Effect of vanadyl doping on relative intensities of factor group split Raman bands in potassium oxalate monohydrate

NAVIN PANT¹, A L VERMA^{1,*} and S D PANDEY²

¹Department of Applied Physics, Amity Institute of Applied Sciences, Amity University, Sector-125, Noida 201313, India

²P.P.N. College, P.G. Center, Kanpur University, Kanpur 208001, India

*Author for correspondence (alverma@amity.edu; alverma@yahoo.com)

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Abstract. We report Raman spectral studies of pure potassium oxalate monohydrate, $K_2C_2O_4 \cdot H_2O$ (POM) and its doped varieties with 1 and 5% vanadyl concentrations at room temperature. Apart from many other interesting changes in the Raman spectra on doping with VO^{2+} , one of the most intriguing observations is the change in relative intensities of factor group split components of several Raman bands including some bands in the lattice mode region. We have explained the relative intensity changes of factor group split components in terms of locking of adjacent $C_2O_4-H_2O-C_2O_4-H_2O$ chains due to vanadyl doping in the POM lattice. The reduction in the intensities of water bands on vanadyl doping also supports this view.

Keywords. Raman spectra; potassium oxalate monohydrate (POM); vanadyl doping; factor group split Raman bands.

1. Introduction

The study of doped ions in a crystalline host has been the subject of scientific interest for a long time. The question arises as to how the neighbouring structure in the lattice is perturbed by the introduction of external impurities. We have chosen potassium oxalate monohydrate (POM) to understand how the bonding pattern in POM is affected on doping with some external impurities. POM plays an important role in nature, is found in many plants and is used in various medical and technological applications [1]. We have therefore tried to understand the structural changes induced in the lattice of POM on introducing vanadyl ions as external impurities using a Raman spectroscopic technique which provides direct evidence of structural changes at the microscopic level including lattice modes.

Moreover, we are interested in studying the structural changes using an electron spin resonance technique and also where paramagnetic vanadyl ions act as useful probes for electron paramagnetic resonance (EPR) investigations [2]. Many optical absorption and EPR studies are reported for vanadyl ions doped in a number of host lattices [3–7] and changes in energy levels/parameters are observed from one host to another.

Though X-ray and neutron diffraction studies are important established tools in crystal structure determination [8–10], when one wants to explore localized defects in crystals, an X-ray technique does not seem much helpful. Vibrational and EPR studies are sometimes of immense help in this direction. The EPR technique [3–7] is quite characteristic of an immediate environment of the cation site and very small changes in

the environment of doped ions could be identified. For such investigations, the vanadyl ion is a powerful probe. This is a linear molecular entity ($V=O$) and can substitute at lattice cationic locations or may occupy interstitial positions.

Raman spectroscopic techniques provide direct evidence of structural changes at the microscopic level including lattice modes. In this paper, we are presenting the results of our Raman study for undoped POM and its 1 and 5% vanadyl doped varieties. It is interesting to find that the doped vanadyl ions do attenuate the intensities of some of the Raman bands and splitting of some bands is also observed.

The Raman studies of pure POM (both in powder and single crystal forms) have been reported from 80 to 3800 cm^{-1} by Eriksson and Nielson [11]. They have also assigned the observed bands in different spectral regions, though their spectral resolution was not adequate to resolve the bands due to O–H stretching modes. Fukushima [12] has conducted infrared (IR) studies on pure POM. If POM is doped with vanadyl ions, the $V=O$ groups are reported to bind oxalate groups in the adjacent $H_2O-C_2O_4-H_2O$ chains, replace two potassium ions and occupy interstitial sites in the lattice, forming the $VO(C_2O_4)_2 \cdot H_2O$ complex [7]. Such a doping would influence the bonding arrangement and may affect the lattice and other vibrational and even rotational/librational motions of different groups in POM. The intensities of different factor group split components may not be affected equally with the above suggested bonding of the $V=O$ group. During our Raman investigations of vanadyl doped POM, we have observed very surprising and remarkable changes in the relative intensities of many factor group split components of Raman bands. We therefore undertook

systematic Raman studies on POM doped with different concentrations of vanadyl ions and have attempted to explain the origin of such changes in this work.

2. Crystal structure

The crystal structure of $K_2C_2O_4 \cdot H_2O$ has been investigated by Hodgson and Ibers [13] from X-ray diffraction and by Chidambaram *et al* [10] using neutron diffraction techniques. $K_2C_2O_4 \cdot H_2O$ crystallizes as per the $C2/c$ (C^6_{2h}) space group in the monoclinic centrosymmetric lattice and the molecular symmetry of the oxalate group is D_{2h} . It occupies the C_i site in the unit cell while the factor group is C^6_{2h} . On the other hand, the water molecule has the C_{2v} molecular point group and occupies the C_2 site in the solid.

The monoclinic crystals of POM consist of chains of oxalate ions with a water molecule present in each chain between the two neighbouring oxalate groups. The water molecule forms a hydrogen bond with the oxygens of the oxalate group. Two such neighbouring chains are held by K^+ ions between them placed in general positions at the C_1 site. The determined crystal parameters [9,10] are: $a = 9.223 \text{ \AA}$, $b = 6.197 \text{ \AA}$, $c = 10.690 \text{ \AA}$ and $\beta = 110.70^\circ$. The unit cell of the crystal has four formula units and each primitive cell contains two formula units.

Group theoretical analysis of different modes in the Raman spectrum of POM has been given by Eriksson and Nielson [11] in terms of internal, rotational (called librational modes in solids) and translational lattice modes including the symmetry correlation diagram. However, we shall give here only pertinent details for the ease of readers. Briefly, one would expect 66 normal modes from 22 atoms in the primitive cell of POM consisting of two formula units. Out of these, there will be 33 Raman active modes distributed as 12 internal vibrational modes of C_2O_4 ($6A_g + 6B_g$), 3 internal vibrations of H_2O ($2A_g + 1B_g$), 6 rotational (librational) modes of C_2O_4 ($3A_g + 3B_g$), 3 rotational/librational modes of H_2O ($1A_g + 2B_g$) and 9 translational modes ($4A_g + 5B_g$). In IR, one would expect 12 internal vibrational modes of C_2O_4 ($6A_u + 6B_u$), 3 internal vibrational modes of H_2O ($2A_u + 1B_u$), 3 rotational/librational modes of H_2O ($1A_u + 2B_u$), 12 translational modes ($6A_u + 6B_u$) and 3 acoustic modes ($1A_u + 2B_u$). The symmetry correlation diagram for $K_2C_2O_4 \cdot H_2O$ solid is shown in table 1.

The XYZ coordinate system for the oxalate group is chosen such that the X – Y plane coincides with the molecular plane and the Y -axis is along the C–C direction. For water, the Z -direction is taken along the two-fold axis and the X -direction lies perpendicular to the molecular plane. Figure 1 shows the projection of the POM crystal structure on the (010) plane as given by Chidambaram *et al* [10] and Kripal *et al* [7] which also shows the orientation of the V=O group.

Being centrosymmetric, the interactions among the molecular units in the unit cell are expected to give rise to splitting of each mode into A_g , B_g , A_u and B_u components which is called

the factor group splitting. Only the A_g and B_g component modes would be active in Raman scattering. The classification of the factor-group split components as symmetric (A_g) and antisymmetric nature (B_g) is visualized with respect to the common plane of the oxalate ion and the position of H_2O . Table 1 shows the symmetry correlation diagram for the $K_2C_2O_4 \cdot H_2O$ solid.

3. Materials and methods

Crystals of pure POM and POM doped with vanadium sulphate were grown from saturated solution at room temperature by slow evaporation. The saturated solution was prepared by dissolving analar grade POM along with 1 and 5% vanadium sulphate by weight in distilled water. After nearly 12–14 days, small crystals were obtained which were ground to a powder form for Raman studies. The Raman spectra of the samples in the powder form were recorded using a JY-Horiba Model R-550 Raman spectrometer with a focal length of 55 cm and an aperture of $f/6.4$. The spectrometer was fitted with a Peltier cooled CCD detector. The Raman spectrometer was fitted with a microscopic arrangement for focusing the laser light to a micron size spot. The 514.5 nm argon ion laser line with ~ 3 mw power at the sample was used as the excitation source. The data were accumulated for 3 s and averaged over 200 scans to improve the S/N ratio.

4. Experimental

Figure 2A and B shows the Raman spectrum of undoped POM and the corresponding spectrum of 5% vanadyl doped POM samples in the spectral region of 50–2000 cm^{-1} , respectively. In the Raman spectrum of undoped POM, the 1443 cm^{-1} Raman band associated with the C=O stretching mode is the strongest followed by the group of external vibrations and a clear doublet at 874 and 879 cm^{-1} associated with the C–C stretching mode. In 5% vanadyl doped POM, Raman bands ascribable to external vibrations are quite strong. We present the Raman spectra of undoped POM along with 5% vanadyl doped samples in figures 3, 4 and 5 on an expanded scale for clarity in the spectral ranges: 50–200, 400–700, 840–910, 1540–1640 cm^{-1} and 2900–3800 cm^{-1} , respectively.

Before attempting to explain changes in the Raman spectra of POM doped with vanadyl ions, it is emphasized that two planar oxalate groups are bound through H_2O molecules in the primitive unit cell of POM (figure 1). Therefore, symmetric and anti-symmetric nature of bands has to be visualized with respect to the water group joining the oxalate groups. Thus C=C stretching will be considered symmetric or anti-symmetric while keeping the position of linked H_2O in mind. Similar implications have to be considered while examining the vibrations of C=O and other groups.

Table 1. Symmetry correlation diagram for $K_2C_2O_4 \cdot H_2O$ solid.

Molecular group $C_2O_4^{2-} (D_{2h})$	Site group C_1	Factor group C_{2h}^6	Spectral activity
A_g	A_g	A_g	Raman
B_{1g}		B_g	Raman
B_{2g}			
B_{3g}			
A_u	A_u	A_u	IR
B_{1u}		B_u	IR
B_{2u}			
B_{3u}			
H_2O molecule (C_{2v})	C_2	C_{2h}^6	
A_1	A	A_g	Raman
A_2		B_g	Raman
B_1	B	A_u	IR
B_2		B_u	IR
K^+ ions ($D_{\infty h}$)	C_1	C_{2h}^6	
Σ^+_u	A	A_g	Raman
		B_g	Raman
Σ^-_u		A_u	IR
		B_u	IR

5. Raman spectral data in different wavenumber regions

In the following, we describe changes in the intensities of Raman bands in different spectral regions on vanadyl doping of POM. There are two traces. The top and bottom for each region corresponds to pure POM and 5% VO^{2+} doped POM, respectively. The Raman intensity units are arbitrary.

5.1 50–200 cm^{-1} region

In the pure POM, five prominent bands and two weak features with the symmetry type A_g/B_g in the parenthesis are observed at different wavenumbers: 79 cm^{-1} (A_g/B_g), 105 cm^{-1} (B_g), 114 cm^{-1} (A_g/B_g), 128 cm^{-1} (A_g), 142 cm^{-1} (A_g/B_g), 151 cm^{-1} (A_g/B_g) and 162 cm^{-1} (A_g/B_g) as shown in deconvoluted Raman bands in figure 3. The intensities of all the bands except for the 105 cm^{-1} band decreases on vanadyl doping. In the VO^{2+} doped samples, additional bands appear at 56 and 68 cm^{-1} . The latter of these bands has also been reported by Fukushima [10] in their IR spectrum. The relative intensity of the 114 cm^{-1} band decreases sharply compared to the intensity of the 105 cm^{-1} band in the Raman spectrum of VO^{2+} doped samples.

5.2 400–650 cm^{-1} region

As shown in figure 4A, the 472 and 555 cm^{-1} bands in pure POM reduce in intensity on vanadyl doping. Again, the 625 cm^{-1} band due to H_2O rocking/librational motion reduce in intensity and is virtually lost in the noise due to reduction of water at regular sites in the 5% vanadyl doped POM.

5.3 840–920 cm^{-1} region

Figure 4B shows the Raman spectrum in the region from 840 to 910 cm^{-1} . The factor group split components of the Raman bands due to the C–C stretching mode at 875 cm^{-1} (A_g) and 879 cm^{-1} (B_g) respectively in pure POM are observed. The intensity of the B_g component at 879 cm^{-1} decreases sharply relative to the A_g component at 875 cm^{-1} on vanadyl doping.

5.4 1540–1640 cm^{-1} region

A doublet at 1598 (B_g) and 1604 (A_g) cm^{-1} corresponding to the C=O antisymmetric stretching mode in pure POM is observed in the Raman spectrum. On doping the POM with

Figure 1. Projection of the crystal structure of POM on the (010) plane (based on references [7,10]) showing the position of the V=O group.

Figure 2. (A, B) Raman spectra of polycrystalline undoped POM and POM doped with 5% vanadyl ions at room temperature in the spectral region of 50–2000 cm^{-1} .

vanadyl ions, the relative intensity of the B_g component at 1598 cm^{-1} reduces greatly compared to the A_g component at 1604 cm^{-1} as is evident from figure 5A.

Figure 3. Relative intensities of different Raman bands of undoped and 5% VO doped POM at room temperature in the spectral region of 50–200 cm^{-1} . This portion of the spectrum has been deconvoluted using Lorentzian line shape function which makes relative intensities and the band position of different components much clear.

5.5 2800–3800 cm^{-1} region

The Raman spectrum in this wavenumber region is shown in figure 5B. The relative intensities of water bands decrease due to reduction in the number of H_2O groups at regular crystal sites due to vanadyl doping in POM. Moreover, the Raman bands arising from stretching modes of OH^- ions created by dissociation of H_2O may be buried in the broad bands in this region and the relative intensity changes and/or shift in band positions are neither significant nor follow any systematic pattern. However, we have observed clearly resolved Raman bands due to symmetric and antisymmetric O–H stretching modes at 3262 and 3400 cm^{-1} respectively while Eriksson and Nielsen [11] observed only one band at $\sim 3250 \text{ cm}^{-1}$ in this spectral region.

6. Discussion

From Raman studies on single crystal of POM, Eriksson and Nielsen [11] have associated the split components of some Raman bands due to factor group splitting. The contribution of the site group splitting in the splitting of the bands arising

Figure 4. (A) Relative intensities of Raman bands of undoped and 5% VO doped POM at room temperature in the spectral region of 400–650 cm^{-1} . (B) Relative intensities of Raman bands of undoped and 5% VO doped POM at room temperature in the spectral range of 840–920 cm^{-1} .

from occupancy of VO^{2+} ions on different sites can be ruled out as, in general, the site group split components in Raman bands are more widely separated than observed in our studies.

If POM is doped with a vanadyl ion, the $\text{V}=\text{O}$ group would bind oxalate groups in the adjacent $\text{C}_2\text{O}_4-\text{H}_2\text{O}-\text{C}_2\text{O}_4-\text{H}_2\text{O}$ chains. Thus VO^{2+} would link with the oxygens O(1), O(2), O(3) and O(4) to form a complex $\text{VO}(\text{C}_2\text{O}_4)_2\cdot\text{H}_2\text{O}$. In this complex, $\text{V}=\text{O}$ would obviously point perpendicular to the plane formed by O(1), O(2), O(3) and O(4) atoms. Such a complex formation was established by Kripal *et al* [7] through their EPR studies in vanadyl doped POM. The orientation of complexed $\text{V}=\text{O}$ in POM and relevant ‘g’ and ‘A’ parameters were also obtained by Kirpal *et al* [7].

6.1 Intensity of B_g type modes

The particular planar and tightly bound atoms in oxalate ions and the orientation of the $\text{V}=\text{O}$ complex with respect to the surrounding oxygens provide a clue that during the B_g type

Figure 5. (A) Relative intensities of Raman bands of undoped and 5% VO doped POM at room temperature in the spectral range of 1540–1640 cm^{-1} . (B) Relative intensities of Raman bands of undoped and 5% VO doped POM at room temperature in the spectral range of 2900–3800 cm^{-1} .

modes, the atomic species move perpendicular to the oxalate plane and their movement would be restricted resulting in a decrease in the polarizability change and intensity of B_g type modes. On the other hand, A_g type modes involve the movement of atoms in the oxalate plane which would not be much affected due to vanadyl doping in POM. This is further clarified as per discussion below.

The orientations of the plane of the oxalate group containing oxygens O(3), O(4), O(5) and O(6) and the planes O(1), O(2), O(3) and O(4) of oxygens in the vanadyl complex can be seen in figure 1.

When vanadyl ions are doped in POM as shown in figure 1, the oxygens O(3) and O(4) are locked to the adjacent O(1) and O(2) oxygens through the V^{4+} ion which forms strong covalent bonds with all the four oxygens O(1), O(2), O(3) and O(4).

From the position of oxygens surrounding V^{4+} and the position of carbon atoms, according to the crystal data [10], it can be estimated that the carbon–O(3) bond makes an angle of 81° with the O(3)–V bond and the carbon–O(4) bond makes an angle of 77° with the O(4)–V bond in the three-dimensional image. With this image, it is easier to visualize that the out of plane movement of the atomic species during B_g type vibrations would be greatly hampered due to tightly bound coupling of oxalate chains through vanadyl bonding.

Table 2. Vibrational data for $K_2C_2O_4 \cdot H_2O$ and VO^{2+} doped $K_2C_2O_4 \cdot H_2O$ at room temperature.

Sl. no.	FTIR (Fukushima)	Raman (Eriksson)	Present work			Mode symmetry	Mode description (approx.)
			Pure POM	1% VO^{2+} doped POM	5% VO^{2+} doped POM		
1	56	—	—	56 vw	57 vw		Lattice modes
2		82 w	79 w	79 w	81 w	A_g, B_g	
3	92	—	—	—	—	—	
4	—	103 vw	105 sh	106 m	107 m	B_g	
5	115	112 m	113 s	113 m	111 sh	A_g, B_g	
6	—	118 m	—	—	—	A_g	
7	129	130 s	129 vs	128 s	128 s	A_g	
8	—	141 sh	142 sh	141 sh	143 sh	A_g, B_g	
9		150 sh	—	—	—	A_g, B_g	
	160	162 sh	163 sh	163 sh	163 sh	A_g, B_g	
10	190	—	—	—	—	—	
11	210	—	—	—	—	—	
12	351	—	—	—	—	—	
13	—	473 s	472 vs	470 vs	470 m	A_g, B_g	Oxalate def. mode, sym. O–C–O bending
14	524	—	—	—	—	—	Oxalate in-plane def. mode mixed with H_2O lattice mode
15	—	556 m	555 wm	555 w	555 vw	A_g, B_g	
16	614	—	—	—	—	—	H_2O rocking/libration
17	—	627 vw	625 vw	620 vvw and diffused	—	B_g	
18	718	720 vw	—	—	—	B_g	H_2O wagging/libration
19		876 vs	875 m	874 s	874 s	A_g	ν_{c-c} , C–C sym. str.
	—	881 vs	879 s	879 s	879 w		
20				980	—	—	$\nu_{v=0}$, $\nu_{=O}$ sym. str.
	—	—	—	1002 vvw	1003 vvw		
21	—	~1095 vw	—	—	—	—	2x 556 cm^{-1} , overtone
22		1342 w	1343 vw	1338 vw	1334 vvw	A_g, B_g	ν_{c-c} sym. Str. +473 cm^{-1} , combination
23	—	1444 vs	1443 vs	1443 vs	1443 vs	A_g, B_g	ν_{c-o} , sym. C–O str.
24		1600 s	1598 m	1600 m	1600 w	A_g	ν_{c-o} , asy. C–O str.
	—	1606 m	1604 sh	1605 sh	1606 w		
25	—	1754 w	—	—	—	A_g	2x ν_{c-c} , str. overtone
26	—	~ 3250 vw, b	3262 m	3260 vw	3251 vw	A_g, B_g	ν_{O-H} , sym. O–H str.
27	—	—	3400 b, sh	3383 w, sh	3390 vw	A_g, B_g	ν_{OH} , asy. O–H str.

Abbreviations: s, strong; m, medium; w, weak; b, broad; sh, shoulder; v, very; vvw, very very weak; str, stretching mode; sym, symmetric; asy, asymmetric.

On the other hand, A_g type modes involving motion of atomic species in the oxalate plane would not be much affected due to vanadyl doping in POM.

The reduction in the intensities of various Raman bands can thus be satisfactorily understood as per discussion given above. Further, as any oxalate ion is linked to a neighbouring oxalate through a water group under inversion symmetry, any decrease in intensities of the B_g mode in one oxalate group will be reflected in the nearest-neighbouring oxalate locked chains also. In other words, doping by single V=O group would thus affect the intensities of B_g modes in six oxalate groups.

6.2 Intensities of H_2O vibrational modes

We observed weak-medium and very weak intensity Raman bands associated with water molecules at 556 cm^{-1} (A_g , B_g), 627 cm^{-1} (B_g) and 720 cm^{-1} (B_g), respectively. When V=O is doped in POM, water groups need to leave regular sites and some of these may even break into H^+ and OH^- ions. The latter ions may coordinate with the displaced K^+ ions. Thus even allowed B_g type vibrations associated with water molecules would decrease in intensity on vanadyl doping, as observed.

The locking of oxalate group chains may alter the local symmetry activating the otherwise some forbidden IR modes in Raman scattering. Further, Fukushima [14] has made lattice dynamical calculations for finding the vibrational modes for POM based on force constants between K^+ and oxalate groups. The data obtained therein have been used to explain the observation of IR bands at 56 and 92 cm^{-1} and predict a band at $\sim 50\text{ cm}^{-1}$. There is a possibility of some combination bands overlapping with the 105 and 113 cm^{-1} Raman bands. The apparent increase in the intensity of the 105 cm^{-1} band relative to the 113 cm^{-1} band on vanadyl doping may be expected with an increase in disorder in the lattice on vanadyl doping.

The vibrational data for pure POM and vanadyl doped POM at room temperature for two vanadyl concentrations are shown in table 2. We have also included the Raman data by Eriksson and Nielsen [11] and IR data by Fukushima [14] along with mode description for easy comparison.

7. Conclusions

The observed changes in the relative intensities of factor group split components of some Raman bands in POM have been

reasonably well explained. The relative intensity changes arise from locking of adjacent $C_2O_4-H_2O-C_2O_4-H_2O$ chains on vanadyl doping in the lattice of POM through the formation of a complex $VO(C_2O_4)_2 \cdot H_2O$. The role of vanadyl doping is further reflected in the appearance of additional very weak Raman features at 57 and 67 cm^{-1} in the V=O doped samples. The appearance of the IR active mode at 56 cm^{-1} suggests that vanadyl linkage inside POM eliminates the inversion symmetry. This may also be responsible for the appearance of some additional weak features in the 5% V=O doped POM samples. The present conclusions thus corroborate EPR results of Kripal *et al* about such complexes in vanadyl doped POM. The intensity changes also support the decrease in water content at regular sites in the VO^{2+} doped POM.

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