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Growth and Characterization of Cobalt Mercury Thiocyanate single crystals grown in silica gel medium

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Abstract: **Single crystals of Cobalt Mercury Thiocyanate belonging to Semiorganic material with nonlinear optical properties have been grown in silica gel medium using gel growth technique. The grown Cobalt Mercury Thiocyanate were subjected to single crystal X-ray diffraction (SXRD) and Fourier transform infrared spectroscopy (FTIR) to elucidate their lattice parameters and functional group confirmation. The dielectric studies at different temperatures and frequency applied are measured and their behavior is analyzed. The crystal exhibit second harmonic generation which was confirmed by the important Kurtz powder test. The crystals are thermally stable up to 280°C, which was analyzed by thermogravimetric and differential scanning Calorimetric analysis.**

Keywords: **Diffusion, Single crystal growth, Metals, Nonlinear optical.**

1. INTRODUCTION

In the promising field of communication, opto-electronic devices play a very important role. Metal complexes offer a large variety of environmental stability and tunable electronic properties. Organometallic materials have attracted the attention in the nonlinear optical field [1–7]. As the materials have the potential for combining the high optical nonlinearity, chemical flexibility of organics with temporal thermal stability, excellent transmittance of inorganics [8–9].

In recent days, thiocyanate compounds have attracted the attention of researchers, due to the NLO properties exhibited by them, when forming complexes with metals of the form $AB(SCN)_4$. In the $AB(SCN)_4$ molecules, metal ions can bind to $(SCN)^-$ through either sulfur or nitrogen [10]. The ligand, (SCN) −ion that is usually S-bonded to a soft and N-bonded to a hard metal center can also act as a bridging bidentate ligand to satisfy the coordination number of the metal. Studies with different AB compounds of various proportions in the $AB(SCN)_4$ complex have exhibited remarkable optical properties. These materials are relevantly chosen such that SCN bending is reduced and CN and CS stretching vibrations are enhanced for obtaining better optical properties [11]. The $CdHg(SCN)_4$ crystal consists of two slightly flattened tetrahedra HgS_4 and CdN_4. The noteworthy factors in this compound namely –NCS– bridge that connects the central atom of the flattened tetrahedra –Cd–N and CS–Hg– networks. Hence, these structural features provide the good optical activities [12,13]. The present work, an attempt has been made to grow Cobalt Mercury Thiocyanate by gel technique. The various characterizations of grown crystals have been studied here.

2. EXPERIMENTAL PROCEDURE (CRYSTAL GROWTH PROCESS)

In gel growth technique, the rate of diffusion is governed by the width of the micropores in the gel medium. The width of the micropores depends upon the density of the gel solution. At higher gel densities the crystallization is restricted appreciably due smaller pore size, thus decreasing the nucleation density [14]. Freshly prepared stock solution of sodium

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metasilicate having density 1.03kg/m^3 is used for the experiments. By varying the pH (4.2, 4.7, 5.2) of the gel, the effect on the crystal were analyzed. The concentration of the inner and supernatant solution is kept a constant. When the pH of the gel is increased, the setting time was found to decrease. Besides, the number of Cobalt Mercury Thiocyanate nuclei also was found to increase. The maximum size crystal of Cobalt Mercury Thiocyanate was grown at 4.7pH. Ammonium thiocyanate and Mercury (II) chloride were added as the inner solution to the gel medium. After the setting of the gel, cobalt chloride was used as the supernatant solution. The reaction between 1 M Mercury (II) Chloride, 4 M ammonium thiocyanate (inner reactant) and 1 M Cobalt chloride (supernatant solution), in gel medium resulted in the growth of Cobalt Mercury Thiocyanate single crystals. The reaction is as follows,

$$HgCl_2 + 4NH_4SCN + CoCl_2 \rightarrow CoHg(SCN)_4 + 4NH_4Cl$$

Crystals grown inside the gel medium is shown in Fig.1a within 7 days of addition of supernatant solution. The as-grown harvested Cobalt Mercury Thiocyanate single crystals are shown in Fig. 1b.

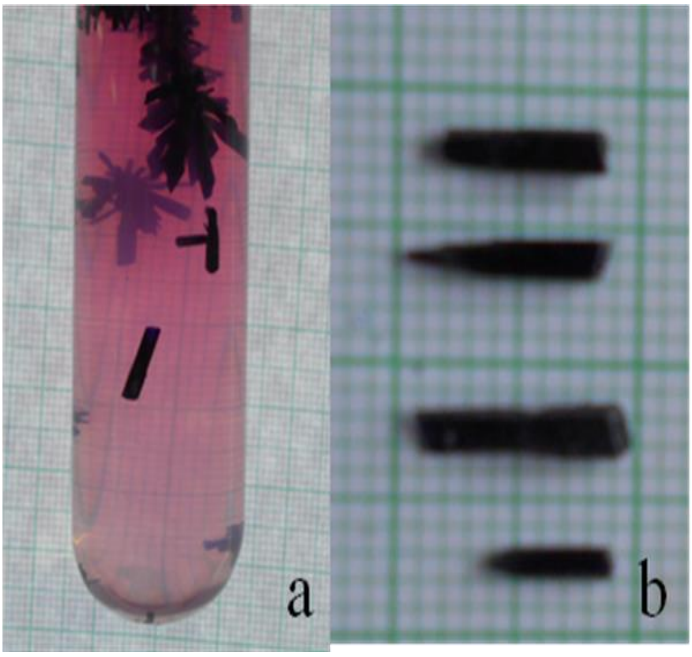

Fig 1: Cobalt Mercury Thiocyanate crystals (a) in the gel medium and (b) Harvested crystal

3. CHARACTERIZATION

3.1 Single crystal X-ray diffraction and fundamental parameters:

The grown crystals of Cobalt Mercury Thiocyanate was subjected to single crystal X-ray diffraction studies using ENRAF NONIUS CAD-4 diffractometer to elucidate their lattice parameters. The title crystal belongs to the tetragonal system. The lattice parameter was determined as a=b= 11.030Å, c= 4.461 Å, cell volume V=587.46 Å^3, which is in good agreement with that of the reported value [15].

3.2 FT-IR spectral analysis:

The FTIR spectra of title Cobalt Mercury Thiocyanate crystal were recorded in the range of 4000–400 cm^{-1} employing a Perkin Elmer spectrometer by KBr pellet method in order to reveal the functional group present in the crystal. Fig. 2 shows the FTIR spectrum. The vibration peaks are consistent with those reported by Wang et al., [16, 17]. The intense peak at 2339, 2169, 2148 and at 1984 cm^{-1} corresponds to CN stretching vibration (ν_{CN}) and the peak observed at 796.26 cm^{-1} is due to the CS stretching (ν_{CS}). The absorption peaks at 460 and 438 cm^{-1} are assigned to SCN bending vibrations (δ_{NCS}) while those at 867 and 923 cm^{-1} corresponds to $2\delta_{NCS}$.

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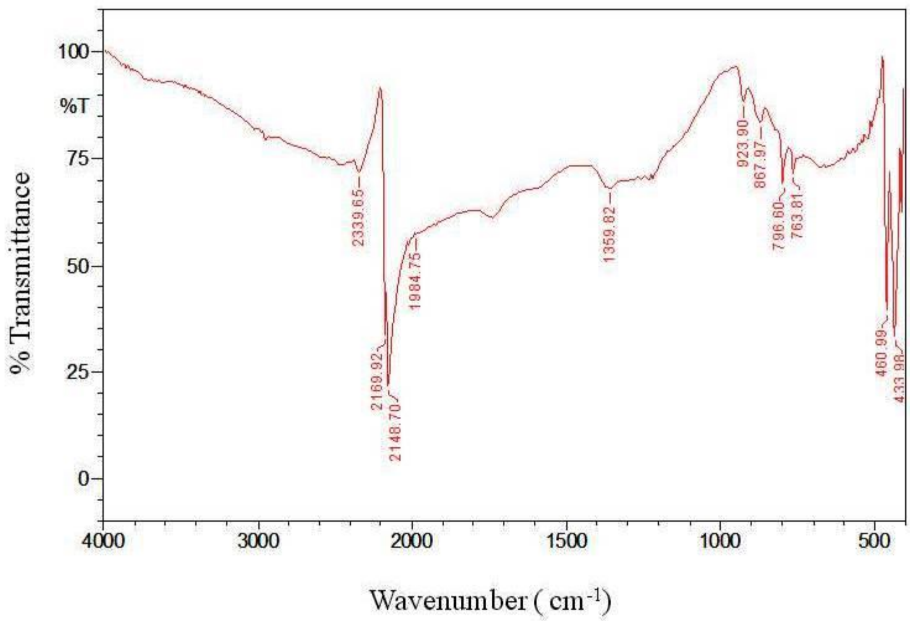

Fig 2: FTIR spectrum of Cobalt Mercury Thiocyanate

3.3 Optical studies:

The optical properties of the title crystal were examined between 190 and 1100 nm using ELICO SL 218 double beam UV–Vis spectrophotometer. When the absorption is monitored from longer wavelength to shorter wavelength, the enhanced absorption is observed between 200 and 480 nm as shown in Fig. 3. From the spectrum, it is noted that at 482 nm a sharp fall of absorbance to nearly zero is observed indicating the cutoff wavelength. It is seen that low percentage of absorption in the entire visible region which is an essential parameter for NLO applications. Optical band gap value was calculated from the Tauc's plot between $(\alpha h\upsilon)^2$ vs photon energy (hυ). The band gap graph of the crystal is shown in insert of Fig. 3 and the optical band gap value of the crystal is 4.01 eV.

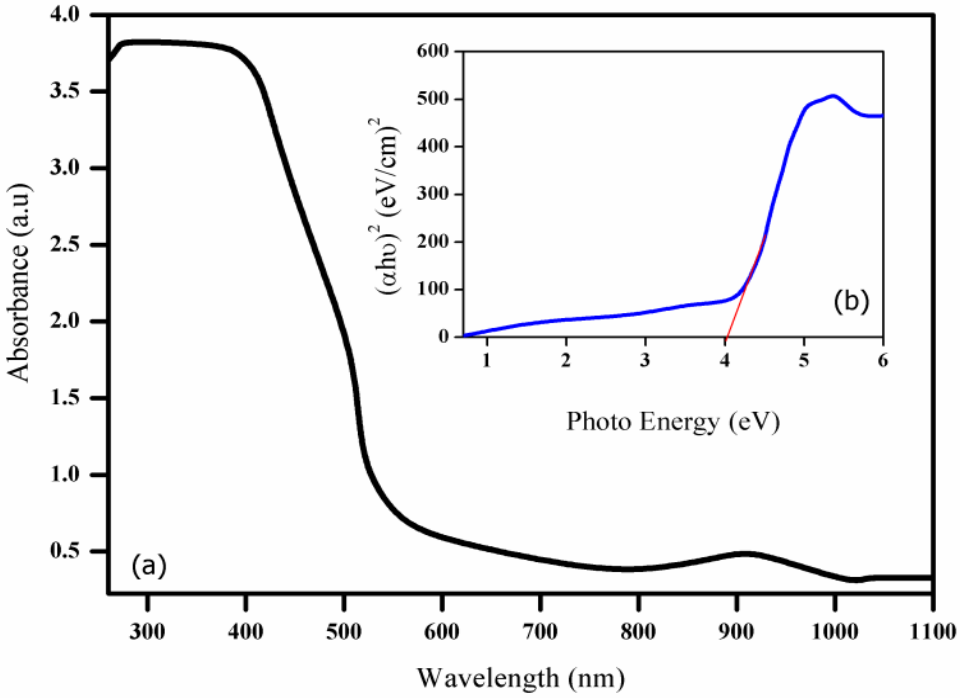

Fig 3 (a): The absorption spectrum and (b) Plot of $(\alpha h\upsilon)^2$ vs Photon Energy for Cobalt Mercury Thiocyanate.

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3.4 Dielectric Properties:

Dielectric measurements give the formation about electro-optical molecular responses, structural changes, molecular anisotropy and transport phenomena within crystalline materials [18-20]. Dielectric measurement of the grown crystal was carried out as a function of the frequency varying from 50 Hz to 5 MHz using a HIOKI 3532-50 LCR HiTESTER meter at room temperature. The dielectric constant value of the crystal was calculated using the following equation:

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A} \quad (1)$$

Where, t is the crystal thickness, C is the capacitance and A is the area of the crystal. Fig. 4 shows the variations of dielectric constant with respect to log frequency. From Fig.4, the values of dielectric constant are high (1500) in the lower frequency region (50Hz), and further, the dielectric constant decreases with increasing frequency. Above, 10KHz the frequency remains a constant value. The high value (1500) of dielectric constant at low frequencies (100 Hz) is a result of the contributions from space charge orientation polarization. At higher frequency, the low value of dielectric constant may be caused by the inability of the dipoles to comply with the external field [21,22]. Fig.5 shows that the dielectric loss decreases with increasing frequency. Thus, the crystal has enhanced optical properties as it has very low values of dielectric constant and dielectric loss at high frequencies. Thus, the crystal could be useful for optoelectronic applications and NLO devices [23]. The Penn gap is calculated by fitting the dielectric constant with the Plasmon energy [24]. The $\hbar\omega_p$ (plasma energy) can be calculated, as given by Jackson et al [25].

$$\hbar\omega_p = 28.8\left(\frac{Z_\rho}{M}\right)^{1/2} \quad (2)$$

Explicitly, the $\hbar\omega_p$ dependent Penn gap (EP) and the Fermi energy (EF) in eV are derived from the following relations [23]

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

And

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

The electronic polarizability (α) can be calculated using the relation [26]

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

Where S_o is a constant for a particular material and which is determined by using the below equation

$$S_0 = 1 - \left[\frac{E_p}{4E_F}\right] + \frac{1}{3}\left[\frac{E_p}{4E_F}\right]^2 \quad (6)$$

The value of α so obtained agrees with that of Clausius-Mossotti equation, given by the equation

$$\alpha = \frac{3M}{4\pi N_a \rho}\,\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} \quad (7)$$

The dielectric constant of materials is a very important parameter for calculating the physical or electronic properties of materials. These values of gel grown crystal are compared with the values of standard material KDP and listed in are shown in Table 1. From the table, it is observed that electronic parameters are found to be higher than those of KDP. As the SHG efficiency depends upon the polarizability, thus the SHG efficiency of the crystal can be more than that of KDP.

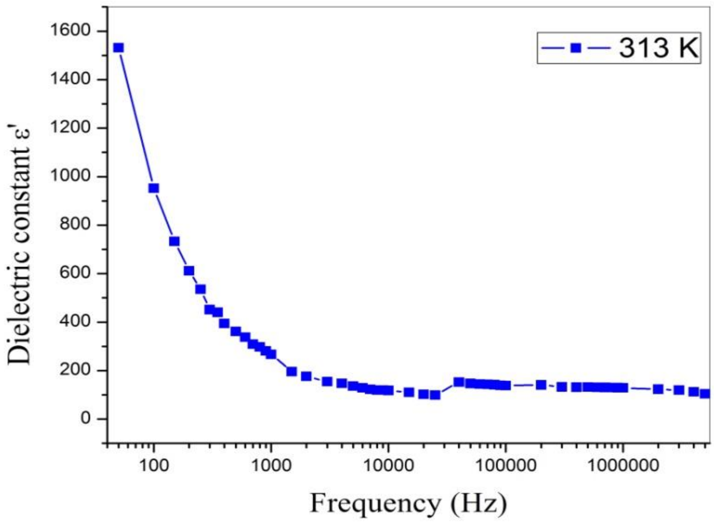

Fig 4: Variation of the dielectric constant with frequency

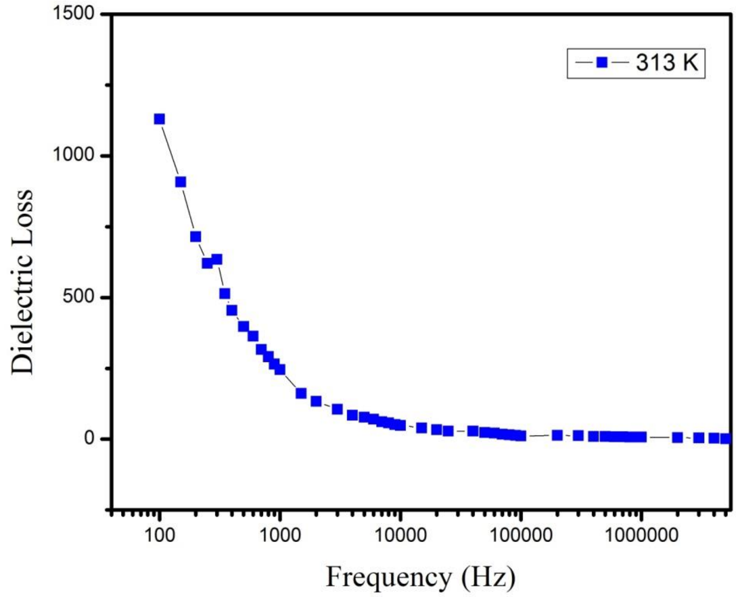

Fig 5: Variation of the dielectric loss with frequency

3.5 Second harmonic generation (SHG) studies:

The Kurtz powder technique is a popular standard method and very important test to evaluate conversion efficiency of an NLO material. In this experimental set up, the crystalline powder was illuminated using Q-switched, mode locked Nd-YAG laser beam of wavelength of 1064 nm with input beam energy 1.1 mJ. The light emitted by the sample was detected by a photodiode detector. SHG signal of intensity 125mV was recorded for our sample. Thus the crystal exhibit second harmonic generation.

Table 1: Comparision of Electronic properties of Cobalt Mercuty thiocyanate and KDP crystal

Parameters	Values of Cobalt Mercury Thiocyanate	Values of KDP
Plasma energy (eV)	21.892	17.28
Penn Gap (eV)	3.4146	2.37
Fermi Gap (eV)	17.636	12.02
Polarizability (cm^3) Penn analysis	$4.902 x 10^{-23}$	2.12×10^{-23}
Polarizability Clausius-Mossotti Equation	$4.94 x 10^{-23}$	2.14×10^{-23}

3.6 Thermal Analysis:

Thermogravimetric and differential thermal (TG/DTA) analyses were carried out in the nitrogen atmosphere to analyse the thermal stability of the crystal. Fig. 6 shows the TG/DTA curves of Cobalt Mercury Thiocyanate. Gel-grown Cobalt Mercury Thiocyanate crystals are thermally stable up to 200°C and decomposition starts only at 230°C. The observed mass loss 3.86% below the decomposition point is due to dehydration. In between the range of 230 to 325°C, the breakdown of the three dimensional steric structure takes place with the evaluation of 7/8 (CN) (cyanogen) which corresponds to mass loss of 5.06%. The mass loss of 75.25% is between the temperature 330 to 525°C corresponds to the evaluation of 1/8 (CN) and $2CS_2$ (carbon disulphide) and above 530°C corresponds to sublimation of Hg with mass loss of 11.41%, while 1/8 N_2 is lost in the final stage [27]. The DTA curves show an exothermic peak at 495 C corresponding to the evaluation of volatile gases corresponding to the TG curve.

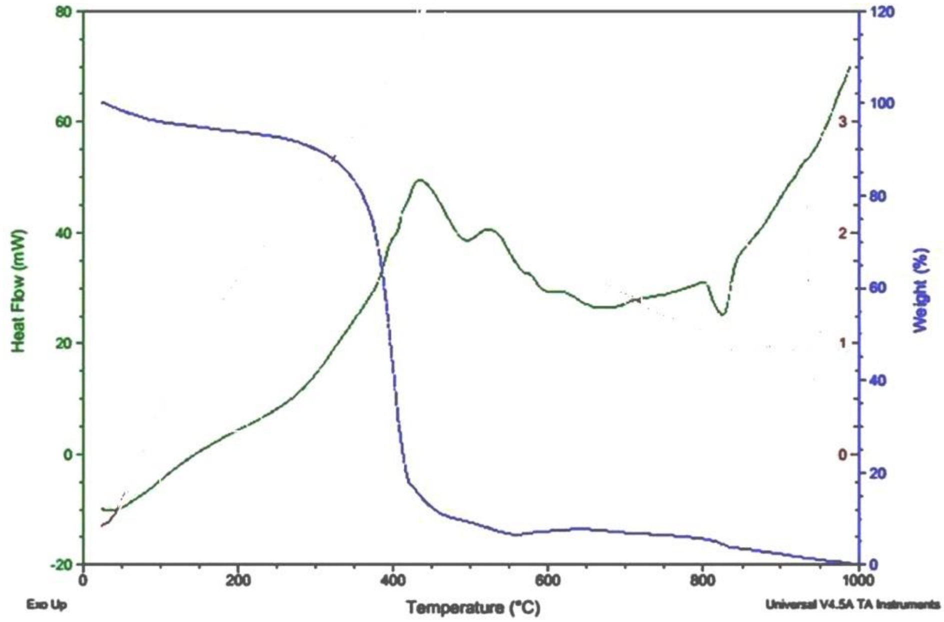

Fig 6: TG/DTA curves of Cobalt Mercury Thiocyanate.

4. CONCLUSION

Cobalt Mercury Thiocyanate single crystals was grown by gel technique at room temperature. The single crystal XRD study confirms the crystalline structure to be tetragonal. The FTIR spectrum shows that SCN ions bridge the 2 metal ions by coordination through both N and S atoms. Important Kurtz powder test confirms the nonlinear optical property of the crystal. Thus the characterization confirms the suitability of the grown crystal for NLO applications. Therefore the crystal has a wide application in the area of photonics, electro-optic and NLO devices. From the thermogram, it is concluded that gel-grown possess high thermal stability. Due to their excellent optical, and thermal properties, these crystals can be used for NLO applications.

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REFERENCES

[1] X.Q. Wang, D. Xu, M.K. Lu, D.R. Yuan, S.X. Xu. Materials Research Bulletin 36 (2001) 879 – 887

[2] G.C. Xing, M.H. Jiang, Z.S. Shao, D. Xu, Chinese Journal of Lasers 14 (1987) 302 (in Chinese).

[3] N. Zhang, M.H. Jiang, D.R. Yuan, D. Xu, X.T. Tao, Z.S. Shao, J. Cryst. Growth 102 (1990) 580.

[4] W.B. Hou, M.H. Jiang, D.R. Yuan, D. Xu, N. Zhang, M.G. Liu, X.T. Tao, Mat. Res. Bull. 28 (1993) 645.

[5] D. Xu, M.G. Liu, W.B. Hou, D.R. Yuan, M.H. Jiang, Mat. Res. Bull. 29 (1994) 73.

[6] B.G. Wang, Cryst. Res. Technol. 31 (1996) 421.

[7] S.G. Bhat, S.M. Dharmaprakash, Mat. Res. Bull. 33 (1998) 833.

[8] N.J. Long, Angew. Chem. Int. Ed. Engl. 34 (1995) 21.

[9] M.H. Jiang, Q. Fang, Adv. Mater. 11 (1999) 1147.

[10] S. Gunasekaranand S. Ponnusamy, Cryst. Res. Technol. 41, No. 2, 130 – 137 (2006)

[11] P. Paramasivam, C. Ramachandra Raja. Spectrochimica Acta Part A 79 (2011) 1109–1111

[12] X.L. Duan, D.R. Yuan, Z.W. Zhong, J.G. Zhang, X.Q. Wang, J. Cryst. Growth 233 (2001) 312.

[13] X.Q. Wang, D. Xu, M.K. Lu, D.R. Yuan, J. Cryst. Growth 245 (2002) 126

[14] C.C. Desai, M.S.V. Ramana, J. Cryst. Growth 102 (1990) 191.

[15] J. W. Jeffery And K. M. Rose, Acta Cryst. (1968). B24, 653.

[16] X.Q. Wang, D. Xu, X.F. Cheng, M.K. Lu, D.R. Yuan, J. Huang, G.W. Lu, H.X. Ning, X.L.Duan, Z.M. Wang, G.T. Lu, S.G. Li, Y. Chen, Y.Q.Zhou, Mater. Res. Bull. 37 (2002) 1859–1871.

[17] X.Q. Wang, D. Xu, M.K. Lu, D.R. Yuan, G.H. Zhang, F.Q. Meng, S.Y. Guo, M. Zhou, J.R.Liu, X.R. Li, Cryst. Res. Technol. 36 (1) (2001) 73–84.

[18] H. M. Lin, Y. F. Chen, J. L. Shen and W. C. Chou,J. Appl. Crystallogr., 2001, 89, 4476.

[19] J. Philip and T. A. Prasada Rao,Phys. Rev. A, 1992, 46, 2163–2165.

[20] H. J. Coles and S. V. Kershaw,J. Chem. Soc., Perkin Trans. 2,1988, 987–996.

[21] B. B. Parekh and M. J. Joshi,Cryst. Res. Technol., 2007,42(2),127–132.

[22] S. A. Mazen, F. Metawe and S. F. Mansour,J. Phys. D: Appl. Phys., 1997, 30, 1799–1808.

[23] C. Balarew and R. Duhlew,J. Solid State Chem., 1984,551,1–6.

[24] N. M. Ravindra, R. P. Bharadwaj, K. Sunil Kumar and V. K. Srivastava,Infrared Phys., 1981, 21, 369.

[25] J. D. Jackson,Classical Electrodynamics, Wiley Eastern, 1978,pp. 321.

[26] N. M. Ravindra and V. K. Srivastava,Infrared Phys., 1980,20,67–69

[27] Z.Blank, J. Cryst. Growth 18 (1973) 281-288.