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Electron spin resonance of MO^{5+} in $KTiOPO_4$

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The ESR spectra from Mo^{5+} ions in $KTiOPO_4$ single crystal were studied at 77 K. The ESR spectra reveal two different types of paramagnetic centers, one due to Mo^{5+} which occupy the Ti (1) position in the crystal and the other, due to Ti^{3+}, formed at position Ti (2) in the crystal. The principal values and direction cosines of the **g** tensor are reported for the former center. © *2000 Kluwer Academic Publishers*

1. Introduction

Potassium Titanyl Phosphate ($KTiOPO_4$ abbreviated as KTP) is a material with interesting non-linear optical properties and has high conversion efficiency for second harmonic generation [1, 2]. Considerable efforts have been made to clarify the structural origin of the optical response of KTP. The principal structural origin of the large optical nonlinearity in KTP has long been considered to be due to anomalously short Ti-O bonds which give rise to highly distorted TiO_6 octahedra [3]. Electron spin resonance (ESR) studies can furnish information about electric field symmetry produced by the ligands around the metal ion. Hence it is interesting to substitute Ti with some paramagnetic impurity and study the ESR thereof.

Vanadium ion (V^{4+}) doped in KTP has been studied to obtain the interaction of the paramagnetic ion with its environment [4]. It has been shown that V^{4+} ion replacing the Ti^{4+} ion occupies two kinds of sites, namely Ti (1) and Ti (2). ESR study of Fe^{3+} ion in KTP has revealed that it occupies the position of Ti (1) only [5]. The complete substitution of Ti with Sn to obtain the structural origin of the optical properties has been carried out [6]. It is known that the Mo^{5+} ($4d^1$) ion can also be used as a sensitive indicator for studying the local symmetry produced by ligands because it is a simple one electron magnetic system [7, 8]. Moreover the ionic radius of Mo^{5+} (0.66 Å) is comparable with the ionic radius of Ti^{4+} (0.68 Å). Therefore the substitution of Ti by Mo does not make any local distortion. Hence the study of Mo^{5+} in KTP was undertaken with information to this effect at hand. Earlier studies on laser damaged KTP have shown the presence of the Ti^{3+} ($3d^1$) paramagnetic centres [9]. In the present study Ti^{3+} center is found to form as a charge compensator.

2. Crystal structure

KTP is orthorhombic and its space group is $Pna2_1$. Its lattice parameters are $a = 12.814$ Å, $b = 10.616$ Å and $c = 6.404$ Å. It has eight molecules in the unit cell. KTP can be described as a complex three-dimensional network of PO_4 tetrahedra and distorted TiO_6 octahedra with short Ti-O distances. Ti occupies two types of chemically inequivalent sites, Ti (1) and Ti (2) in the lattice. The lattice contains several 'holes' in which the loosely bound K^+ ions are present in two chemically inequivalent sites [3].

3. Crystal growth

In the present study, KTP crystals grown by spontaneous nucleation of high temperature solution were used [10]. The flux employed was $K_6P_4O_{13}$. The growth solution was prepared by mixing the precursors viz., KH_2PO_4, K_2HPO_4 and TiO_2 in proper proportions in a platinum crucible. The dopant molybdenum was added to the solution in oxide form (MoO_3). The concentration of MoO_3 in the starting composition is about 1.0 mole %. The crucible was then loaded into a furnace preheated to 1050 °C. After an equilibrium time of 15 hours, the temperature was brought down to the growth temperature of 950 °C. The solution was then cooled at a rate of 0.3 °C/hour down to 925 °C. The solution was then cooled at a rate of 1 °C/hour. After the growth regime, the solution was then cooled at a faster rate to room temperature. The crystals formed on the surface of the solidified solvent were removed by bleaching in hot water.

4. Experimental

ESR measurements were performed using a Varian E-112 X-band spectrometer with 100 kHz field

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modulation. The measurements were carried out at 77 K. The ESR spectra were recorded by rotating the crystal at 10° intervals in three mutually perpendicular planes. The x-axis was chosen to be parallel to the crystallographic c-axis, the y and z-axis parallel to the a and b-axes respectively. The g-value of DPPH (2.0036) was used as an internal standard for evaluating the g parameters. Temperature variation studies were performed using a Varian E-257 variable temperature accessory.

5. Results and discussion

Molybdenum has two types of isotopes, the even isotopes, $^{94,\,96,\,98,\,100}$Mo with nuclear spin $I = 0$ (abundance 75%) and the odd isotopes $^{95,\,97}$Mo with a nuclear spin $I = 5/2$, the nuclear moments differing by only 2%. Hence the ESR spectrum of Mo^{5+} (4d^1 electron) should consist of a strong line at the centre arising due to the even isotopes of Mo and six hyperfine lines arising from the interaction of the 4d^1 electron with the nuclei of odd isotopes. Due to the similar magnetic moments of ^{95}Mo and ^{97}Mo, the hyperfine lines due to these two isotopes will overlap.

Fig. 1 shows the observed ESR spectrum of KTP single crystal, when the magnetic field is parallel to the c-axis of the crystal. The spectrum revealed six doublets along with a central intense doublet and a triplet having $1:2:1$ intensity pattern. The central intense doublet is due to $^{94,\,96,\,98,\,100}$Mo isotopes having $I = 0$. The six doublets arise due to $^{95,\,97}$Mo isotopes having $I = 5/2$. The doublets formation is due to the interaction of the Mo^{5+} with a single ^{31}P nucleus having $I = 1/2$. When the crystal is rotated away from the crystallographic c-axis each doublet is further split into two more doublets. This further splitting is due to the two physically equivalent but magnetically non-equivalent Mo^{5+} ion sites.

The paramagnetic center which gives rise to a triplet with intensity ratio $1:2:1$ is assigned to the titanium ion which is in the Ti^{3+} state (3d^1 electron) [9]. Ti has even isotope with abundance 87%, odd isotope ^{47}Ti with $I = 5/2$, abundance 7.75%, and another odd isotope ^{49}Ti with $I = 7/2$, abundance 5.5%. Hence it is difficult to see the individual ESR lines due to odd Ti isotopes separately. Ti^{3+} formation is to take care of the charge compensation within the lattice while doping with molybdenum. Comparing the principal g-values of Mo^{5+} centers obtained from this work with those of Ti^{3+} reported by Roelofs [9], one can see that they are very close to each other. Experimentally it means that in this study, the resolved lines of Ti^{3+} are seen only in a specific orientation of magnetic field, such as the magnetic field is along the c-axis. Any direction away from the c-axis allows the intense lines of Mo^{5+} to overlap with the weak lines of Ti^{3+} making the analysis extremely difficult. Hence the detailed analysis for Ti^{3+} line is not performed.

The spin Hamiltonian appropriate to a Mo^{5+} ion in KTP can be expressed as [8].

$$\mathcal{H} = \beta \mathrm{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} + \mathbf{S} \cdot \mathbf{A}^{\mathrm{p}} \cdot \mathbf{I}^{\mathrm{p}} \qquad (1)$$

where **A** is the hyperfine tensor due Mo nuclei with $I = 5/2$, $\mathbf{A}^{\mathrm{p}}$ is the superhyperfine tensor due to phosphorus nuclei. The other symbols have their usual meaning.

Isofrequency plot of Mo^{5+} ions having nuclear spin $I = 0$, when the magnetic field is in the ab plane is shown in the Fig. 2. The hyperfine lines from the relatively low abundant magnetic nuclei of Mo having spin $I = 5/2$ are very weak and hence it is not possible to plot their angular variation.

The $\mathbf{g}^2$ matrices were calculated by least square fitting procedures [11]. The principal values and direction cosines were calculated by Jacobi method. The principal values of the **g** tensor and the direction cosines are given in the Table I. The powder spectra is used to determine the principal A values of Mo since the spectra

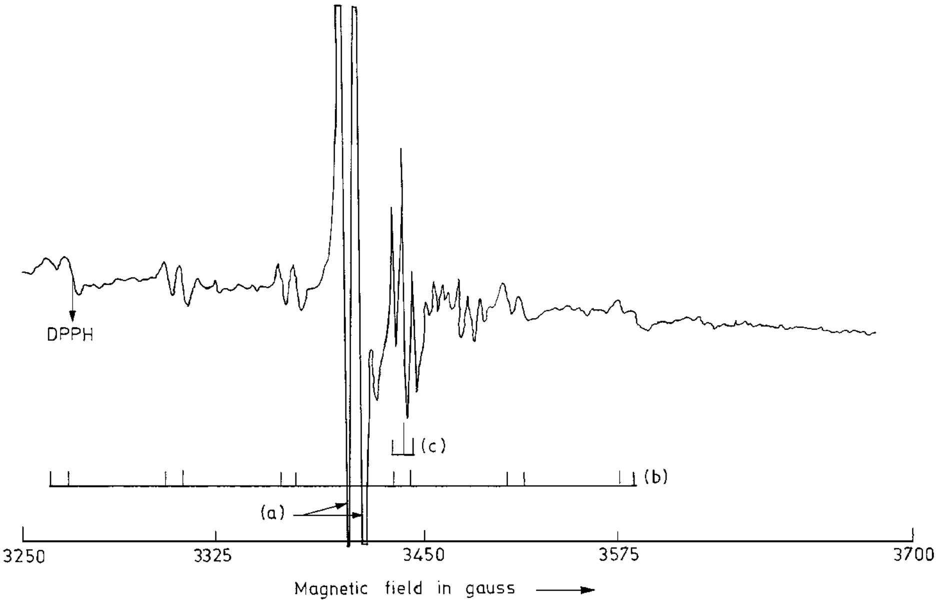

Figure 1 ESR spectra of Mo doped KTP in the X-band at 77 K when the magnetic field is along the c-axis. (a) Due to Mo^{5+} with Mo isotopes $I = 0$. (b) Due to Mo^{5+} with Mo isotopes $I = 5/2$. (c) Due to Ti^{3+} center with two equivalent phosphorus nucleus of $I = 1/2$ (frequency $\nu = 9.01$ GHz).

TABLE I The principal values of the **g** tensor for Mo^{5+} in KTP at 77 K and corresponding direction cosines relating the principal axes to the crystallographic axes

	Direction cosines		
Principal value	*a*	*b*	*c*
$g_{xx} = 1.868 \pm 0.002$	0.9662	0.2498	−0.0627
$g_{yy} = 1.885 \pm 0.002$	−0.1706	0.8031	0.5708
$g_{zz} = 1.905 \pm 0.002$	0.1930	−0.5409	0.8186

TABLE II Calculated bond lengths (Å) between Ti and P atoms in $KTiOPO_4$ crystals [3]

Ti (1)	–	P (1)	=	3.3664
Ti (1)	–	P (2)	=	5.9775
Ti (2)	–	P (1)	=	3.2503
Ti (2)	–	P (2)	=	3.2637

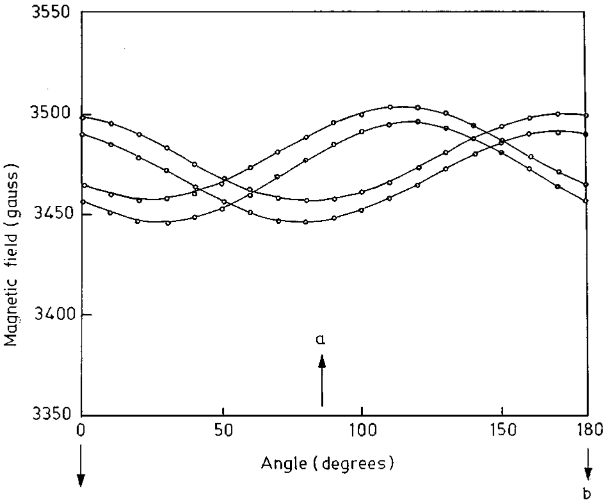

Figure 2 Isofrequency plot of Mo^{5+} center corresponding to nuclear $I = 0$, when the magnetic field is in the *ab* plane.

recorded on single crystals do not reveal all six doublet at all angles. The principal values obtained from the powder spectra are found to be axially symmetric, the values are $|A_{\|}| = 88 \pm 2G$ and $|A_{\perp}| = 43 \pm 2G$. From the main doublet it is observed that superhyperfine splitting, $|A^{p}|$ is almost isotropic, with a value of $A^{p} = 10 \pm 2G$.

From Table II, it can be seen that the phosphorus atoms (P (1) & P (2)) are situated nearly equidistant from Ti (2) [3]. From this, it could be inferred that the triplet spectra (Fig. 1c) arise due to interaction of the above two equivalent phosphorus nuclei (I value of phosphorus nucleus is 1/2) with Ti^{3+} ion ($3d^1$ electron) and also that this ion (Ti^{3+}) is forming at the Ti (2) site. With respect to Ti (1), one of the phosphorus nuclei (P (2)) is situated quite far compared with the other. This explains the doublet formation of the Mo lines which arises due to the interaction between Mo^{5+} ion and phosphorus nucleus that is situated closer (P (1)). It can also infer that the Mo^{5+} ($4d^1$ electron) ion occupies the Ti (1) site. Since Mo^{5+} is gets substituted only at Ti (1) sites, four sets of doublets are possible in general orientation. When the magnetic field is applied in the crystal principal plane *ab*, *bc*, and *ca* (*yz*, *zx* and *xy* respectively), four sets merge to become two sets and when magnetic field is along crystallographic axes *a*, *b* and *c* the lines merge to become one set.

The Mo^{5+} ion in KTP replaced for Ti (1) is surrounded by a distorted oxygen octrahedra. The distorted oxygen ligands (low symmetry ligand field) lifts all the degeneracies of d-orbitals (t2g & eg). The ground state wave function is most probably d_{xy} orbital or linear combination of d_{xz} and d_{yz}. It is assumed that the ground state is d_{xy}. The split component of this orbital (t2g) can be calculated from the principal g values by using the following Equation 7.

$$g_{xx} = 2.0023 - \frac{2\lambda}{\Delta E_1} \tag{2a}$$

$$g_{yy} = 2.0023 - \frac{2\lambda}{\Delta E_2} \tag{2b}$$

$$g_{zz} = 2.0023 - \frac{8\lambda}{\Delta E_3} \tag{2c}$$

where ΔE_1, ΔE_2 and ΔE_3 are energy splitting between the ground state orbital and d_{xz}, d_{yz} and $d_{x^2-y^2}$ orbital state respectively. We estimate the energy splitting from the observed g values using the spin-orbit coupling constant for the free ion, $\lambda = 1013\ \text{cm}^{-1}$ [12] and assume reduction to $900\ \text{cm}^{-1}$ due to the covalency effect [7]. The calculated values are $\Delta E_1 = 19823\ \text{cm}^{-1}$, $\Delta E_2 = 15679\ \text{cm}^{-1}$ and $\Delta E_3 = 12679\ \text{cm}^{-1}$. This indicates a large distortion from the cubic symmetry.

6. Conclusion

The ESR of Mo doped KTP have been studied. Two types of paramagnetic centers were observed, Mo^{5+} and Ti^{3+}. The Mo^{5+} is situated at Ti (1) site and Ti^{3+} is forming at Ti (2) site. The principal values of the **g** tensor and their direction cosine of Mo^{5+} have been evaluated. These principal g-values reveal the tetragonally distorted octahedral symmetry of Mo^{5+} ion.

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