International Journal of Engineering Trends and Technology (IJETT) - Volume 67 Issue 3- March 2019

Electron Paramagnetic Resonance and Optical Study on VO(II) Ion Doped Triaquapotassiumbismalonatonickelate (TPMN)

K. Senthil Kumaran[#1], S. Jayakumar[*2,3]
[#1]Assistant Professor, Department of Chemistry, SNS College of Engineering, Coimbatore, Tamilnadu, India
[*2]Assistant Professor, Department of Physics, SNS College of Engineering, Coimbatore, Tamilnadu, India
[3]Center for Materials Research and Energy, Udumalpet, Tiruppur, Tamilnadu, India

Abstract

The EPR spectroscopic investigation of VO(II) ion doped in a paramagnetic host lattice, Triaquapotassiumbismalonatonickelate complex has been carried out at room temperature using X-band spectrometer to gain information about location of the impurity and bond characters. Single crystal rotated along the three orthogonal crystallographic axes has yielded spin Hamiltonian parameters g and A as: $g_{xx} = 1.979$, $g_{yy} = 1.968$, $g_{zz} = 1.936$ *and* $A_{xx} = 6.92$, $A_{yy} = 6.02$, $A_{zz} = 18.12$ *mT respectively. Single crystal EPR spectra further indicate the presence of vanadyl impurity in a single site. Angular variation studies in all the three orthogonal planes confirm that the VO(II) ion has occupied an interstitial position in the lattice. The spin Hamiltonian parameters indicate orthorhombic nature of the impurity. The analysis of powder spectrum also reveals the presence of only one site. The isofrequency plots and powder spectrum have been simulated to confirm the spin-Hamiltonian parameters. The percentage of covalency of metal-oxygen bond has been estimated. The admixture coefficients have also been calculated.*

Keywords *Inorganic complex, vanadyl ion, crystal growth, Electron Paramagnetic Resonance*

I. INTRODUCTION

Electron Paramagnetic Resonance (EPR) yields a great deal of information about the magnetic properties of paramagnetic ion in different host lattices. They also lead to some understanding of the nature of the bonding of the metal ion with its ligands. The EPR studies of paramagnetic ion doped in diamagnetic host yields important information about the magnetic properties of matter, chemical bonding, dynamic interactions of spins with lattice, nuclear moments, the possibility of nuclear alignment and orientational properties of the host lattice [1-4]. Vanadium is one of the transition group elements that have been studied with EPR spectroscopy in divalent, trivalent and tetravalent states. The tetravalent state, V^{4+} exists as VO(II) ion with a single unpaired d-electron. The $3d^1$ configuration of vanadyl ion allows electron paramagnetic resonance to be observed at ambient temperatures [5-7]. The behaviour of vanadyl complex is dictated by the strong V=O bonding and most of the complexes possess C_{4v} symmetry. EPR studies of VO(II) ion in a variety of host lattices have been reported [7]. However, in a recent work both substitutional and interstitial sites for VO(II) impurity are reported. Therefore, interest is developed to ensure the location of the impurity ion and nature of bonding in TPMN single crystal. In this chapter we report the EPR and optical absorption studies of VO(II) ion in TPMN single crystal and deduce the spin Hamiltonian, spin-lattice relaxation time measurement and molecular orbital (MO) coefficients. These MO coefficients are further used to discuss the nature of bonding of VO(II) ion with different ligands in the crystal. Triaquapotassiumbismalonatonickelate is abbreviated here as TPMN.

II. MATERIALS AND METHODS

A. *Preparation of single crystal of VO(II)-doped* $[K(H_2O)_{3/2}]_2[Ni(mal)_2]$

Malonic acid, nickel(II) basic carbonate, potassium hydrogen carbonate were purchased from commercial sources and used as received. $[K(H_2O)_{3/2}]_2[Ni(mal)_2]$ was synthesized by adding solid nickel(II) basic carbonate to an aqueous solution of malonic acid under continuous stirring. The suspension was heated at 40 – 50 °C, until a colourless solution was obtained. This solution was filtered and mixed with an aqueous solution of potassium hydrogen carbonate. The solution was then filtered and doped with five different concentrations of vanadyl sulfate (0.05, 0.1, 0.15, 0.2 and 5.0%). All the crystals were transparent and blue colour with well shaped and separated out on concentrating the solution at room temperature.

B. Characterization

The EPR spectra are recorded at 300 K on a JEOL JES-TE100 ESR spectrometer operating at X-band frequencies, having a 100 kHz field modulation to obtain the first-derivative EPR spectrum. 1,1-Diphenyl-2-picrylhydrazyl (DPPH) with a g-value of 2.0036 is used as a reference for g-factor calculations.

The optical spectrum has been recorded at room temperature using a Varian Cary 5000 ultraviolet-visible (UV-Vis) near-infrared spectrophotometer in the range of 200-1300 nm. In the present investigation, the FT-IR spectra are recorded for doped and undoped materials on a Shimadzu FT-IR-8300/8700 spectrometer, in the frequency range of 4000-400 cm^{-1}. The measurements are made using almost transparent KBr pellets containing fine-powdered samples at room temperature. In the current study, powder XRD studies are carried out for doped and undoped materials on a PANalytical X'pert PRO diffractometer with Cu Kα radiation of wavelength λ = 0.15406 nm, 2θ values between 5-75°, at room temperature.

III.RESULTS AND DISCUSSIONS

A. EPR Studies

A typical EPR spectrum of VO(II) doped in TPMN, when the applied external magnetic field (B) is parallel to crystallographic axis a is given in Fig. 1. It consists of sharp eight resonance lines. Fig. 2 is showing the EPR spectrum recorded in ac plane, when the applied magnetic field (B) is 140° away from the axis c, corresponding to maximum hyperfine separation. The bc plane is almost identical with ac plane. Fig. 3 is showing an EPR spectrum of bc plane, when the applied magnetic field (B) is 50° away from the axis c, corresponding to broad resonances, due to the presence of dipolar-dipolar interaction between the host–guest paramagnetic centres. In single crystal of TPMN doped with VO(II), reasonably sharp EPR lines are observed in all the three crystallographic planes except in few orientations, having dipolar broadening due to the paramagnetic host–impurity interaction. However, the line width of the hyperfine lines of TPMN is found to be larger than those found in the corresponding diamagnetic lattice. This is due to the presence of the Ni(II) ion interaction with the vanadyl ion. Crystal rotations are done in all the three planes and to obtain isofrequency plots, for all the three planes, calculate the spin Hamiltonian parameters (g and A matrices).

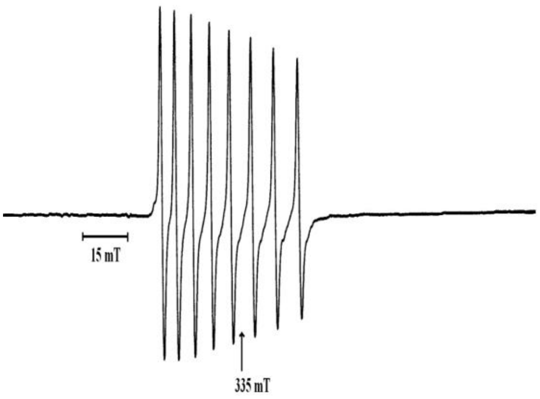

Fig. 1 Single crystal EPR spectrum of VO(II)/TPMN when the applied magnetic field is 50° away from the crystallographic axis a in ab plane. Frequency = 9.05989 GHz.

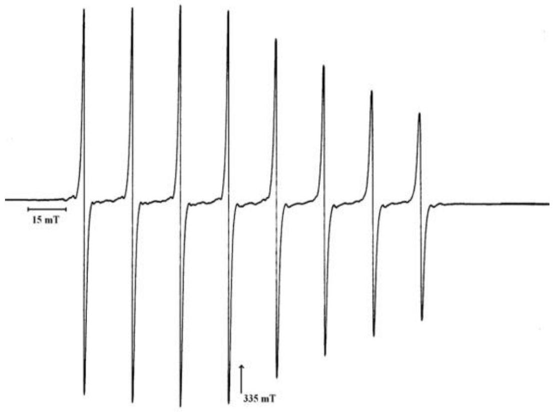

Fig. 2 Single crystal EPR spectrum of VO(II)/TPMN recorded at room temperature when the magnetic field is perpendicular to crystallographic axis c in ac plane. Frequency = 9.06020 GHz.

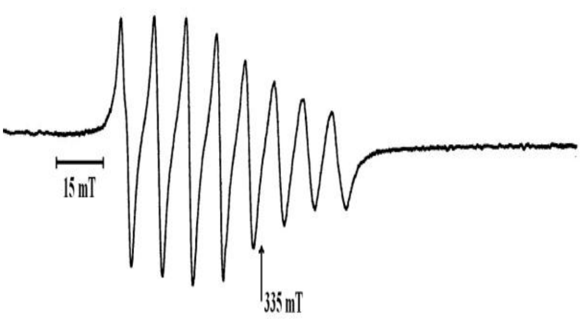

Fig. 3 Single crystal EPR spectrum of VO(II)/TPMN recorded at room temperature when the applied magnetic field is parallel to crystallographic axis c. Frequency = 9.05926 GHz.

B. Calculation of spin-Hamiltonian parameters

In order to obtain spin Hamiltonian parameters, the spectra obtained on the orthogonal planes for VO(II) ion was fitted with the following spin Hamiltonian.

$$\hat{H} = \beta(g_x B_x S_x + g_y B_y S_y + g_z B_z S_z) + A_x S_x I_x + A_y S_y I_y + A_z S_z I_z \qquad (1)$$

The spin Hamiltonian parameters (g and A matrices), calculated using the program EPR-NMR [8], with orthorhombic g and A matrices, are given in Table 1 along with the direction cosines. The direction cosines of the principal g and A are nearly coincident. Since the maxima and minima of g and A variation are obtained at the same angle. For comparison, the direction cosines of Ni –O bonds in TPMN are given in Table 2. These are helpful to predict the location of the paramagnetic impurity. If the direction cosines of g match with one of the direction cosines of Ni – O bonds, a substitution location can be suggested. Otherwise, the impurity might have entered an interstitial location. In other words, one can suggest that the vanadyl ion might have entered the lattice in an interstitial location. The spin Hamiltonian values agree well with the literature values.Using the g and A matrices, the angular variation plots are simulated and it is found to fit with the experimental values. In general, if a paramagnetic system exhibits axial symmetry, the isofrequency plots in ac and bc planes will be identical, whereas the resonance lines in ab plane show invariance. Most of the systems studied so far for VO(II) fall under this category. On the other hand, a slight deviation from axial symmetry makes the resonance lines in ab plane show angular dependence. In the present system, the isofrquency plot in ab plane is angle dependent and isofrequency plots in ac and bc planes are not identical. This immediately confirms that the impurity has rhombic symmetry. In the Figs. 4 – 6, the solid lines indicate the theoretical values and the solid circles indicate the experimental values. A good agreement is obtained.

Table I : The Spin Hamiltonian Parameters Obtained From The Single Crystal Rotations For Vo(Ii) Doped In Tpmn Using Program Epr-Nmr

	Principal values	**Direction cosines**		
		a	b	c
g matrix 1.959 0.006 0.016 1.964 -0.014 1.959	1.979 1.968 1.936	-0.4249 -0.7041 - 0.5689 .	0.5354 -0.7022 0.4692	-0.7298 -0.1052 0.6755
A matrix (mT) 10.87 -3.18 -4.45 9.43 3.85 10.77	6.92 6.02 18.12	0.3459 -0.7198 -0.6017	-0.5429 -0.6767 0.4973	0.7651 -0.1547 0.6249
Powder spectrum $g_\parallel$ = 1.995 $g_\perp$ = 1.973 $A_\parallel$ = 18.31 mT $A_\perp$ = 6.99 mT				

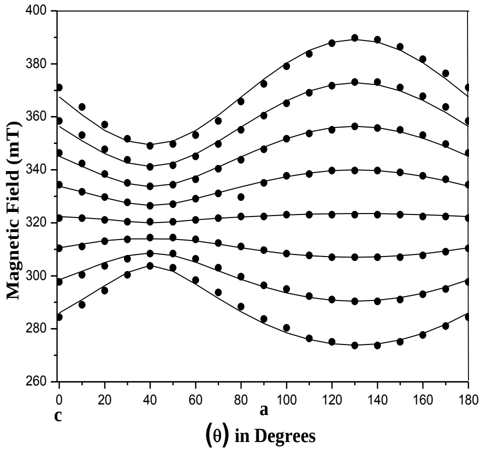

Fig. 4 angular variation of hyperfine lines for c axis rotation of the vo(ii)/tpmn single crystal at room temperature. The solid circles and lines correspond to experimental and theoretical values respectively. Frequency = 9.05989 ghz.

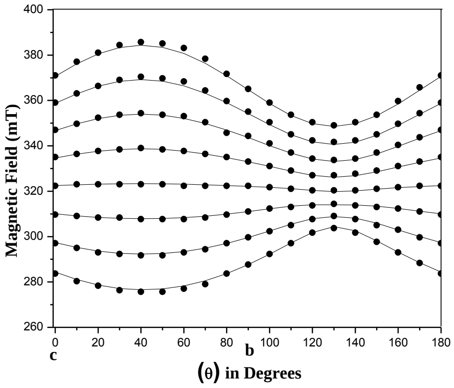

Fig. 5 Angular variation of hyperfine lines for b axis rotation of the VO(II)/TPMN single crystal at room temperature. Frequency = 9.06020 GHz

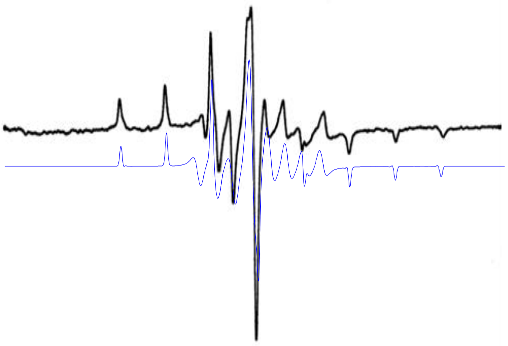

Fig. 6 Angular variation of hyperfine lines for a axis rotation of the VO(II)/TPMN single crystal at room temperature. Frequency = 9.05926 GHz.

C. *Evaluation of MO coefficients*

The spin-Hamiltonian parameters are related to the molecular orbital coefficients by the following expression

$$g_{\parallel} = g_e - 8\beta_1^2\beta_2^2\,\lambda/\Delta E_1\,(b_2 - b_1^*) \qquad (2)$$

$$g_{\perp} = g_e - (2\lambda\beta_2^2\,e_\pi^2/\Delta E_2\,(b_2 - e_\pi^*) \qquad (3)$$

$$A_{\parallel} = -pk - (4/7)\beta_2^2\,p - (g_e - g_{\parallel})P - (3/7)(g_e - g_{\parallel})P \qquad (4)$$

$$A_{\perp} = -pk + (2/7)\beta_2^2 p - (11/14)(g_e - g_{\perp})P \qquad (5)$$

Where β_1^2 , β_2^2 and e_π^2 are molecular orbital coefficients. The isotropic EPR parameters, using the relations

$$g_0 = (1/3)(g_{\parallel} + 2g_{\perp} \qquad (6)$$

$$A_0 = (1/3)(A_{\parallel} + 2A_{\perp}) \qquad (7)$$

Using the above equation, the value of Fermi contact term is calculated. The Fermi contact term is directly related to the isotropic hyperfine coupling and represents the amount of unpaired electron density at the nucleus [9-10]. Combining Eq. (8) and (9) and eliminating κ one can get an expression for β_2^2 in term of the g and A tensor values.

$$\beta_2^2 = (-7/6)[A_{\parallel} - A_{\perp})/P + (g_e - g_{\parallel}) - (5/14)(g_e - g_{\perp})] \qquad (8)$$

Using the above relation β_2^2 is calculated. The deviation of β_2^2 from unity usually represents the degree of admixture of the ligand orbital and increase in the degree of covalency. The present value of β_2^2 = 0.93 clearly indicates that the bonding is nearly ionic and represents poor π bonding of the ligands. The β_2^2 should be equal to unity for a nonbonding orbital in the case of pure $VO(H_2O)_5^{2-}$ complex [11-12].

β_1^2 indicate the delocalisation in the σ system. The in-plane σ bonding varies from compound to compound and decreases from unity as the covalency of the bond increases. From Eq. (6), the value of β_1^2 is calculated and found to be 0.94. β_1^2 values reported in different hosts are collected and are compared with the present value. Considerable contribution of 4s spin density to κ is predicted from the value of β_1^2. The out-of-plane π bonding represented by e_π^2 is calculated from Eq. (7). The calculated value of 0.89 is comparable with many other systems.

D. *Optical studies*

The optical absorption spectrum of vanadyl doped TPMN single crystal is recorded at room temperature is given in the Fig. 10. The spectrum consists of three characteristic bands at 272, 382 and 689 nm, respectively. The first two peaks correspond to d –d transitions in vanadyl. The band at 689 nm corresponds to the transition $b_2 – e_\pi^*$ and the band at 382 nm is due to the transition $b_2 – b_1^*$ levels. The higher energy band at272 nm can be assigned to a charge transfer (CT) band due to the promotion of the electron from the filled bonding level (oxygen orbital) to the nonbonding orbital (d_{xy}) level [13-14].

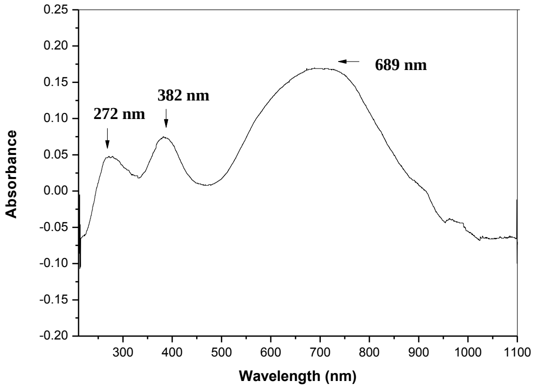

Fig. 7 Optical absorption spectrum of VO(II)/TPMN recorded at room temperature.

IV. CONCLUSIONS

Single crystal vanadyl ion doped TPMN has been studied at room temperature using EPR technique indicates that only one site in the lattice and the number of sites seems to be independent of concentration of the impurity. The spin Hamiltonian parameters indicate that the impurity is rhombically distorted and entered the lattice in an interstitial position. The angular variation plot and the powder EPR spectrum have been simulated, which authenticates evaluated spin Hamiltonian parameters. The optical absorption spectrum at room temperature shows three bands characteristic of vanadyl ions in distorted octahedral symmetry. By using EPR and optical data, admixture coefficients, molecular orbital coefficients, Fermi contact term and dipolar interaction parameter have also been calculated.

REFERENCES

[1] *R*.S. Alger, Electron Paramagnet Resonance: Techniques and Application, Wiley, New York, 1968.

[2] J.A. Weil, J.R. Bolton, Electron Paramagnetic Resonance, Wiley, New York, 1994.

[3] V. Somasekharm, P. Sivaprasad, K. Ramesh, Y.P. Reddy, “Electronic Spectra of VO^{2+} and Cu^{2+} Ions in Rubidium Zinc

Sulphate Hexahydrate", Phys. Scr., vol 33(2), pp. 169 – 172, 1986.

[4] S. Jayakumar, G.K.D. Prasanna Venkatesan, K. Senthilkumaran, J. Poongkothai "Photoluminescence of Reactive Plasma Synthesized ZrO2 Nanoparticles", International Journal of Advance Engineering and Research Development, vol. 4(6), pp. 1-16, 2017

[5] S. Dhanuskodi, A.P. Jeyakumari, "EPR studies of VO^{2+} ions in kainite single crystals", Spectrochim. Acta A, vol. 57(5), pp.971-975, 2001.

[6] S. Deepa, K. Velavan, I. Sougandi, R. Venkatesan, P.S. Rao, "Single crystal EPR study of VO(II) in magnesium potassium phosphate hexahydrate: a case of two substitutional vanadyl ion", Spectrochim. Acta A,vol. 61(11), pp. 2482 – 2487, 2005.

[7] B. Karabulut, A. Tufan, "An EPR and optical absorption study of VO^{2+} ions in sodium hydrogen oxalate monohydrate ($NaHC_2O_4{\cdot}H_2O$) single crystals", Spectrochim. Acta A, vol. 65(4), pp. 742 – 748, 2006.

[8] A.K. Viswanath, "EPR studies of VO^{2+} in single crystals of $ZnSO_4{\cdot}7H_2O$ and certain polycrystalline sulfates", J. Chem. Phys.,vol. 67(8),pp. 3744 – 3757, 1977.

[9] S. Jayakumar, P.V. Ananthapadmanabhan, K. Perumal, T.K. Thiyagarajan, S.C. Mishra, G. Suresh, L.T. Su, A.I.Y. Tok, J. Guo," Nanosize stabilization of cubic and tetragonal phases in reactive plasma synthesized zirconia powders", Materials Chemistry and Physics. vol. 140, pp. 176 – 182, 2013.

[10] F. Clark, R.S. Dickson, O. B. Fulton, J. Isoya, A. Lent, D. G. Mc Gavin, M. J. Mombourquette, R. H. D. Nuttall, P. S. Rao, H. Rinnerberg, W.C. Tennant, J. A. Weil, EPR-NMR Program, University of Saskatchewan, Saskatoon, Canada, 1996.

[11] A. Kasiviswanath, S. Radhakrishna, "EPR and optical properties of impurity centers in low-symmetry crystals", J. Phys. Chem. Solids, vol. 52(1), pp. 227 – 248, 1991.

[12] S. Jayakumar, K. Senthil kumaran, "Synthesis of Spherical Nano ZnO Particles by Modified Precipitation Method for Dye-Sensitized Solar Cell Applications", International Journal of Advanced Research trends in Engineering and technology, vol.5(12,) pp. 424 – 427, 2018

[13] S.G. Sathyanarayana, V.G. Krishnan, G.S. Sastry, "Single crystal ESR of VO^{2+} in hexa-urea aluminium perchlorate", J. Chem. Phys., 65(10), pp. 4181 – 4183, 1976.

[14] A.B.P. Lever, Inorganic Electronic Spectroscopy, 2nd ed, Elsevier, New York, 1986.