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ORIGINAL RESEARCH PAPER

Synthesis of Cuprous Oxide by Thermal Treatment in Liquid Paraffin

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Abstract

Cu_2O nanoparticles were synthesized by thermal treatment in liquid paraffin without any inert gas protection using nano structures of Schiff base copper (II) complex (1) as precursor. Liquid paraffin was used as solvent and reductant. Span 80 was applied to control the morphology of cuprous oxide nanoparticles. The nano structure of the complex was characterized by X-ray diffraction measurements, UV–visible spectroscopy and Fourier transforms infrared spectroscopy. Thermal stability of Cu complex in its nano size form has also been studied by thermal gravimetric and differential scanning calorimetry analysis. The obtained cuprous oxide nanoparticle has been characterized by XRD measurements and FT-IR spectroscopy. The morphology, structure and size of the nano structure of 1 and Cu2O are investigated by scanning electron microscopy. The resulted cuprous oxide nanoparticles with average diameter about 30-40 nm were obtained and they have uniform morphology and stable when exposed to air.

1. INTRODUCTION

In the last decade metal oxides has extensively studied by materials scientists due to their useful optical, electrical, magnetic, mechanical, and catalytic properties [1, 2].

Among metal oxides, cuprous oxide (Cu_2O) nanoparticles have attracted attention because of their low cost and novel properties such as optical, catalytic, mechanical, electrical, and magnetic as well as heat conduction properties [3]. Cuprous oxide is an important metal-oxide *p*-type semiconductor and has a direct small band gap of 2.2 eV [4-6]. It has diverse applications in solar energy conversion, catalysis, gas sensors, electrodes for lithium-ion batteries and magnetic storage [7-11]. To synthesis of uniform Cu_2O nanoparticles with different morphologies many efficient approaches has been carried out such as sonochemical preparation [12], microwave irradiation [13] and liquid phase reducing [14] sol–gel [15] and electrochemistry [16].

This paper describes a new method, without any inert gas protection, to prepare stable nano cuprous oxide with uniform morphology structure. In contrast to conventional chemical reduction, paraffin was used as reductant and solvent to prepare well dispersed cuprous oxide nanoparticles. Here, nano structure salicylaldehyde Schiff base complex is used as a precursor and Span 80 is used to control the morphology of cuprous oxide nanoparticles.

2. Experimental procedure

2.1. Materials and measurements

The involved samples were prepared using $Cu(NO_3)_2.3H_2O$ from Merck India Ltd, 2-hydroxybenzaldehyde and 2-amino-2-methyl-propan-1-ol from Sigma–Aldrich, USA. All the chemicals and solvents employed for the synthesis were of analytical grade and used as received without further purification.

FT-IR spectra of the ligands and the complexes were recorded in the 4000–400 cm^{-1} wavenumbers region by using KBr disks as standard on a Thermo SCIENTIFIC model NICOLET iS10 spectrophotometer. The UV-Vis absorption spectra were obtained by using a PG instruments Ltd, T70/T80 series (UV–Vis) spectrometer in the range of 800–200 nm wavelength with HPLC grade methanol as solvent. A Brucker Avance DPX 400 MHz instrument was used to record the NMR spectra with TMS and $CDCl_3$ as the internal standard and the solvent, respectively. The simulated XRD powder pattern based on single crystal data were prepared using Mercury software [17]. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with monochromatic Cu-Kα radiation to investigate the crystalline structure and phase identification. The nano samples were characterized by a scanning electron microscopy (SEM) (Philips XL 30). Ultrasonic generator was carried out on an ultrasonic bath wiseclean-wvc-A02H (frequency of 50 kHz). Thermogravimetric analysis (TGA) and differential thermal analysis (DSC) of the Cu complex was performed on a computer-controlled NETZSCH model PC Luxx 409 apparatus. A single-phased powder sample of **1** was loaded into alumina pans and heated with a ramp rate of 10 ^{o}C/ min from room temperature to 800 ^{o}C under an argon atmosphere.

2.2. Synthesis

2.2.1. Synthesis of the Schiff base ligand [2-[(2-hydroxy-1, 1-dimethyl-ethylimino) methyl] phenol] (H_2L)

The Schiff base ligand was prepared by standard methods. The solution of 2-hydroxy-benzaldehyde (2 mmol, 0.224 g) was mixed with 2-amino-2-methyl-propan-1-ol (2 mmol, 0.178 g) to preparation of H_2L in ethanol (20 mL). The bright yellow solution was stirred and heated to reflux for 1 h. The desired yellow solution was precipitated by mixing with diethyl ether and then filtered off and dried in air. H_2L: Yield: 84%, m.p. = 63-66 ^{o}C, Selected FT-IR data, ν(cm^{-1}): 3371 (O–H), 2964 (C–H), 1601 (C=N), 1550 (C=C). ^{1}H NMR (δ): 1.31 (s, 6H, 2(CH_3)), 1.96 (br s, aliphatic OH), 3.59 (2H, CH_2), 6.86 (d of tri, ArH, *J*=7.2 and *J*=0.8 Hz), 6.92 (d, ArH, *J*=8 Hz), 7.25–7.32 (m, 2H, ArH), 8.37 (s, 1H, HC=N) and 13.94 (br s, Aromatic OH). ^{13}C NMR (δ): 23.56 (2CH_3), 60.92 ((CH_3)2CCH_2), 71.14(CH_2), 117.34, 118.69, 118.36 131.65, 132.44 and 161.95 (aromatic C), 162.23(HC=N).

2.2.2. Synthesis of [$Cu(HL)(H_2O)NO_3$] (1) nanostructure by a sonochemical process

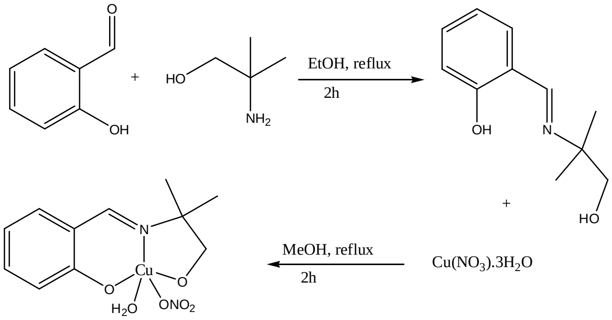
A tetrahydrofuran (THF) solution of the Schiff base ligand, H_2L (0.962 g, 5 mmol) was poured drop wise into to a copper nitrate three hydrate (1.126 g, 5mmol) in chloroform during 40 min under ultrasonic irradiation. By the end of the titration process, the solution was kept in the ultrasonic bath for a period of 40 min. The obtained precipitates were filtered and then dried. Yield (Nano Cu complex): 88%, m.p.: >250 ^oC. FT-IR (KBr disc, cm^{-1}): 1624($\nu_{C=N}$), 1535($\nu_{C=C}$), 598(ν_{Cu-O}) and 481(ν_{Cu-N}). The structural formula of Cu (II) Schiff base complex was shown in Scheme 1.

2.2.3. Synthesis of Cu_2O nanoparticles

6.70 g Cu (II) Schiff base complex and appropriate content of span 80 as surfactant (15 ml) were added into a 500 mL distillation flask with 150 mL paraffin in it. The mixed solution was slowly heated to 250 ˚C under vigorous stirring without any inert gas protection and gradually cooled to room temperature after 3 h of reaction. Then the particles were filtrated by centrifugation and washed successively with petroleum ether, deionized water, and absolute ethanol and dried in air.

3. Results and discussion

The pure ligand, [2-[(2-hydroxy-1,1-dimethyl-ethylimino)methyl]phenol] (H_2L), was obtained and isolated during the condensation reaction of the 2-amino-2-methyl-propan-1-ol with 2-hydroxybenzaldehyde in ethanol and the obtained ligand being stable in air was characterized by the FT-IR, ^1H NMR, and ^{13}C NMR spectra. The formation of the ligand and its complex is shown in Scheme 1. Nanostructures of the copper complex were obtained by sonochemical method. This Cu(II) complex containing the tridentate Schiff base ligand was characterized by FT-IR, UV-Vis spectroscopy and XRD analysis. Thermal decomposition of compound **1** as nanostructure in paraffin at 250 ^oC for 3 h results in Cu_2O nanoparticles.



Scheme 1. Schematic representation of the synthesis of title compound.

The FT-IR spectra of ligand and the nanostructure Cu complex prepared by the sonochemical method are shown in Fig. 1. The spectra in KBr matrix confirm that the strong absorption band at about 1624- 1627 cm^{-1} can be assigned to the imine stretching frequency of the coordinated ligand, whereas for the free ligand the same band is observed at 1601 cm^{-1}. The shift of this band towards upper wavenumber upon complexation with the metal can be attributed to the coordination to the metal ion through imine nitrogen atom [18, 19]. Ligand coordination to the metal center is substantiated by the single bands appearing at about 590 and 480 cm^{-1} which can correspond to the vibrations of Cu-O and Cu-N bonds, respectively [20]. Coordination of the nitrate to the copper(II) ion is also supported by the FT-IR spectra, displaying two strong bands due to the nitrate group,: ν_{sym} and ν_{as} at about 1440 and 1290 cm^{-1} respectively. This bands indicate that the nitrate ion is coordinated to the copper(II) ion as monodentate ligand [21]. The broad band near 3450 cm^{-1} shows the existence of water molecule [21, 22].

An electronic spectrum of the Cu complex was recorded in MeOH. In the electronic spectrum the bands in the spectral range 200-300 nm, of ligand origin, have become blue shifted upon complexation(Fig.2).

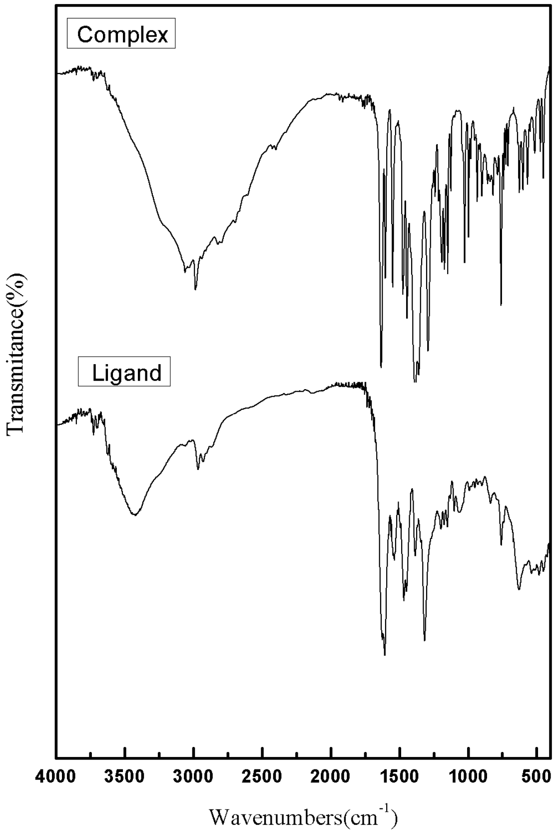


Fig. 1. FT- IR spectra of the ligand and nano complex produced by sonochemical method.

They can be attributed to n→π*, π→π* transitions of the phenyl ring and π→π* of the azomethine moiety respectively. The band at approximately 355 nm reveals coordination of the ligand to metal center. This band is due to MLCT (metal to ligand) and LMCT (ligand to metal) charge transfer transitions. In five coordinated Cu(II) complexes Visible spectrum can be used for predicting preferred geometry. SP or distorted SP geometries exhibit a band in the 550-660 nm range that is assigned to dxz,yz→dx2- y2 while TBP structures have a characteristic band around >800 nm is related to d_{xz}, $d_{x^2-y^2} \rightarrow d_{z^2}$. The spectrum of [Cu(HL)(H_2O)NO_3] shows a broad band at about 660 nm, Thus Cu central atom in this complex is closer to SP [23].

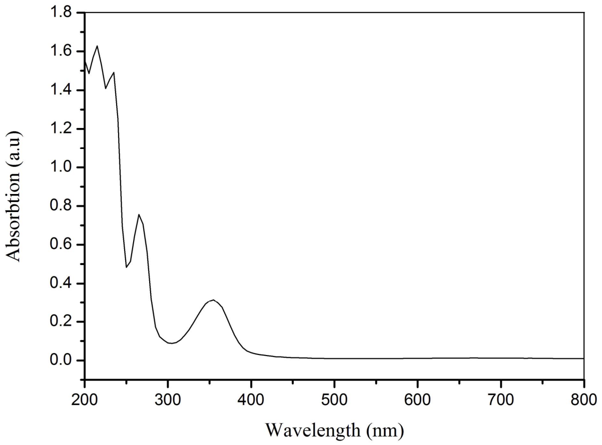


Fig. 2. Electronic spectra of the Cu complex.

The reaction between [2-[(2-hydroxy-1,1-dimethyl-ethylimino)methyl]phenol] (H_2L) and copper (II) nitrate three hydrate provided a crystalline material of the general formula [Cu(HL)(H_2O)NO_3] (**1**). The morphology and grain (crystalline) size of compound **1** prepared by the sonochemical process was studied by X-ray diffraction (XRD) techniques and scanning electron microscopy (SEM). Fig. 3 shows the simulated XRD pattern from single crystal X-ray data of compound **1** in comparison with the XRD pattern of the typical sample of compound **1** prepared by the sonochemical process. Acceptable matches, with slight differences in 2θ, were observed between the simulated and experimental powder X-ray diffraction patterns. This indicates that the compound obtained by the sonochemical process as nanoparticles are identical to that obtained by single crystal diffraction. The significant broadening of the peaks indicates that the particles are of nanometer dimensions.

The morphology and size of the nanocompound **1** are investigated by scanning electron microscopy (SEM) (see Fig. 4). As can be seen from this figure some nanoparticles of compound **1** with average diameter about 40-50 nm were obtained.

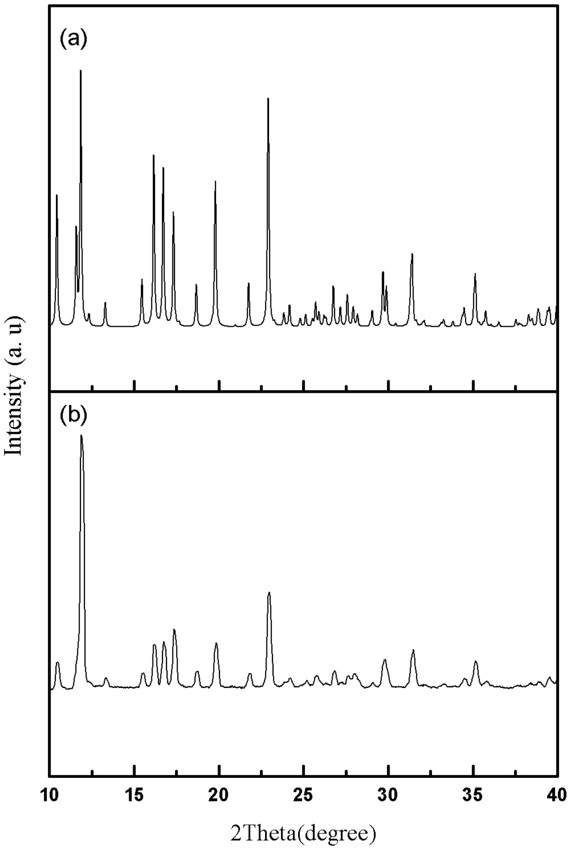


Fig. 3. XRD patterns: (a) simulated pattern based on single crystal data of compound **1** (b) nano structure of compound **1** prepared by sonochemical process.

Fig. 6 shows FT-IR spectra of Cu_2O nanoparticles formed via thermal decomposition of nanostructure **1** at 250 °C. The peak at 601 cm^{-1} is assigned to Cu-O stretching [24]. Existence of free precursor is ruled out due to the absence of stretching vibration of CH, C=N and other groups of the ligand.

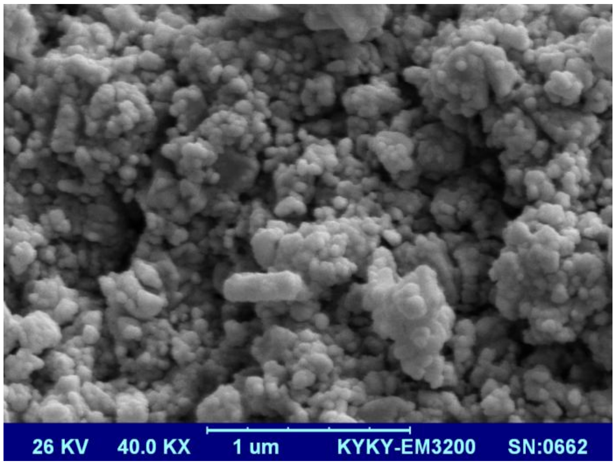


Fig. 4. SEM photographs of compound **1** nano structures.

The thermal behavior of the nanocompound **1** was investigated by thermal gravimetric analysis (TGA). Fig. 5 shows that the Cu complex starts to decompose at 140 °C and the weight loss occurs in the temperature range 140-490 °C. The weight loss is ascribed to the decomposition of the Schiff base ligand. The weight loss is about 54.23%. The decomposition of the compound ultimately results in a solid that appears to be Cu_2O. The DSC curves displays two distinct endothermic effects at 140 and 410 °C and three exothermic effects at 160, 220 and 275 °C for the compound **1.**

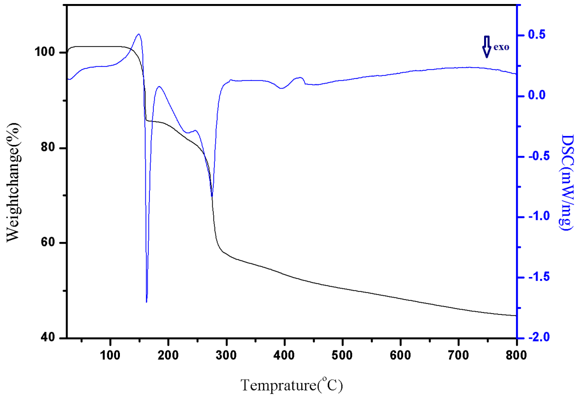


Fig. 5. Thermal behaviour of compound **1**.

The phase composition and structure of the sample with Span 80 as surfactant were determined via XRD. Fig. 7 shows an XRD pattern of freshly produced copper (I) oxide. All peaks in the XRD patterns matched well with Cu_2O standard data (JCPDS 05-0667). No impurities are present. The sharp and strong peaks reveal Cu_2O nanoparticles are highly oriented.

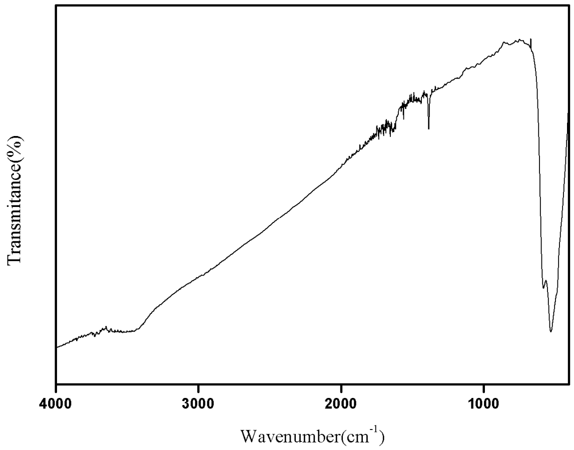


Fig. 6. FT-IR absorption spectra of copper oxide.

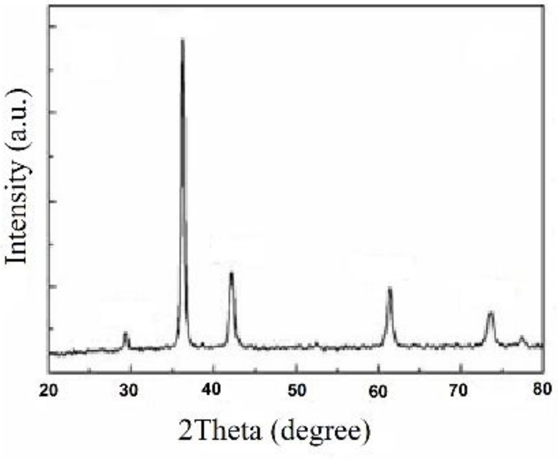


Fig. 7. XRD pattern of Cu_2O nanoparticles prepared by thermal decomposition of compound **1**.

The morphology and size of the product were characterized by SEM. Fig. 8 shows SEM image of the samples thermal treated for 3 h with Span 80. From this image, we can conclude that the formation of nanoparticle morphology structure should be attributed to Schiff base complexed with Cu (II). Sample prepared in the presence of Span 80 are composed of well dispersed nanoparticle (as shown in Fig. 8). This result reveals that Span 80 acts as surfactant to disperse nanoparticles. As can be seen from this figure some nanoparticles of Cu_2O with average diameter about 30-40 nm were obtained.

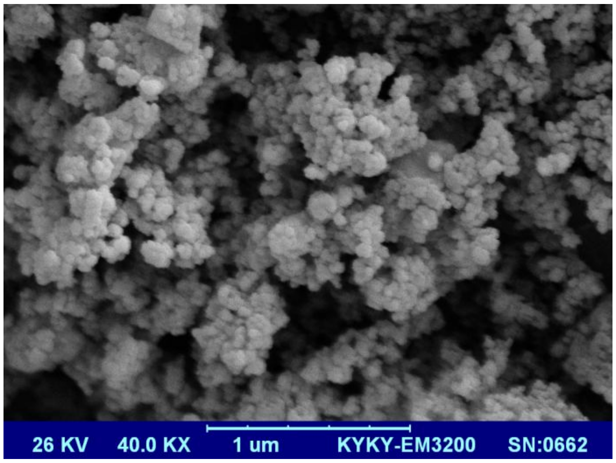


Fig. 8. Scanning electron microscopy (SEM) images of Cu_2O nanoparticles prepared by thermal decomposition.

4. Conclusion

Cu_2O nanoparticles have been successfully synthesized via thermal treatment in paraffin by using copper (II) Schiff base complex as precursor. This method is an effective route for the synthesis of Cu_2O nanoparticles in the present of Span 80 as surfactant.

References

[1] C. Burda, X.B. Chen, R. Narayanan, M. A. El-Sayed, Chem. Rev. 105(4) (2005) 1025–1102

[2] M. Y. Masoomi, A. Morsali, Coord. Chem. Rev. 256 (2012) 2921– 2943

[3] J. Wen, J. Li, S. Liu, Q. Chen. Colloid. Surf. A 373(1-3) (2011) 29–35.

[4] I. Grozdanov, Mater. Lett. 19 (1994) 281-285.

[5] M.Y. Shen, T. Yokouchi, S. Koyama, T. Goto, Phys. Rev. B 56 (1997) 13066-13227.

[6] W. Shi, K. Lim, X. Liu, J. Appl. Phys. 81 (1997) 2822-2827.

[7] H. Zhang, X. Ren, Z. L. Cui, J. Cryst. Growth.04 (2007) 206–210.

[8] B. White, M. Yin, A. Hall, D. Le, S. Stolbov, T. Rahman, N. Turro,S. O'Brien, Nano. Lett. 6(9) (2006) 2095–2098.

[9] J. T. Zhang, J. F. Liu, Q. Peng, X. Wang, Y. D. Li, Chem Mater, 18(4) (2006) 867–871.

[10] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J. M. Taracon, Nature 407(28) (2000) 496–499.

[11] C. H. Kuo, M. H. Huang, J. Am. Chem. Soc. 130(38) (2008) 12815–12820.

[12] R. V. Kumar, R. E. Elgamiel, Y. Diamant, A. Gedanken, Langmuir. 17 (2001) 1406–1410.

[13] S. Li, X. Guo, Y. Wang, A. Xie, F. Huang, Y. Shen, X. Wang. Dalton. T. 40 (2011) 6745–6750.

[14] L. Feng, C. Zhang, G. Gao, D. Cui. Nano. Res. Lett. 7(276) (2012) 1–10.

[15] M. Sen, E. Erboz. Food. Res. Int. 43 (2010) 1361–1364.

[16] S. Yallappa, J. Manjannan, M. Sindhe, N. Satyanarayan, S. Pramod, K. Nagaraja. Spectrochim. Acta. A. Mol. Biomol. Spectrosc. 110 (2013) 108–115.

[17] Mercury 1.4.1 2001- 2005 Copyright Cambridge Crystallographic Data Centre 12 Union Road CambridgeCB2 1EZ UK

[18] L. Bessais, C. Djega-Mariadassou, V. H. Ky, N. X. Phuc. J. Alloys. Comp. 426 (2006) 22.

[19] R. Ruzitschka, M. Reissner, W. Steiner, P. Rogl. J. Magn. Magn. Mater. 806 (2002) 242-245.

[20] P. Schobinger-Papamantellos, K. H. J. Buschow, C.H. de Groot, F. R. de Boer, G. Böttger and C. Ritter. J. Phys. Condens. Matter. 11 (1999) 4469-4481.

[21] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th ed., Wiley, New York, 1997.

[22] B. Ding, Y.Y. Liu, X.J. Zhao, E.C. Yang, X.G. Wang, J. Mol. Struct. 920 (2009) 248-251.

[23] K.M. Vyas, R.N. Jadeja, D. Patel, R.V. Devkar, V.K. Gupta, Polyhedron. 65 (2013) 262-274.

[24] A. El-Trass, H. Elshamy, I. El-Mehasseb, M. El- Kemary, Appl. Surf. Sci. 258 (2012) 2997-3001.