Digest Journal of Nanomaterials and Biostructures Vol. 8, No. 3, July - September 2013, p. 965 - 971

LOW TEMPERATURE MAGNETIC SUSCEPTIBILITY STUDY ON TRIS THIOUREA COPPER (I) CHLORIDE CRYSTAL

S.ARIPONNAMMAL[a*],S.CHANDRASEKARAN[a],S.ARUMUGAM[b], S.ESAKKI MUTHU[b]
[a] *Department of Physics, Gandhigram Rural Institute, Deemed University, Gandhigram – 624302, Dindigul District, Tamilnadu, India.*
[b] *Centre for High Pressure Research, School of Physics, Bharathidasan University, Tiruchirappalli-620024, Tamilnadu, India.*

Single crystals of the organometallic material tris thiourea copper(I) chloride(TTCC) have been grown from aqueous solutions of copper(II) chloride by slow evaporation technique. The grown crystals have been characterized by powder X-ray diffraction (XRD). They have been crystallized in tetragonal structure. The thermal properties of the crystals have been investigated by thermo gravimetric (TGA), differential thermal (DTA) analysis and differential scanning calorimetry(DSC). A study of electron spin resonance (EPR) spectrum confirms the presence of Cu (II) ions in the TTCC crystal. The low temperature magnetic susceptibility study on TTCC crystal confirms the diamagnetic behavior of the crystal.

(Received May 1, 2013; Accepted July 16, 2013)

Keywords: Semiorganic, XRD, TGA, DTA, DSC, EPR, Low temperature magnetic susceptibility

1.Introduction

Materials exhibiting large optical nonlinearity are of great interest for applications such as frequency conversion, telecommunication, optical computing, optical information processing and high optical disc storage [1-3]. Organic materials show prominent properties due to their fast and large nonlinear response over a broad frequency range, inherent synthetic flexibility and large optical damage threshold. However, organic materials may suffer from problems, such as volatility, low thermal stability and mechanical weakness etc. Inorganic materials possess excellent mechanical and chemical properties but most of them have shown low nonlinear efficiency. The need for materials which combine large nonlinear optical characteristics with resistance to physical and chemical attack has led to the investigation of semiorganics [4-8]. The advantages of semiorganic materials are that they can be grown from aqueous solution and form large three dimensional crystal. The crystals can be easily cut and polished with specific phase matching loci, acceptance angle and the effective non linear coefficient. Ligands like thiourea and thiocyanate with S and N donors are capable to combine with metal to form stable complexes through coordinated bonds. These complexes show ligand to metal charge transfer by an electron movement from ligand to metal and metal to ligand in addition to л – л* conjugation metal with d^{10} configuration like zinc, cadmium, mercury readily combine with thiourea resulting in stable semiorganic compounds with good physio chemical behavior. Some well known organo metallic crystals are ZTS, ZTC and BTCC [9-11]. Therefore, TTCC crystals have been crystallized for the present study and the study of structural, thermal, electron paramagnetic resonance and low temperature magnetic susceptibility study of TTCC crystal have been reported in this paper.

*Corresponding author: ariponnammal@yahoo.co.in

2.Experimental Details

Synthesis and Crystal growth : Tris thiourea Copper (I) chloride (TTCC) compound was synthesized by the reaction of GR(99%pure Merck) grade thiourea with Copper (II) chloride dihydrate in stoichiometric ratio 1:4. The calculated quantities of thiourea and Copper (II) chloride salts were dissolved in the mixed solvent of water-methanol taken in the ratio of 1:1. The synthesized salt was purified by recrystallization process for three times. Saturated solution of synthesized TTCC compound was allowed to evaporate at room temperature. And, the good quality seed crystals were obtained by slow evaporation technique.

Characterization : The powder X-ray diffraction (XRD) analysis has been performed with Richseifert diffractometer using CuKα radiation. The TGA and DTA scans were performed using Perkin Elemer, Diamond TG / DTA thermal analyzer in the temperature range 42ºC to 1200º C. High temperature DSC was carried out in Mettler Toledo DSC 822e instrument in the temperature range of 40ºC to 460ºC. The rate of heating in all thermal scans was 10ºC per min. The EPR powder spectrum of Cu (II) ion in the TTCC crystal was recorded with Bruker EMX plus model spectrometer at room temperature. Optical absorption spectrum of TTCC was recorded with Perkin Elmer Lamda35 model spectrophotometer. The magnetization and magnetic hysteresis measurements on TTCC crystal have been performed in a Quantum Design PPMS equipped with a continuous low temperature control with temperature varying from helium temperature 4K to 300K.

3.Results and Discussions

XRD analysis The Fig.1 has shown the recorded XRD powder pattern for the grown TTCC crystal and the data is analyzed by the method of least square fitting. The crystal is found to be crystallized in tetragonal structure with a=b=13.409±0.02Å, c=13.774±0.02Å, V=2476.58Å^3 and α=β=γ=90˚. The particle size of the crystal has been calculated using Scherrer formula [12] as 39 nm.

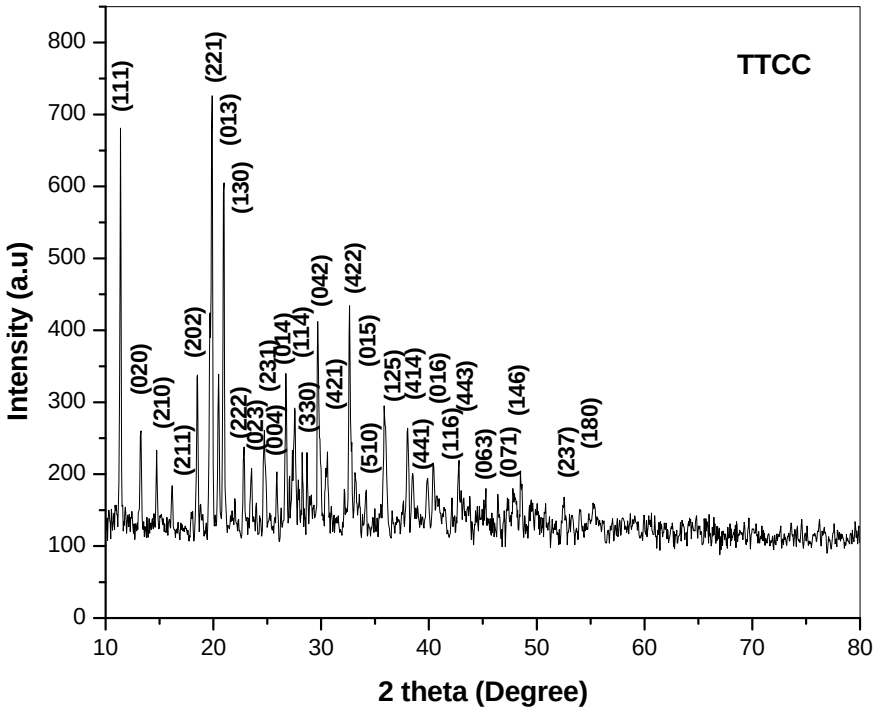

Fig.1. X-ray powder diffraction pattern of TTCC crystal.

Thermal analysis The Fig.2 has shown the TGA curve of TTCC. When the TTCC crystal is heated from ambient temperature to 1200ºC, a prolonged decomposition starts at 205ºC and extends upto 593ºC leading to a total weight loss of 75%. The weight loss of 75% equivalent to 327 molecular units at this temperature range can be accounted for the liberation of CS_2, S, CH_4, N_2 and H_2. The decomposition reaction is formulated as given below

205-593ºC

$Cu[CS(NH_2)_2]_3\ Cl \rightarrow CuCl + CS_2 + S + 2CH_4 + 3N_2 + 2H_2$

Molecular mass units: 327 99 228 [76+32+32+84+4]

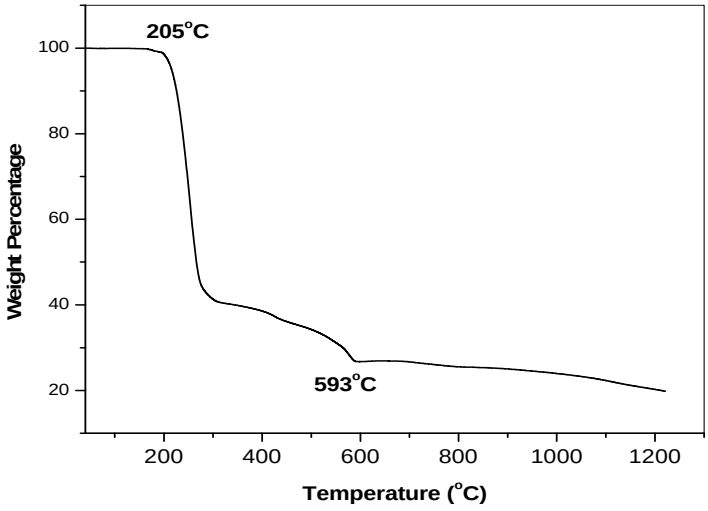

Fig.2. TGA curve of TTCC crystal

The CuCl residue is stable beyond 593ºC. The above decomposition pattern fits well with the formula of the compound.

The Fig.3 has shown the DTA curve of TTCC. The DTA analysis confirms the melting point of the sample through sharp endothermic peak at 172ºC. The endothermic peak at 258ºC reveals the volatile nature of the sample. The peak at 589ºC indicates the large energy requirement for the decomposition process that starts at 205ºC.

The high temperature DSC scan run from room temperature to 460ºC(Fig.4) have shown two sharp peaks. The endothermic peak at 178.8ºC corresponds to melting of compound. The exothermic peak at 294.9ºC indicates a structural phase transition of the residue CuCl which is also observed in DTA thermogram.

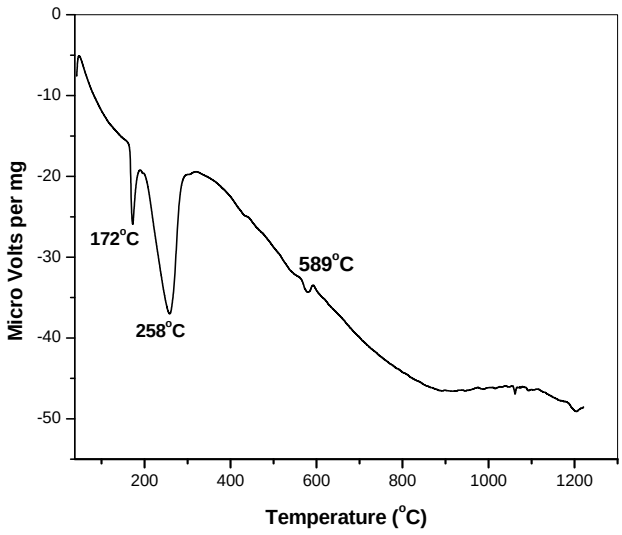

Fig.3. DTA curve of TTCC crystal.

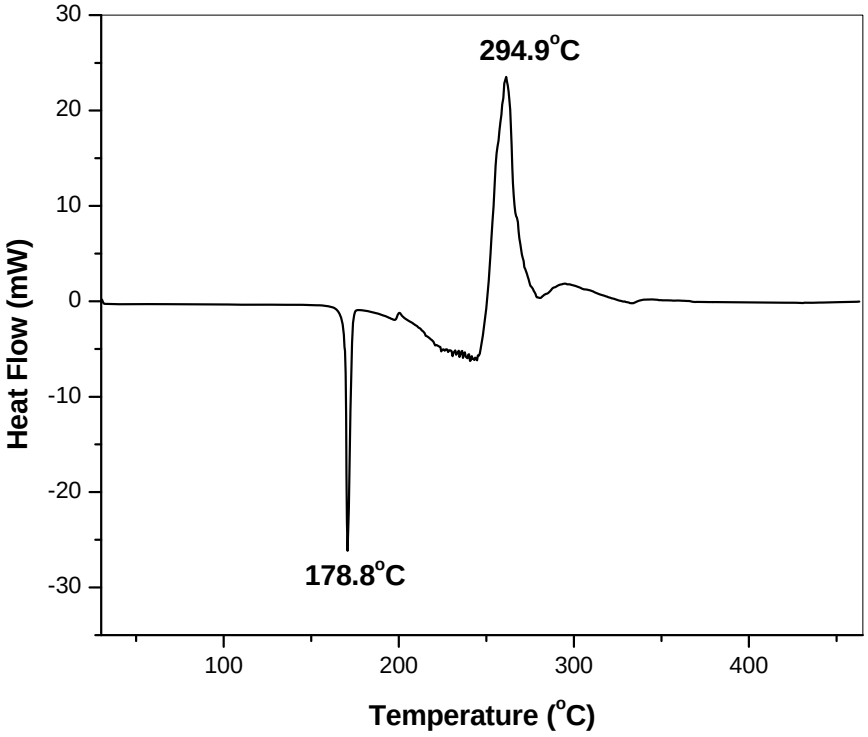

Fig.4. High Temperature DSC curve of TTCC crystal.

EPR Spectral analysis Generally, the EPR spectrum does not exhibit signals due to the absence of unpaired electrons in the copper (I) compounds. But, since the present TTCC crystal has been prepared from copper (II) chloride, EPR active signals have been observed as shown in Fig.5. This may be due to Cu^{2+} ions entering from copper (II) chloride to the host lattice substitutionally and therefore the exhibited resonance lines are observed to be weak. Cu (II) has S=1/2 and nuclear spin I=3/2 (for both ^{63}Cu and ^{65}Cu naturally abundant isotopes). A group of four resonance lines is expected per complex. In any general orientation, the number of such resonance lines will provide the number of distinguishable complexes in the host lattice [13]. The $3d^9$ ion Cu (II) exhibits four lines from single complex. Generally, Cu^{2+} ion can enter the lattice substitutional or interstitially. In this present structure, it is assumed that Cu^{2+} ion enters substitutionally [14,15]. The observed EPR powder spectrum (Fig.5) is quite unusual, complex and difficult to interpret. It starts from 3300 Gauss to 3600 Gauss. It shows that the symmetry of the complex in the crystal is not axial. The powder EPR spectrum was partially resolved into three components. The measured values are g_{xx}=2.051, g_{yy}= 2.000 g_{zz}= 2.098; A_{xx}= 2.37mT, A_{yy} = 2.33mT, A_{zz} = 2.37mT. It is notable that the coupling constant A_{xx}=A_{zz} which favours tetragonal crystal structure deduced from XRD study. Since the lines are quite weak and the spectrum is complex in appearance, the ^{63}Cu and ^{65}Cu hyperfine lines are not clearly resolvable [16].

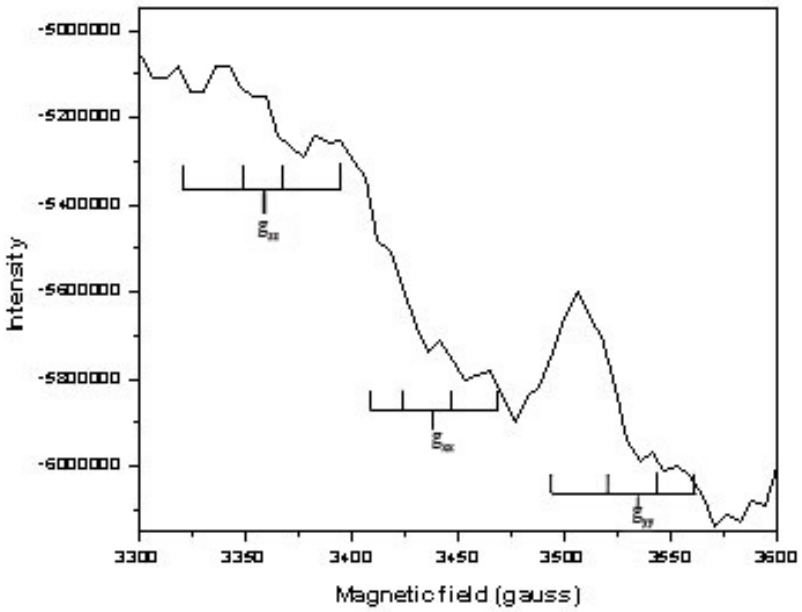

Fig.5. EPR powder spectrum of TTCC crystal

Optical absorption study The Fig.6 has shown the absorption spectrum of the diffused Cu^{2+} ion in the crystal. The broad absorption at about 850 nm is identified as the d-d transition band due to Cu^{2+} ions. The broad absorption band on the right side has not yet been assigned. The crystal may include various kinds of defects other than Cu^{2+} sites such as colour centers [17, 18]. The spectrum contains intense and broad absorption band in the UV range at 336 nm, which may be, probably charge transfer transition bands since it arises from the higher lying energy levels. The four bands at γ_1=14,514cm^{-1}, γ_2=17,153 cm^{-1}, γ_3=17,889cm^{-1} and γ_4=21,598 cm^{-1} in the visible range are weak in intensity. They may be regarded as d-d transfer bands which show the uniqueness of the presence of Cu^{2+} ion [14, 15] due to the preparation of the crystal from copper (II) chloride.

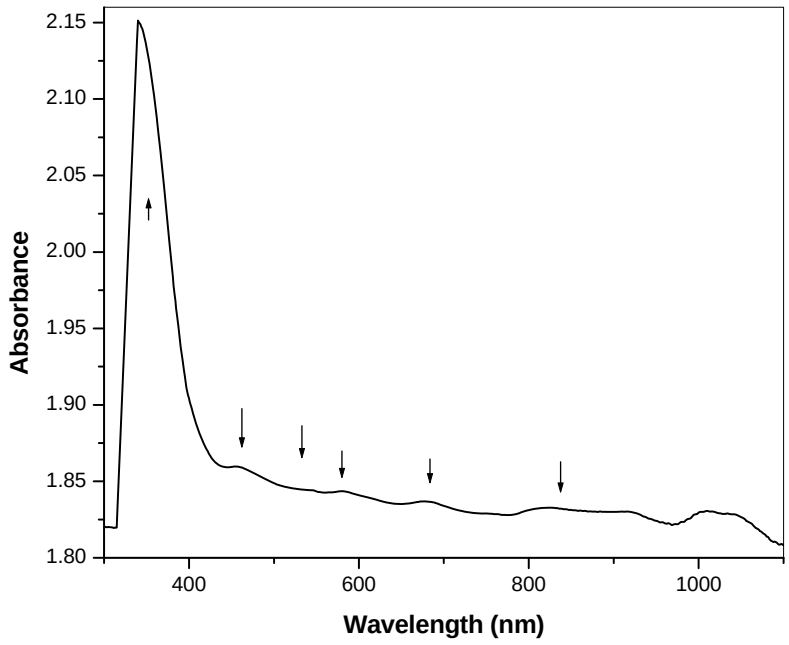

Fig.6. Optical absorption spectrum of TTCC crystal

Low Temperature Magnetic Susceptibility study Magnetic susceptibility measurements provided the field dependence magnetization for TTCC crystal at room temperature 300K. It has been recorded ranging from 0 to 10000 Oe (figure 7) which clearly shows the diamagnetic behavior of the crystal[19-21]. The temperature dependence of magnetic susceptibility measurements has been performed on TTCC crystal at temperatures extending from room temperature to helium temperature (300K-4K) at field strength of 500 Oe and the behavior is well clearly shown in figure 8. The magnetic susceptibility is found to be negative and seems to be constant throughout the temperature range which confirms the diamagnetic nature of the crystal.

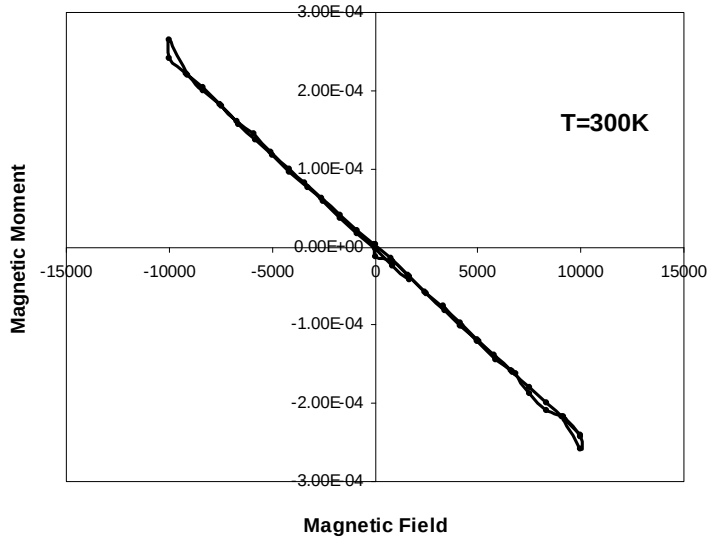

Fig.7. Field dependence magnetization of TTCC crystal at T=300K

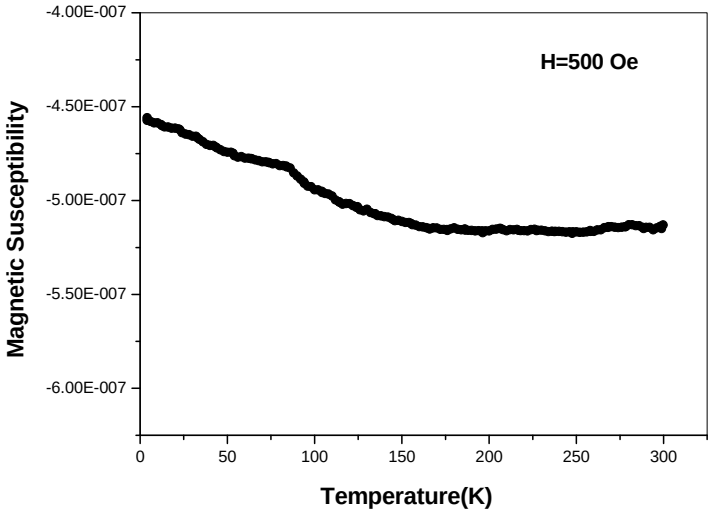

Fig.8. Low temperature magnetic susceptibility of TTCC crystal at H=500 Oe

4.Conclusions

The coordination complex compound tris thiourea Copper (I) chloride was prepared from Copper (II) chloride and pure single crystals of TTCC were grown by slow evaporation technique. The powder XRD data confirms the tetragonal crystal structure. The decomposition patterns in the thermogravimetry gives the molecular formula of the compound. The decomposition starts from 205ºC and extends up to 593ºC. The DTA peaks illustrate the large energy requirement of decomposition. The endothermic peak found in high temperature DSC scan indicates the melting temperature as 178.8ºC. The exothermic peak found in DSC scan indicates the structural phase

transition of the decomposition residue CuCl. The copper (I) complexes are EPR inactive which evinces that the complex is diamagnetic. The present recorded EPR spectrum exhibits weak four lines which indicates the presence of copper (II) centers. Since the crystal has been prepared from copper (II) chloride, copper (II) ions enter the host lattice substitutionally. The +2 oxidation state of the copper which is a d^9 electronic system of unpaired electrons is confirmed by the peaks present in EPR spectrum. Kivelson and Neimann [13, 22] pointed out that compounds having $g_{\parallel} < 2.3$ are covalent in nature where as the compounds having $g_{\perp} > 2.3$ are ionic. The g - values obtained from present EPR spectral study suggests that the compound is having covalent character. The optical absorption spectrum confirms the uniqueness of Cu^{2+} ion combination by the presence of d-d transition bands. The study of low temperature magnetic susceptibility and the field dependence magnetization confirm the diamagnetic nature of the crystal. The magnetic susceptibility is found to be negative throughout the temperature range from 300K to 4K. Thus, the characterization of the TTCC crystal has been made and reported in this paper.

Acknowledgements

Authors are thankful to UGC and DST, Government of India for financial support.

References

[1] I.Ledoux , Synth. Metal. **54,** 123 (1993).
[2] D.R.Yuan, D.Xu, N.Zhang, M.G.Liu and M.H.Jiang, Chin. Phys. Lett. **13**, 841(1996).
[3] M.Iwai, T.Kobayashi, H.Furya, Y.Mori and T.Sasaki, Jpn. J. Appl. Phys. **36,**L276(1997).
[4] A.Baskaran, C.M.Ragavan , R.Sankar, R.Mohankumar and R.Jeyavel, Cryst. Res. Technol. **42**,477(2007).
[5] G.P.Zhang., Phys. Rev. Lett. **86,** 2086 (2001).
[6] H.O.Marcy, L.F.Warren, M.S.Webb, C.A.Ebbers, S.P.Velsko, G.C Kennedy G.C.Catella, Appl. Opt. **31**,5051 (1992).,
[7] B.Ramabadran, D.E.Zelmon and G.C.Kennedy. Appl. Phys. Lett. **60,** 2589(1992).
[8] P.M.Ushasree, R Jeyavel, C.Subramanian and P.Ramasamy, J. Cryst. Growth **197**,216.(1997).
[9] S.Ariponnammal, R.Selva vennila, S.Radhika and S.Arumugam, **40**, 896 (2005).
[10] S.Ariponnammal, R.Selva vennila, S.Radhika and P.M.Ushasree., Modern Physics Letters **B21**,675 (2007).
[11] S.Ariponnammal, S.Radhika, R.Selva vennila and N.Victor Jeya, Cryst.Res. Technol. **40**,786 (2005).
[12] B.D.Cullity, Elements of X-ray Diffraction, Second edition, Addison-Wesley Publishing company Inc. USA, 1978.
[13] V.Rao Padmavathi, K.V.Natasimhulu and Y.Nataraja Naidu, Spectrochemica Acta **A51,**2531 (1995).
[14] Ram Kirpal and Sanjay Misra,. Journal of Physics and Chemistry of Solids **65**,939 (2004).
[15] I.Kartal, B.Karabulet, F.Koksal and H.Icbudak, Z.Naturforsch. **55A**,887 (2000).
[16] B.P.Maurya, Alex Punnoose and R.J.Singh, Solid State Communications. **94**,231(1995).
[17] Tadashi Kobayashi, Katsutoshi Muto, Junj iro Kai and Asako Kawamori, J. of magnetic resonance.(1979)34:459-466.
[18] K.V.NaraSimhulu, C.S.Sunandana and J.L.Rao, Journal of Physics and Chemistry of Solids **61**,1209 (2000).
[19] EWm Pugh, B.R Coles, A. Arrott and J.E..Goldman, Phys. Rev. **105**, 814 (1957).
[20] B.D.Cullity and C.D.Graham, Introduction to Magnetic Materials, Second Edition, IEEE Press, John Wiley and Sons, Inc., Publication, USA. 2009.
[21] N.Sengottuvelan, J.Manonmani and M.Kandaswamy, Polyhedron **21,** 2767 (2002).
[22] Daniel Kivelson and Robert Neiman., J. of Chem. Phys. **35**,149 (1961).