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Gel growth and characterization of pure and vanadyl-doped strontium tartrate tetrahydrate single crystals

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Pure and vanadyl-doped single crystals of $SrC_4H_4O_6 \cdot 4H_2O$ ($SrTr \cdot 4H_2O$) were grown by controlled diffusion in silica gel. The crystals were characterized by EPR and electronic absorption techniques. The angular variation EPR spectra showed that the VO^{2+} ion has a fixed orientation in the lattice. The g and A tensors and their direction cosines were evaluated from the EPR analysis. The above parameters for the observed sites were analysed assuming a spin Hamiltonian corresponding to a tetragonal symmetry. Electronic absorption studies carried out at 300 K as well as at 80 K showed three characteristic absorption bands at 12 500, 13 201 and 18 348 cm^{-1} which were assigned to crystal field (*d–d*) transitions and the site symmetry of the ion has been estimated to be tetragonal. To confirm the ascribed transitions, the band positions were calculated by solving the energy expressions corresponding to the tetragonal symmetry and compared with the observed band positions. The crystal field parameters (*Dq*) and tetragonal distortion parameters (*Ds* and *Dt*) were obtained from the best fit of the observed and calculated band positions. The EPR and electronic spectral results showed that the VO^{2+} ion has occupied the interstitial site having C_{4V} symmetry.

1. Introduction

Some pure and impurity-doped tartrate compounds have been characterized by electron paramagnetic resonance (EPR) and electronic absorption studies [1–7]. The ferroelectric phase transitions exhibited by some of these compounds [5–7] have been investigated using 3d transition metal ions as impurity probes and EPR as an experimental tool [6, 7]. Among the 3d transition metal ions, the VO^{2+} is the most stable molecular cation and it can exist in different complex forms [8]. The VO^{2+} ion is found to have random orientation in some single crystals and vanadyl complexes [9–11]. Also it is found to have fixed orientations, forming different coordinations in different lattices with the oxygen and other ligands [12–15]. From the electronic absorption spectra, one can obtain a better understanding of the structure of the complexes and draw further information about the site symmetry of the ion [16, 17]. Hence, the present work is aimed at (1) the growth of pure and VO^{2+} ion-doped $SrTr \cdot 4H_2O$ single crystals by controlled diffusion in silica gel, and (2) locating and establishing the site symmetry of the impurity ion in the lattice using the EPR and electronic absorption techniques.

2. Crystal growth and structure

Most of the tartrate compounds are insoluble in water and decompose before melting. Hence, single crystals of such type of compounds cannot be grown by either slow evaporation or melt techniques, but can be grown by silica gel method. Hence, the gel method has been used to grow the pure and impurity (VO^{2+}) doped $SrTr \cdot 4H_2O$ single crystals. Gels were prepared by mixing one molar solution of tartaric acid and sodium metasilicate solution (specific gravity 1.04) with proper pH value. After mixing, the solution was allowed to set for about 24 h in pyrex glass test tubes. After setting the gel, 1 M $SrCl_2$ (feed) solution was poured on the top of the gel, which diffuses into

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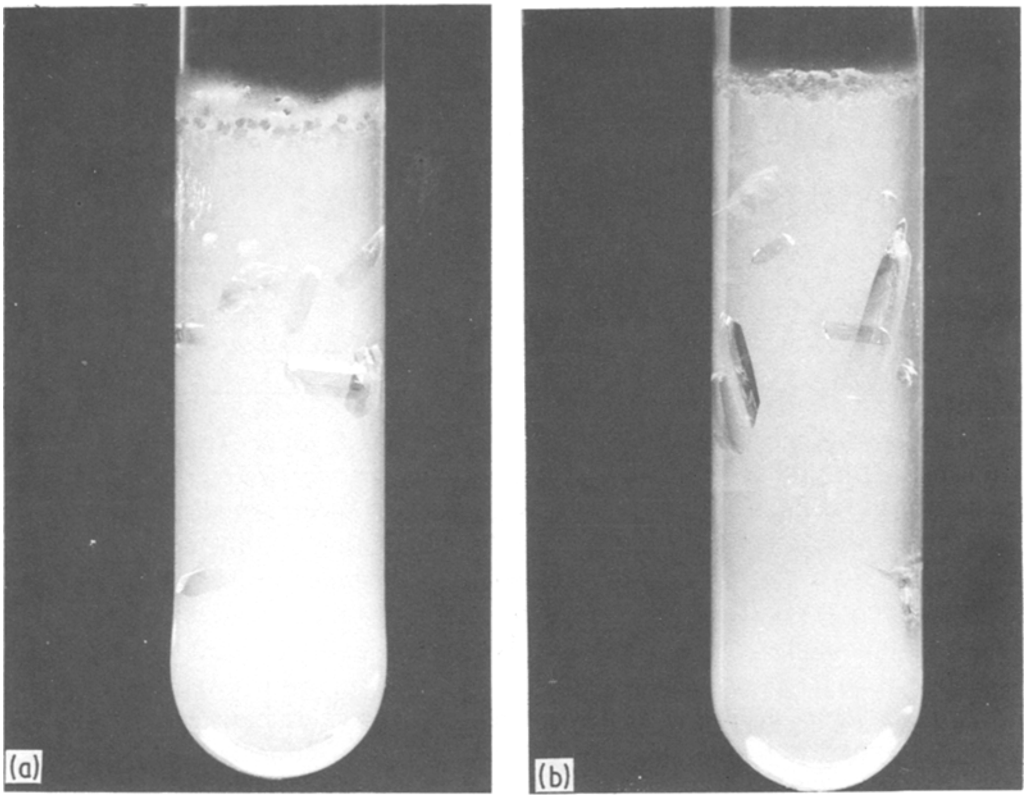

Figure 1 Single crystals of $SrC_4H_4O_6 \cdot 4H_2O$ growth in silica gel. (a) Pure single crystals, (b) VO^{2+} ion-doped single crystals.

the tartaric acid set gel. In order to obtain the impurity-doped crystals, 0.1 to 1.0 mol wt % vanadium chloride solution was added to the feed solution. In the present case, good quality pure and impurity doped $SrTr \cdot 4H_2O$ single crystals were obtained for a gel pH between 5.0 to 5.5. The impurity concentration was found to change the growth rate. The best batch of pure and impurity-doped $SrTr \cdot 4H_2O$ single crystals are shown in Fig. 1. Single crystals were checked by X-ray diffraction and the crystallographic axes identified by taking oscillation photographs.

The $SrTr \cdot 4H_2O$ crystal belongs to orthorhombic space group $P2_12_12_1$ [18]. The unit cell of this compound contains four molecules and has dimensions $a = 0.948$ nm, $b = 1.096$ nm, and $c = 0.946$ nm. According to structure analysis, the divalent cation (Sr^{2+}) has eight-fold coordination with the eight oxygen ligands forming a highly distorted dodecahedron [19]. Of these ligands six are provided by four tartrate ions, i.e. 01, 03, 06C, 04C, 02B and 05B and the other two belong to the two water molecules 08C and 010C. The available interstitial site in the lattice is formed by the following six oxygen ligands, 03C, 04C, 010C, 07C, 06C and 01C. These atoms form an approximate octahedron and the distances from the interstitial centre to each oxygen ligand are also reported [19].

3. Experimental techniques

The EPR spectral measurements were performed on a Varian E-4 Spectrometer, operating at X-band frequencies with a 100 kHz field modulation. The $SrTr \cdot 4H_2O:VO^{2+}$ crystals were mounted at the end of the single circle goniometer which can fit into the EPR cavity operating at TE_{102} mode. The operating frequency was obtained by magnetic field calibrations using the resonance line due to DPPH, which was taken as a standard g-marker ($g = 2.0036$).

A Cary-14 spectrophotometer was used for recording the electronic absorption spectra. A cold finger type cryostat was used for recording the absorption spectra at low temperature (80 K). All EPR and electronic absorption spectral data were analysed on an IBM 370/155 computer.

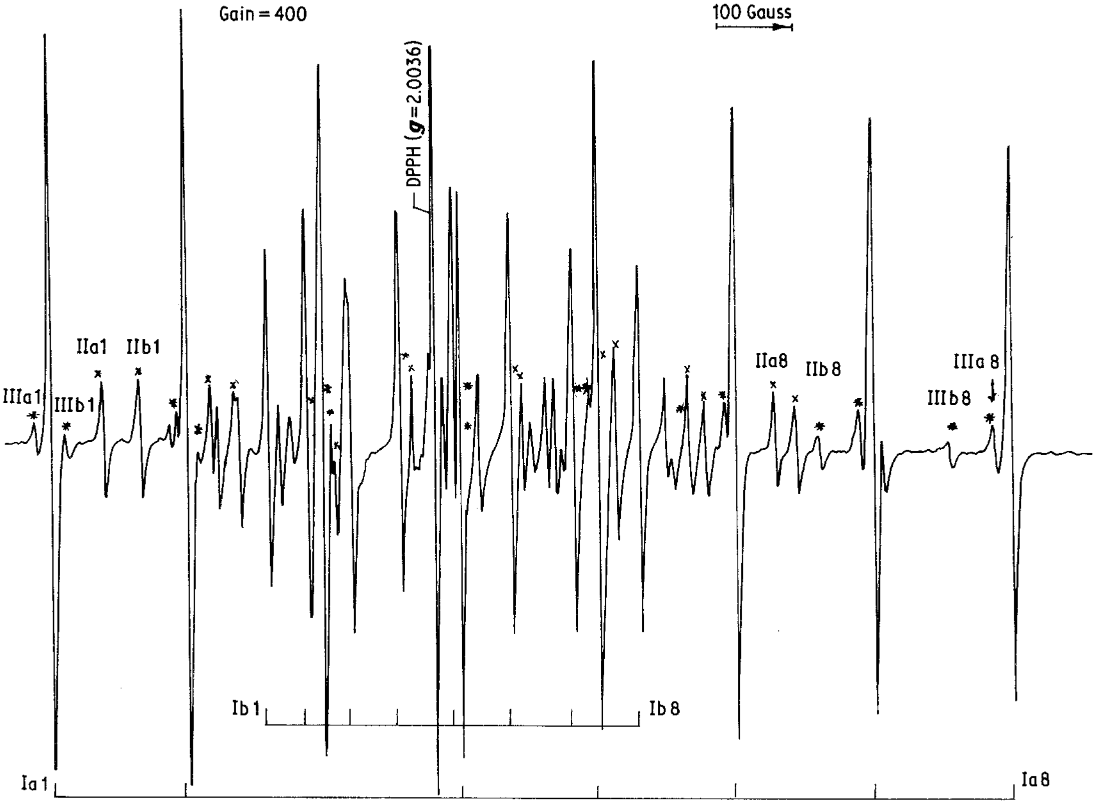

Figure 2 EPR spectrum of $SrC_4H_4O_6 \cdot 4H_2O:VO^{2+}$ crystals with H 50° away from the b-axis.

4. Electron paramagnetic resonance studies

Fig. 2 shows a typical EPR spectrum of a VO^{2+} ion in the $SrTr \cdot 4H_2O$ lattice recorded with the magnetic field (H) 50° away from the b-axis in the ab plane. As can be seen in the figure, there are six sets of eight lines indicated as sites Ia, Ib, IIa, IIb, IIIa and IIIb. Out of these only the sites Ia and Ib are prominent in intensity. The VO^{2+} ion belongs to the $3d^1$ system having a single unpaired electron in the outermost orbital. The above observed eight lines in each group are due to the interaction of a single unpaired electron with the vanadium nuclear spin ($I = 7/2$). The observed six sites are due to the different distinguishable vanadyl complexes present in the lattice. The difference in the intensity of the hyperfine (hf) lines of different sets indicate the difference in the population of VO^{2+} ion in different orientations in the lattice. The above six sites merged into three sites when spectra were recorded with H parallel to three crystallographic a-, b- and c-axes. A typical spectrum recorded with $H \| b$-axis is shown in Fig. 3, where the three sites are indicated as Sites I, II and III. In order to know the behaviour of the VO^{2+} ion in the lattice, the angular variation of EPR spectra was recorded for every 10° of rotation in three planes. The plots of variation of magnetic field position of the hf lines with the angle θ, in all the three planes were drawn, and a typical plot is shown in Fig. 4. In all three planes, only in a few orientations, the sites IIa, IIb, IIIa and IIIb were observed. In order to avoid ambiguity in analysing the EPR spectra, only two prominent intensity sites Ia and Ib were considered and the angular variation plots drawn only for these two sites (Fig. 4). As can be seen in the figure, the hf lines are highly angular dependent and indicate that the VO^{2+} ion has fixed orientations in the lattice.

From the experimentally observed spectra, the g and A parameters were calculated for all orientations in the three planes. Least square fit and the diagonalization procedures [20, 21] have been used to determine the principal g_{xx}, g_{yy}, g_{zz}, A_{xx}, A_{yy}, A_{zz} parameters and their direction cosines with respect to three crystallographic axes, which are given in Table I. The evaluated principal g and A parameters were fitted to the spin Hamiltonian corresponding to the tetragonal symmetry.

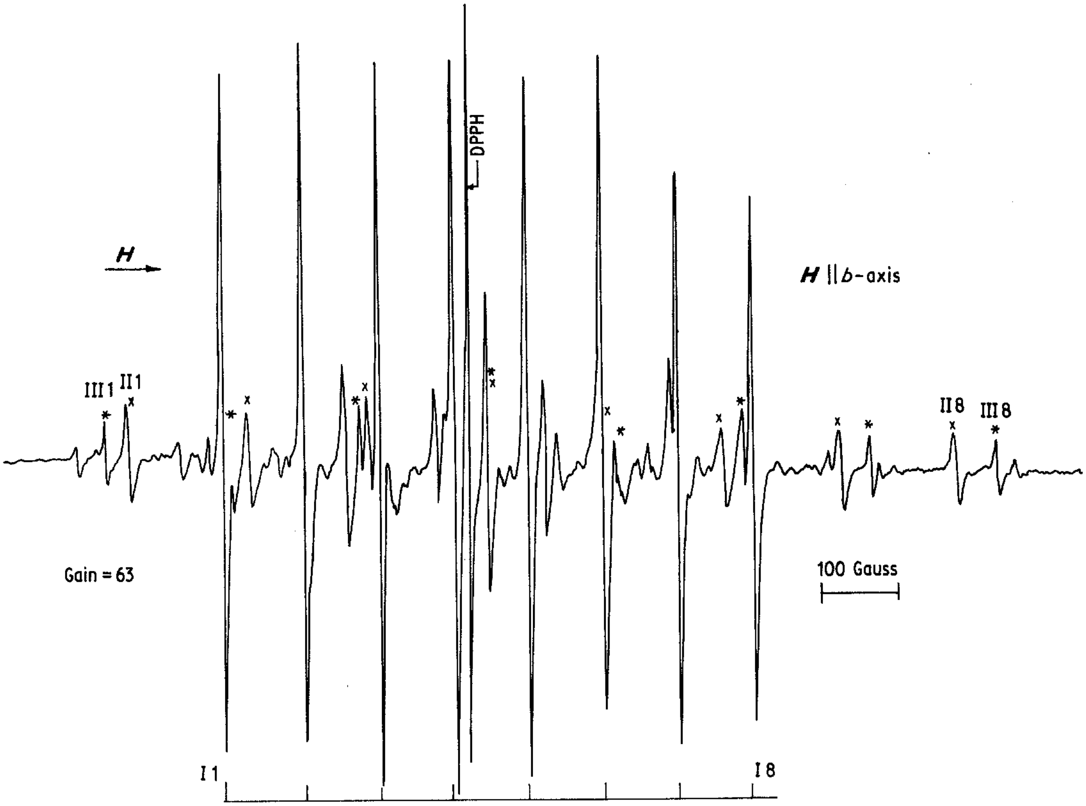

Figure 3 EPR spectrum of $SrC_4H_4O_6 \cdot 4H_2O$ crystals doped with VO^{2+} ion recorded when the magnetic field is parallel to *b*-axis.

$$\begin{aligned}\mathscr{H} &= g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y)\\ &\quad + A_{\parallel} I_z S_z + A_{\perp}(I_x S_x + I_y S_y)\end{aligned}$$

A fine powder sample was prepared by crushing single crystals of $SrTr \cdot 4H_2O:VO^{2+}$ and the EPR spectrum was recorded at 300 K (Fig. 5). The spectrum consists of eight parallel and eight perpendicular hf lines which are indicated as A_1 to A_8 and B_1 to B_8 respectively. The principal $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$ and $A_{\perp}$ parameters have been calculated directly from Fig. 5, and are given in Table II. The above parameters compare well with those obtained from the single crystal data.

4.1. Discussion

According to the crystal structure, the site symmetry of the Sr^{2+} ion is the distorted dodecahedron. If the VO^{2+} ion enters the Sr^{2+} site, the low symmetry effects should reflect on the EPR spectrum as well as on principal *g* and *A* parameters, but the evaluated principal *g* and *A* parameters from the single crystal spectra as well as the polycrystalline spectrum showed tetragonal crystal field symmetry. In addition, the calculated direction cosines did not coincide with the direction cosines obtained from the EPR single crystal data. Therefore, the observed EPR spectra may not be due to the

TABLE I Spin Hamiltonian (*g* and *A*) parameters and their direction cosines for the two sites of VO^{2+} ion in $SrTr \cdot 4H_2O$ lattice

Site	*g*	*A*	Direction cosines		
			a	*b*	*c*
Site I	$g_{zz} = 1.9467 \pm 0.0002$	$A_{zz} = 186 \pm 3G$	0.7658	−0.3323	0.5515
	$g_{yy} = 1.9963 \pm 0.0002$	$A_{yy} = 68 \pm 3G$	0.1019	0.9080	0.4063
	$g_{xx} = 2.0094 \pm 0.0002$	$A_{xx} = 72 \pm 3G$	−0.6349	−0.2550	0.7292
	$g_{zz} = 1.9423 \pm 0.0002$	$A_{zz} = 186 \pm 3G$	0.7161	−0.4361	0.5449
	$g_{yy} = 1.9990 \pm 0.0002$	$A_{yy} = 69 \pm 3G$	0.2588	0.8910	0.3729
	$g_{xx} = 2.0023 \pm 0.0002$	$A_{xx} = 70 \pm 3G$	−0.6482	−0.1260	0.7509

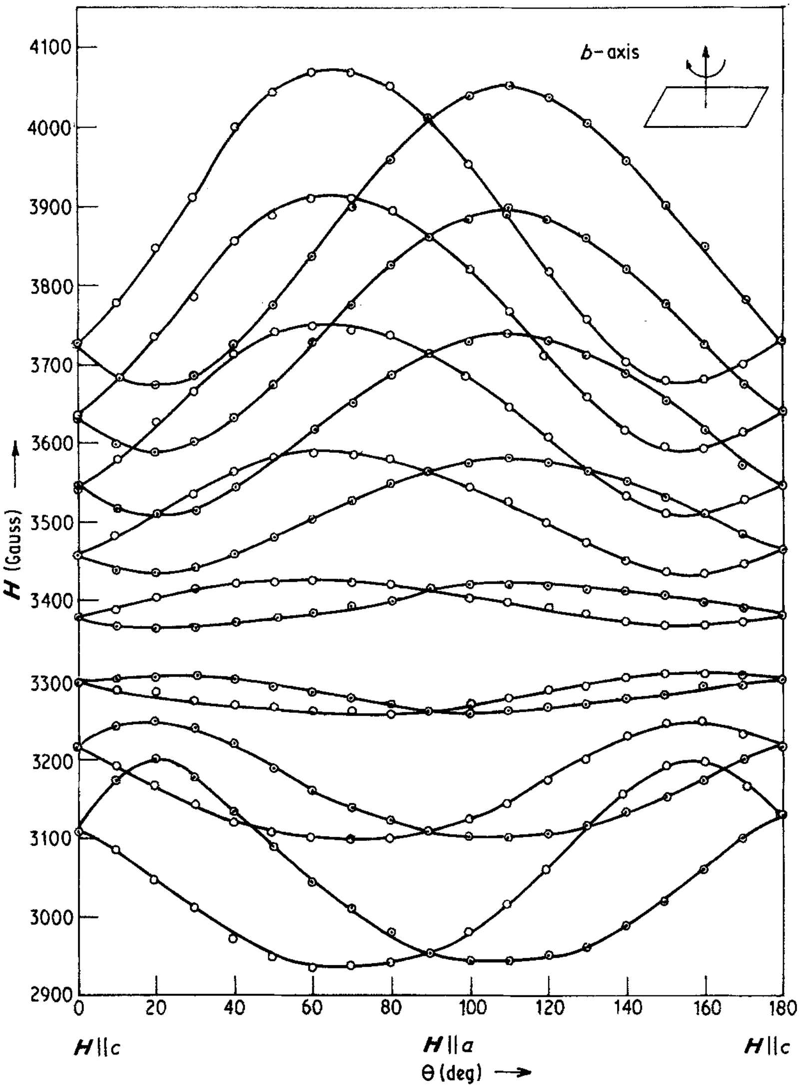

Figure 4 Angular variation of hyperfine lines of site Ia and site Ib in the ac-plane of $SrTr \cdot 4H_2O:VO^{2+}$ crystals.

substitution of the VO^{2+} ion in an Sr^{2+} site, which is also confirmed from the previous studies [4, 22, 23]. Hence, the above EPR spectra were analysed assuming an interstitial site for the VO^{2+} ion in the lattice. There are four interstitial sites available which are formed by six oxygen ligands having an approximately octahedral symmetry. If the VO^{2+} ion enters the interstitial site, the EPR spectrum should show four sets of eight hf lines in any arbitrary orientation. Since the EPR spectrum was recorded in different orientations about the three crystallographic axes, only two of the four symmetry related sites were observed in any orientations and shown in Fig. 2. Hence, the observed six sites are effectively due to the orientation of VO^{2+} ion in three directions. This is the reason why the evaluated principal parameters for Sites Ia and Ib are equal and also the hf lines corresponding to the above sites merged only when the EPR spectra were recorded with H parallel to the crystallographic axes, as shown in Fig. 4. In order to avoid ambiguity, we have analysed only two prominent sets of eight hf lines. The other four sites merged and showed two sets of eight hf lines when the spectra were recorded with H parallel to the crystallographic axes (Fig. 3). These two sites also might be due to the orientations of V–O bond along two different ligand directions available

TABLE II Principal g and A parameters obtained from the polycrystalline $SrTr \cdot 4H_2O:VO^{2+}$ sample

$g_{zz} = g_{\parallel} = 1.9433$	$A_{zz} = A_{\parallel} = 185.43$
g_{yy}, g_{xx} $= g_{\perp} = 1.9902$	A_{yy}, A_{xx} $= A_{\perp} = 68.5$

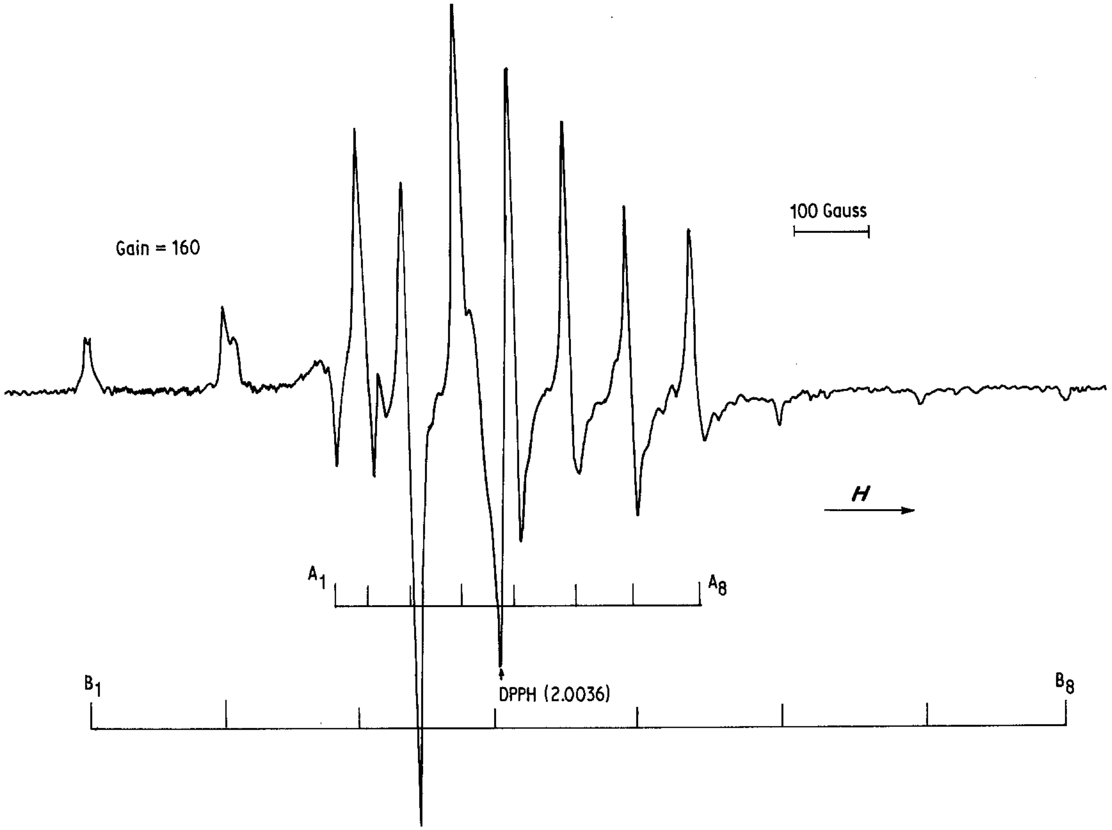

Figure 5 EPR spectrum of polycrystalline SrTr·4H$_2$O:VO^{2+} sample recorded at 300 K.

in the lattice. The exact V–O orientations could not be assigned because the complete crystal structure data are not available. For further confirmation of the site symmetry of the VO^{2+} ion in the lattice, electronic absorption studies were carried out.

5. Electronic absorption studies

Fig. 6 shows the electronic absorption spectrum of the VO^{2+} ion in the SrTr·4H$_2$O lattice recorded at 300 K (Curve 1) and 80 K (Curve 2) in the region 7500 to 25 000 cm^{-1}. At both temperatures, the spectrum showed three absorption bands at 12,500, 13 201 and 18 348 cm^{-1}. On cooling down to 80 K, there was little change in the intensity of the absorption bands and there was also no additional structure. This shows that the observed bands are not vibronic in nature and are purely due to the electric dipole transitions.

In order to interpret the observed absorption spectrum to the particular symmetry, one should have sufficient information about the host lattice. If the VO^{2+} ion enters the Sr^{2+} site then the site symmetry of the ion will be less than C$_{4v}$ in which case one should obtain four absorption bands. On the other hand, the observed absorption spectrum showed only three bands. Similarly, the g and A parameters evaluated from the EPR analysis did not show the low symmetry effects and showed only tetragonal symmetry. Hence, the possibility of the VO^{2+} ion entering the substitutional Sr^{2+} site in the lattice was ruled out. Now one has to look at the next alternative site available in the lattice. Suppose the VO^{2+} ion enters the interstitial site formed by six oxygen ligands. The site symmetry of the ion will be distorted octahedral (tetragonal) symmetry. In this case, one may expect to obtain three absorption bands. Hence, the above absorption spectrum has been analysed assuming the tetragonal crystal field symmetry for the VO^{2+} ion in the lattice.

In the free ion state, the single electron gives rise to the ^{2}D state. When the ion is in octahedral symmetry, the above level will split into $^2T_{2g}$ and ^2E_g levels of which $^2T_{2g}$ is the lower one. These levels can split further when the symmetry of the ions is lower than octahedral. In tetragonal symmetry (C$_{4v}$), the $^2T_{2g}$ splits into $^2B_2$ and $^2E_2$,

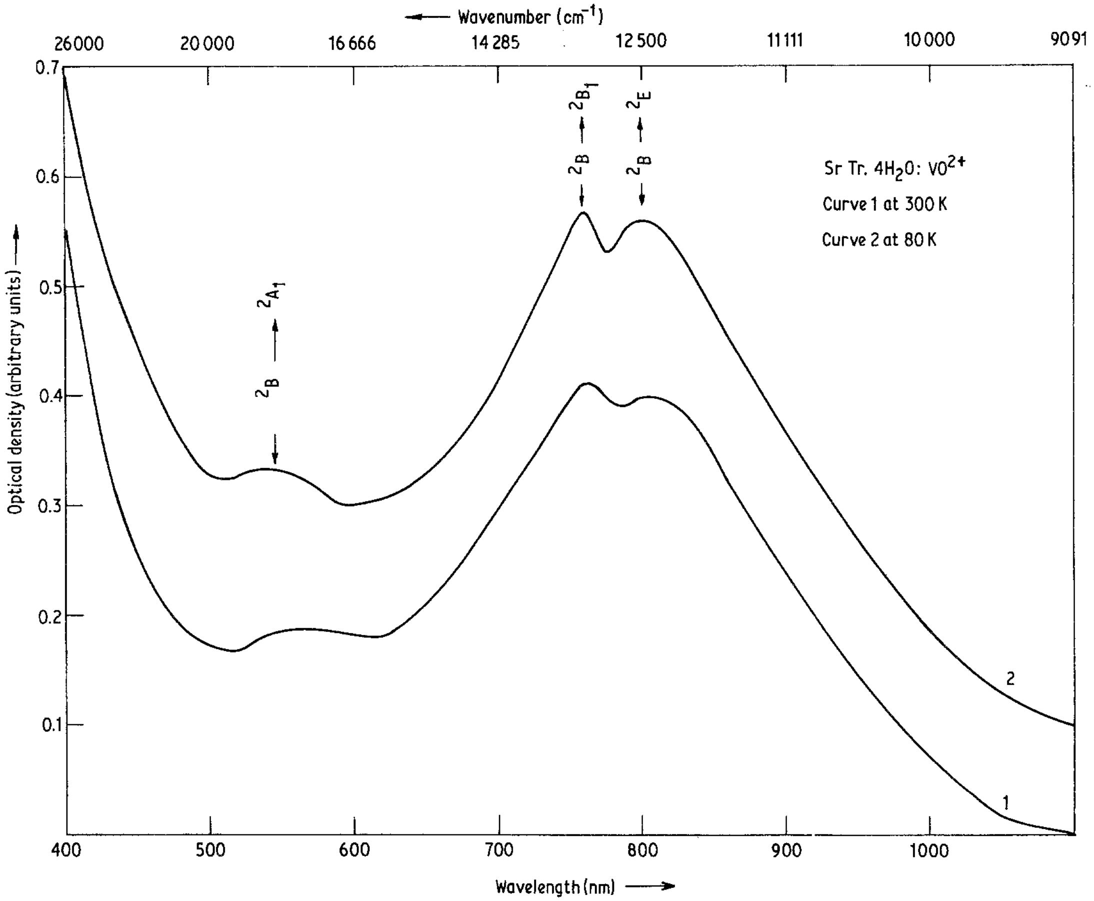

Figure 6 Electronic absorption spectrum of VO^{2+} ion in $SrTr{\cdot}4H_2O$ lattice recorded in the region 400 to 1100 nm at two temperatures: Curve 1 at 300 K; Curve 2 at 80 K.

whereas ^2E_g splits into two non-degenerate $^2B_1$ and $^2A_1$ levels. In this case, the $^2B_2$ is the lowest one having a single unpaired electron.

Assuming the tetragonal crystal field symmetry for the VO^{2+} ion, the observed spectrum has been interpreted in terms of available theories, i.e. molecular orbital theory (MO, BG) and revised crystal field theory (CFT, OSM) [17, 24]. Based on the above MO and CFT schemes, all three bands are assigned to d–d transitions, as given in Table III.

In order to confirm the above assigned transitions, band positions were calculated by solving the energy matrices using the diagonalization procedure and compared with the experimentally observed band positions. For the best fit of the experimentally observed and calculated band positions, the following crystal field parameter (Dq) and tetragonal distortion parameters (Ds and Dt) were evaluated. $Dq = 1305\,\text{cm}^{-1}$, $Ds = -2512\,\text{cm}^{-1}$ and $Dt = 987\,\text{cm}^{-1}$. Table III gives the observed and calculated band positions along with their assignments of transitions in terms of MO and revised crystal field theories. The evaluated

TABLE III Band positons and assignments of transitions of VO^{2+} ion in $SrTr{\cdot}4H_2O$ lattice: $Dq = 1305\,\text{cm}^{-1}$; $Ds = -2521\,\text{cm}^{-1}$; $Dt = 987\,\text{cm}^{-1}$

Serial No.	Band Positions		Assignments	
	Observed band positions (cm^{-1})	Calculated values (cm^{-1})	MO (BG) scheme in C_{4v} symmetry	Crystal field theory (OSM) in C_{4v} symmetry
1	12500	12498	$^2B_2 \rightarrow {}^2E$	$d_{xy} \rightarrow d_{xz}, d_{yz}$
2	13201	13205	$^2B_2 \rightarrow {}^2B_1$	$d_{xy} \rightarrow d_{x^2-y^2}$
3	18348	18354	$^2B_2 \rightarrow {}^2A_1$	$d_{xy} \rightarrow d_{z^2}$

parameters from EPR and electronic absorption studies are well comparable with the reported parameters for the VO^{2+} ion in different low symmetry crystalline field environments [12, 13, 17, 25].

6. Conclusions

Pure and impurity-doped $SrTr \cdot 4H_2O$ single crystals were grown by controlled diffusion in silica gel. The crystal structure of this compound was confirmed by X-ray diffractometry. To find the presence of the impurity (VO^{2+} ion) and its location in the lattice, EPR and electronic absorption techniques have been used. By analysing the above spectral data, the site symmetry of the VO^{2+} ion is estimated to be the C_{4v} (tetragonal) and it is found to enter the interstitial site in the lattice.

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