as amidosulfonic acid with molecular formula, H_3NSO_3. Like amino acid, it alos exist in zwitterionic configuration in solid state. Sulphamic acid finds application in MSF (Multi-stage flash evaporation) desalination plants for cleaning demisters, heat exchangers and cooling water systems [15]

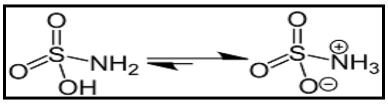

Figure 1: Zwitterionic configuration of Sulfamic acid

However no systematic efforts have been made on sulfamate which is a metal organic compound of sulphamic acid for NLO applications. So in our present work, we made an attempt to grow cobalt sulfamate single crystals by slow evaporation techniques. The grown crystals were analyzed for it’s various physio-chemical properties. And all the results are discussed in detail.

2. Growth of CSM Single Crystals

Analytical reagent (AR) grade samples of Sulfamic acid (99%), and cobalt II sulphate hepta hydrate as purchased from Aldrich were used. Double distilled water was used as solvent.

Sulfamic acid and cobalt sulphate heptahydrate taken in 1: 1 molar ratio were dissolved in double distilled water at ambient temperature to prepare supersaturated solution. The solution was stirred for 2 hours for making homogenous mixing. Then the solution is tightly closed with perforated filter paper so that the rate of evaporation could be minimized. The reaction to produce Cobalt sulfamate tetrahydrate crystals is as follows.

$H_3NSO_3 + CoSO_4.7H_2O \rightarrow Co\,[NH_2SO_3]_2.4H_2O + H_2SO_4$

Slightly reddish, high transparent, defect free crystals were obtained in 15 days. The photograph of the grown crystal is shown in Figure 2.

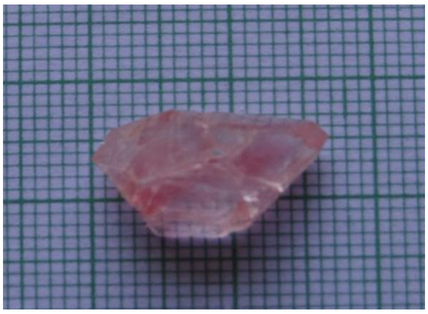

Figure 2: Photograph of as grown CSM crystal

3. Characterization Made

The freshly ground powder samples of CSM crystals were subjected to Powder X- ray diffraction (PXRD) analysis, using an X-ray powder diffractometer, Rigaku ultimaIII XRD (NIT TRICHY)with scintillation counter and monochromated Cu K_α ($\lambda = 1.54056$ Å) radiation. The FT-IR spectrum was recorded in the range of 4000 – 450 cm^{-1} using Perkin Elmer make model spectrum Rx1(st jospesh college trichy). Morphology of the grown crystal has been studied by SEM analysis using LEO 440 STEROSCAN (LEICA) ANNA UNIVERSITY CHENNAI. The optical absorption spectrum was recorded in the range of 200-800 nm using Perkin Elmer make model Lambada 35 UV-Vis-NIR SPECTROPHOTOMETER(St.Jospesh college ,Trichy). The NLO efficiency of LAPC crystals were evaluated by Kurtz and Perry powder technique [16] using Q-switched Nd:YAG laser emitting 1.06 µm (Quanta ray series), 8 ns laser pulses with spot radius of 1 mm supplied by Spectra Physics, USA and coherent Molectron power meter The thermogravimetric analysis is carried out between 40^{o}C and 1400^{o}C at a heating rate of 20^{o}C/min. in nitrogen atmosphere (CLRI CHENNAI) .Electrical measurements were done on the polished crystals using HIOKI 3532-50 LCR HITESTER for various frequency ranging from 100-5 MHz.

4. Results and Discussion

4.1 Powder X-ray Diffraction Analysis

The recorded PXRD pattern of CSM is depicted in Figure 3. The Bragg's diffraction peaks were indexed for the orthorhombic system with the space group Pcab. The h k l planes were indexed using the Jcpds (#080483) pattern of pure sulfamic acid(SA). PXRD pattern of CSM crystal (Figure 3) is well matched with the pure SA also some intensity peaks are slightly shifted and newly raised (marked in astrik). The peaks at 44.38, 50.52 and 55.78 degrees conforms the incorporation of cobalt in SA lattice. The lattice parameters obtained from the PXRD patters are a= 8.115, b=9.145 c = 8.247 Å and V= 612.130 Å^3.

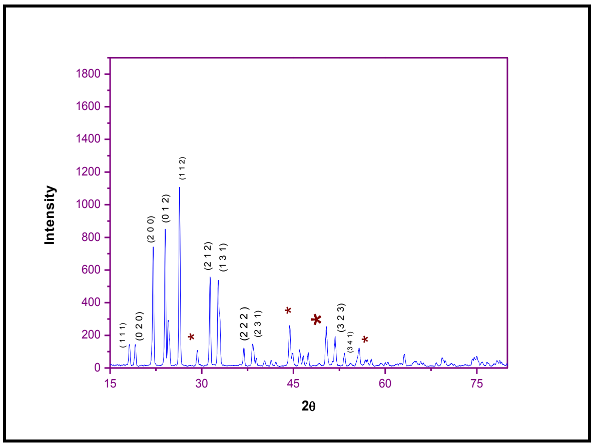

Figure 3: PXRD pattern of CSM single crystal

4.2 FTIR Analysis

Figure 4 shows the FTIR transmission spectrum of CSM crystal in the region 4000-450 cm^{-1}.Various functional group present in the given spectrum supports the formation of CSM crystal. The frequency assignment for the functional groups are given in table 1.

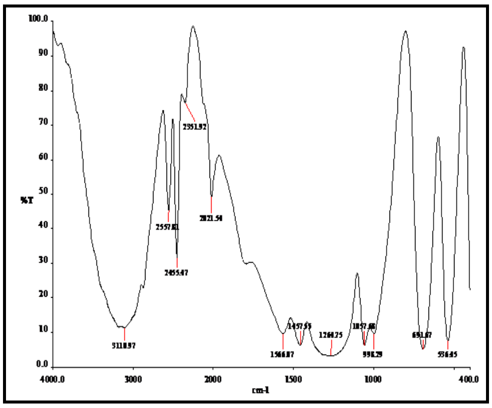

Figure 4: FTIR for CSM

Table 1: Band assignment for CSM crystal

Wave number (cm-1)	Assignment
2557	S-H stretch
1264	S= O asymmetric stretch
1017	S=O symmetric stretch
691	C-S stretch
550	S-S stretch

4.3 SEM Analysis

SEM analysis gives information about the nature and suitability for device fabrication and also it is used to check the presence of imperfections. SEM analysis was carried out using LEO 440 STEROSCAN (LEICA) scanning electron microscope. SEM image of CSM crystal is shown in Figure 5.The images show step-like growth, which suggests the existence of grain boundaries and striations. The micrographs also show the presence of few cracks and visible inclusions on the surface of the crystal. This may be due the temperature oscillations during the crystal growth

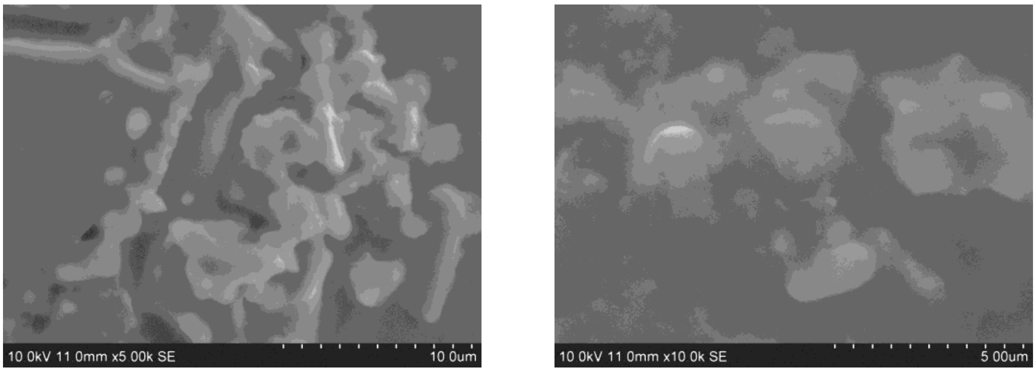

Figure 5: SEM micrographs of CSM single crystals

4.4 UV-VIS spectral Analysis

The absorption of UV and visible light involves excitation of the electron in the orbital from the ground sate to higher energy states which gives the limited information about the molecular structure [1]. The recorded transmission and absorption spectra are shown in Fig. 6. From the graph, the cut off wavelength of the crystal is around 218nm

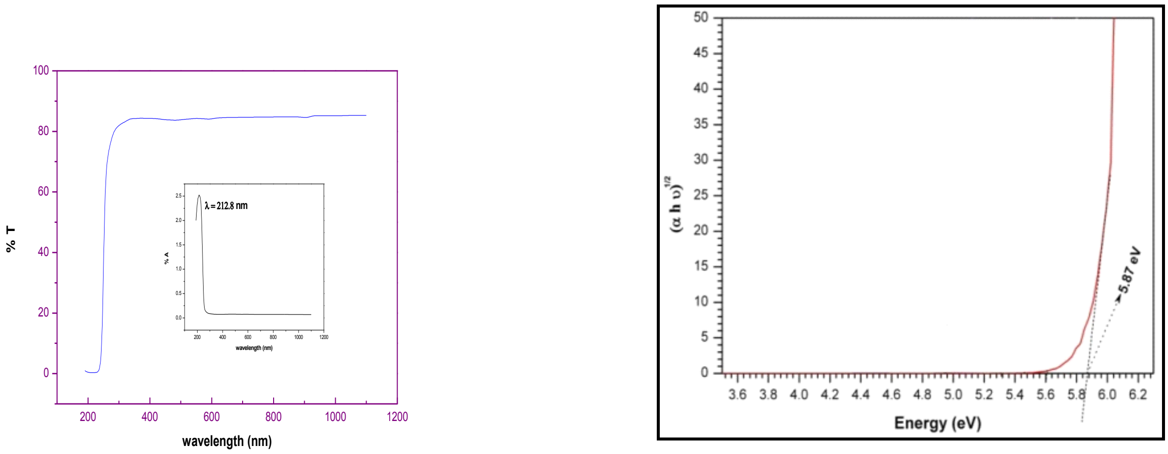

Figure 6: a) UV-VIS spectrum and b) Plot of optical bandgap determination from UV-Vis

The absence of absorption bands in the visible region and the wide bandgap of the grown crystal attest to the suitability of the grown crystal for photonic and optical applications. The low value of cutoff wavelength, the wide transmittance window and the absorbance nearly equal to zero in the entire visible region are the most desirable properties of the crystals used for NLO applications. The value of optical bandgap is calculated by extrapolating the straight line portion of $(\alpha h\upsilon)^{\frac{1}{2}}$ *vs* hυ graph to hυ axis (Figure 6 (b)). The bandgap energy of the CSM crystal is found to be 5.87 eV.

4.5 Thermo gravimetric–differential thermal analysis

The TG–DT analysis trace of dried powder of single crystal of CSM obtained is shown in Fig. 7.TG Analysis of CSM was carried out between 20o-800^{o}c at a heating rate of 15^{o}C/min with nitrogen atomosphere. There is a sharp weight loss at 375^{o}C , which corresponds to about 97.98% of the sample and no other loss is observed further, this conforms the decomposition of the sample at 375^{o}C. The DSC traces shown in figure, gives the sharp endotherm close to 250^{o}C which gives the melting point of CSM.

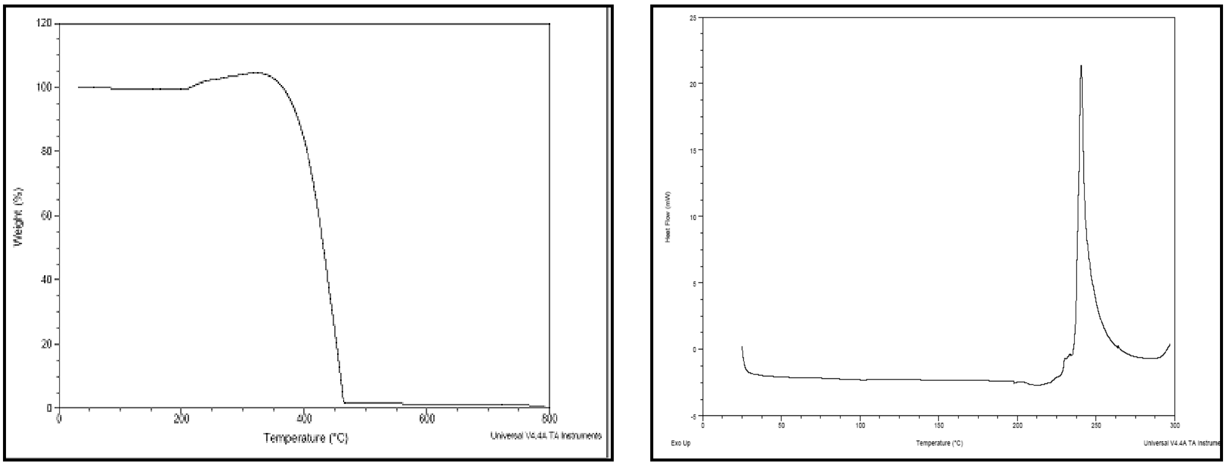

Figure 7: TG and DSC thermo gram for CSM single crystals

4.6 Dielectric and Conductivity Measurements

The electrical studies were carried out and the capacitance, dielectric loss (tan δ) and *ac* conductivity of the sample as a function of frequency (100 Hz–5 MHz) and temperature (in the 40, 50 and 60°C). The dielectric constant was calculated using the relation ε_r = Cd / εoA, where εo is the permittivity of the free space, C is the capacitance, d is the thickness of the sample and A is the area of cross section. The variation in the dielectric constant, loss factor and Ac conductivity with frequency at different temperatures is illustrated in Fig 8. The decrease of dielectric constant with increasing frequency is a normal dielectric behavior and this may be due to the presence of all the polarizations, namely space charge, orientation, electronic and ionic polarizations; minimum value at higher frequencies is attributed to the slow loss of significance of these polarizations [17]. The influence of temperature leads to increase in dielectric constant with increasing temperature and is due to the presence of electronic polarization. It is clear that the conductivity increases with increasing frequency and can be expressed as σac = ωεr tanδεo and, where ω=2πf. It is observed that at a given temperature, the magnitude of conductivity is high at higher frequencies, there by supporting the small polaron hopping model [18]. As temperature rises, more and more defects are created, and as a result, the conductivity increases, which is predominantly due to moment of defects produced by thermal activation.

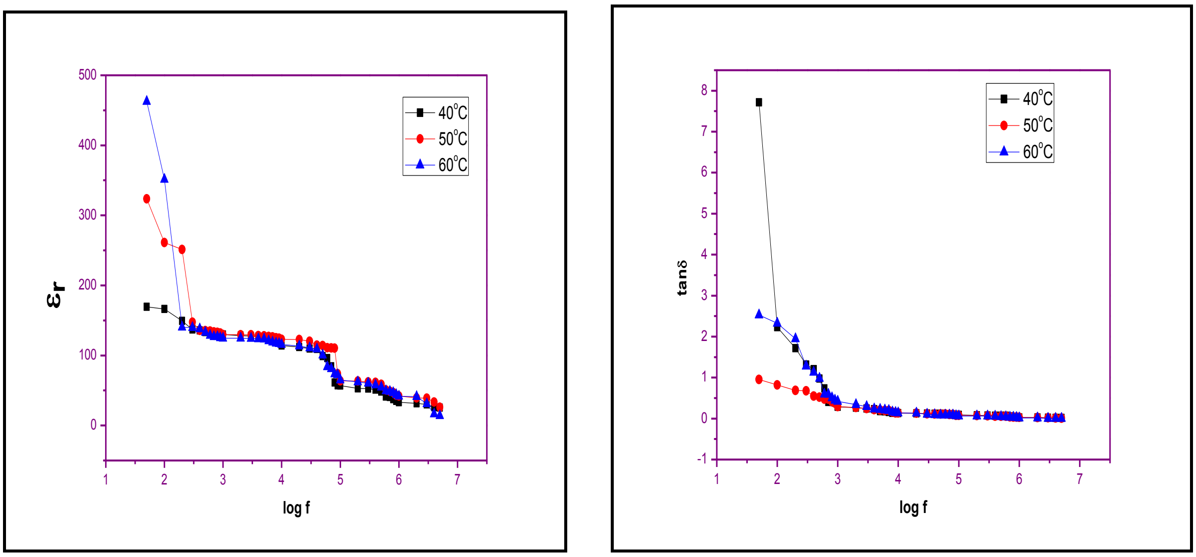

Figure 8a: Variation of dielectric constant and Loss factor with frequencies for different temperature

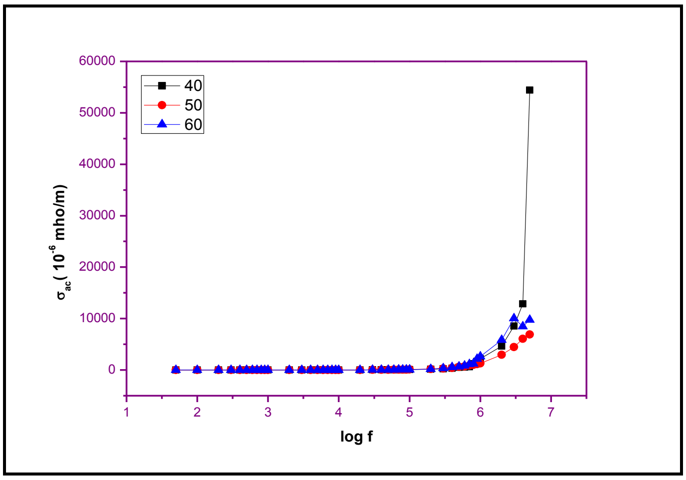

Figure 8b : Variation of Ac conductivity with frequencies at different temperatures.

5. Conclusions

In our present study, defect, optically transparent crystals of Cobalt sulfamide (CSM) were grown by slow evaporation technique. The grown crystal was subjected to Structural characterization, PXRD data revealed that, grown crystal belongs to orthorhombic system with the space group Pcab. The chemical composition of the grown crystal was confirmed by FTIR analysis. Optical absorption studies confirm the UV cut-off wavelength of LLS at 213 nm. The band gap energy of the sample is calculated and it is found to be 5.8 eV. The T variation of dielectric constant and dielectric loss are studied with varying frequency at different temperature. Thus, the optical and electrical properties of the crystal indicate the suitability of this crystal for photonic device fabrication.

References

1. R. Valluvan, K. Selvaraju, S. Kumararaman (2006) Matrials Chem & Physics 97,81-84.
2. Ramesh Kumar, S. Kumaresan, N. Vijayan, M. Gunasekaran, R. Gopalakrishnan, P. Kannan, et al. J. Cryst. Growth 256 , 2003 , 387-392 (2004)
3. M. N. Bhat and S. M. Dharmaprakash, J. Cryst. Growth, 235 (2002) 511.
4. M. Kumar, S. Tamilselvan, M. Vimalana, P. Saravanana, S. Arunab, R. Kanagaduraic, Archives of Applied Science Research, 2013, 5 (5):220-227.
5. R.R.Saravnan, S.Seshadri, M.Murugan and V.Manivannan, Indian J.Pure and Applied Physics 51 (2013)254-259
6. D.Xu, M. H. Jian, X. T. Tao, Z. S. Shao, J. Synth. Cryst. 16, 1987, 1
7. Zhang N., Jiang M.H., Yuan D.R., Xu D., Tao X.T. and Shao Z.S., J.Crystal Growth102(1990) 581
8. Xinqiang Wang, Xu D, Lu M.K, Yuan D R, Xu S.X, Guo S.Y, Zhang G.H, Liu J R J. Crystal Growth, 224(2001c), pp.284
9. Xinqiang Wang, Xu D., Lu M.K., Yuan D.R., Zhang G.H., Meng F.Q., Guo S.Y., Zhou M., Liu J.R.and Li X.R., Cryst. Res. Technol., 36(2001) 73.
10. R. Rajasekaran, R. Mohan Kumar, R. Jayavel, P. Ramasamy. J. Cryst. Growth 252, 2003, 317- 327.
11. P. M. Ushasree, R. Jayavel, P. Ramasamy, Mater. Sci. Eng. B65, 1999, 153.
12. V. Venkataramanan, S. Maheswaran, J. N. Sherwood, H. L. Bhat, J. Cryst. Growth 179, 1997, 605.
13. V. Venkataramanan, C. K.Subramanian, H. L. Bhat, J. Appl. Phy. 77 , 1995, 6049
14. V. Venkataramanan, C. Dhanaraj, V. K. Wadhawan, J. N. Sherwood, H. L. Bhat, J. Cryst. Growth 154, 1995,92.
15. M. SenthilPandian a, UritCharoenIn b, P.Ramasamy a,n, PrapunManyumb, M.Lenin c, N. Balamurugan, Journal ofCrystalGrowth 312 (2010) 397–401.
16. S. K. Kurtz, T. T. Perry, J. Appl. Phys 39 , 1968, 3798-3813.
17. Reicha F.M., El-Hiti M., El-Sonabati A.Z., Diab M.A., J. Phys. D: Appl. Phys., 1991, 24, 369.
18. Smyth C.P., Dielectric Behaviour and Structure, Mc Graw Hill, New York, 1995.

*****