

Structural, spectroscopic and dielectric properties of KVO_3

N K MISRA, R N P CHOUDHARY* and K L YADAV*

Department of Physics, P.K.H.N. College, Howrah 711 410, India

*Department of Physics, Indian Institute of Technology, Kharagpur 721 302, India

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Abstract. Polycrystalline samples of KVO_3 , a member of the pyroxene structural family have been synthesised with high-temperature solid-state reaction technique. Preliminary structural and spectroscopic and detailed dielectric properties have been studied in different conditions. No dielectric anomaly or hysteresis loop has been observed in a wide temperature range (30°C to 450°C). Basic structural and spectroscopic (IR and Raman) studies suggest that at room temperature, KVO_3 is centrosymmetric as reported earlier. This and other observations do not support the recent report of ferroelectric phase transition in the compound.

Keywords. X-ray diffraction analysis; Raman and IR spectra; dielectric constant; ferroelectric phase transition.

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1. Introduction

Potassium metavanadate KVO_3 is a member of pyroxene structural family with a general formula AMO_3 (A = mono or divalent cations and M = Si, Ge, V or P) which has a wide structural flexibility, distortion, variant and interesting properties [1–6]. For example metavanadates (AVO_3) with small alkali cations like Li^+ and Na^+ , have monoclinic or clino pyroxene centrosymmetric structures (space group $C2/c$) and with larger ions like K^+ , Rb^+ , Cs^+ orthorhombic centrosymmetric (space group $Pbcm$; D_{2h}^{11}) structures [7]. These centrosymmetric structures at room temperature have been supported by others [8–9] from their spectroscopic (IR and Raman) studies. However, recently ferroelectric phase transition and other related properties in some vanadates have been reported [10–12] which is contradictory to all the above previous studies. Further, if reported crystal structures are correct, ferroelectric properties should not be observed. Therefore, it was felt necessary to reinvestigate the structural, dielectric, spectroscopic and thermal properties of AMO_3 family to solve the above contradictory report. In this paper, we report our preliminary structural and spectroscopic, and detailed dielectric properties of the titled compounds.

2. Experimental

Polycrystalline samples of potassium vanadate were prepared from K_2CO_3 (99.9% pure) and V_2O_5 (99.99% M/s Sigma Ltd.) by high-temperature solid-state reaction technique. Before weighing, these compounds were dried to remove their moisture contents. The oxides were mixed in a suitable stoichiometry in an agate mortar. After

thorough mixing in ball milling, the mixture was calcined at 750°C for 20 h. The calcined material was again mixed to make fine powder of the sample. Finally, powders were cold pressed into pellets at a pressure of about 5×10^6 kg/m². These pellets were sintered in a platinum crucible at 500°C for 20 h and then quenched to room temperature (25°C).

At room temperature X-ray diffractogram of the pellet sample were recorded by Rigaku (Miniflex, Japan) X-ray powder diffractometer with CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$) in the 2θ range of $10 \leq 2\theta \leq 35^\circ$ ($\theta =$ Bragg angle). The surface morphology, grain shape microstructure and final compositional ratio were studied by the help of 'CAMSCAN' scanning electron microscope (SEM) equipped with energy dispersive X-ray microanalysis (EDX) system.

Measurements of dielectric constant (K) and loss ($\tan \delta$) were carried out by GR-1620 capacitance measuring assembly as a function of temperature (room temperature to 450°C).

Infrared spectra were recorded using KBr pellet in a wide range of wave numbers (200 cm^{-1} to 4000 cm^{-1}) using a Perkin Elmer 598 spectrometer. The Raman spectra were recorded in the frequency range 20 to 4000 cm^{-1} with laser Raman spectrometer (Cary Model 82) consisting of Ar-ion laser and double grating monochromator with photon counting detector. The Raman spectrum was excited with the 541.3 nm line at a power of 200 mW.

3. Results and discussion

The sharp single X-ray profiles of all the reflections of the compound suggest the formation of single phase compound. Using d -values of all the reflection peaks, cell parameters of KVO₃ have been determined and refined by least-squares method which were consistent with those of the reported values. These are: $a = 5.176(1) \text{ \AA}$, $b = 10.794(1) \text{ \AA}$ and $c = 5.780(1) \text{ \AA}$ (estimated errors in parentheses). The calculated d spacing (from refined cell parameters and indexed reflections) are in very good agreement with those observed experimentally (table 1) which suggests the correctness of cell configuration and structures.

Table 1. Comparison of observed and calculated ' d ' values (\AA) (estimated error 10^{-4} \AA) of some reflections of KVO₃ at room temperature

hkl	d_{obs}	d_{cal}	I/I_0
020	5.4049	5.3970	23
100	5.1852	5.1760	100
021	3.9171	3.9125	9
120	3.7385	3.7357	26
111	3.6187	3.6060	3
121	3.1210	3.1211	75
002	2.8488	2.9400	23
040	2.6983	2.6985	20
131	2.6212	2.6210	14
200	2.5887	2.5880	94

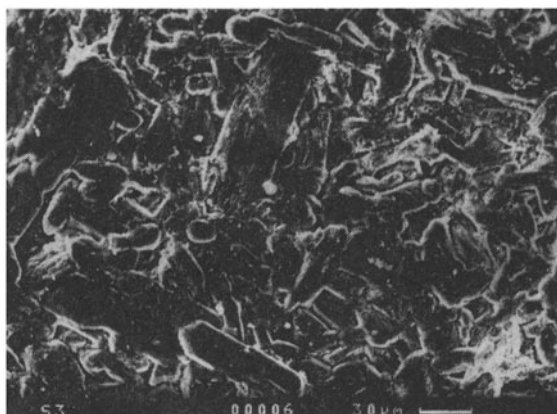


Figure 1. Scanning electron micrographs of KVO_3 sintered pellet.

Table 2. Raman and infrared active modes in the KVO_3 .

Raman		Infrared	
of Raman active mode	Assignment	of I.R. active mode	Assignment
947] 940] 930] 920]	$\nu_s(VO_2)$	962] 940] 923]	$\nu_s(VO_2)$
910] 637]	$\nu_{as}(VO_2)$	892] 862] 680]	$\nu_{as}(VO_2)$ $\nu_{as}(V-O-V)$
525] 497]	Combination of $\nu_s(V-O-V)$ and $\nu_{as}(V-O-V)$	498]	Combination of $\nu_s(V-O-V)$ and $\nu_{as}(V-O-V)$

In figure 1 the SEM photograph of KVO_3 indicate that particles are not spherical. Elemental analysis from EDX recording has shown that the chemical formula of the prepared compound is very close to that of KVO_3 .

Detailed and careful spectroscopic analysis of (IR and Raman) of KVO_3 at room temperature has confirmed the reported centrosymmetric group $PbCm (D_{2h}^{11})$ and configuration of pyroxene structure. In this structure there are two chains per unit cell running parallel to c -axis. These chains are held together by K -ions. The site symmetry of the chains in the unit cell is C_{2v} . The backbone consists of V_2O_2 , the line group of which is D_{2h} . Details of the correlation scheme and assignments of the band have been discussed elsewhere [2, 3] which are in good agreement with our observed spectral data.

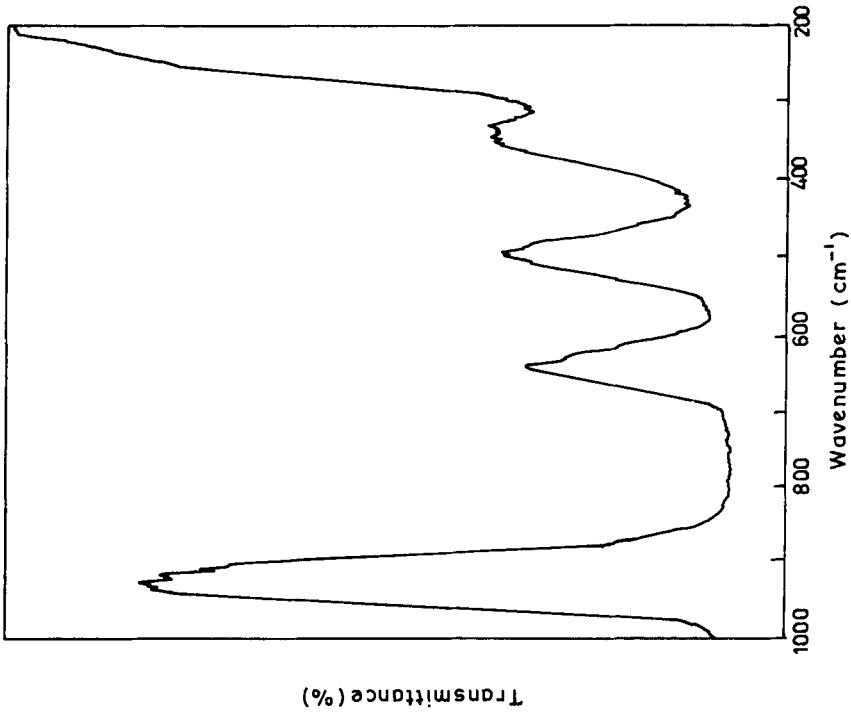


Figure 3. Raman spectra of KVO_3 at room temperature.

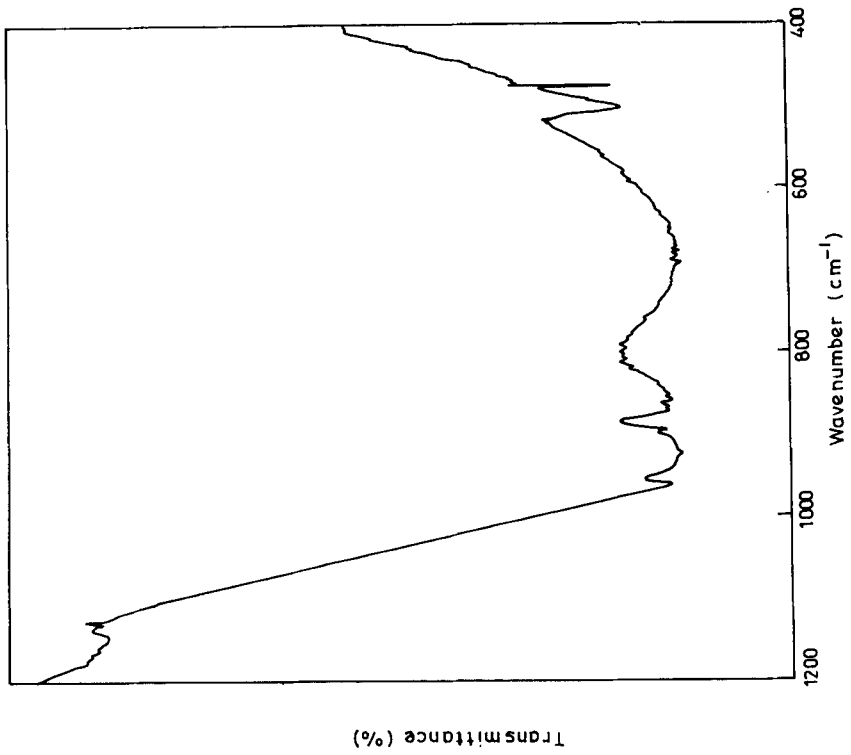


Figure 2. Infrared spectra of KVO_3 at room temperature.

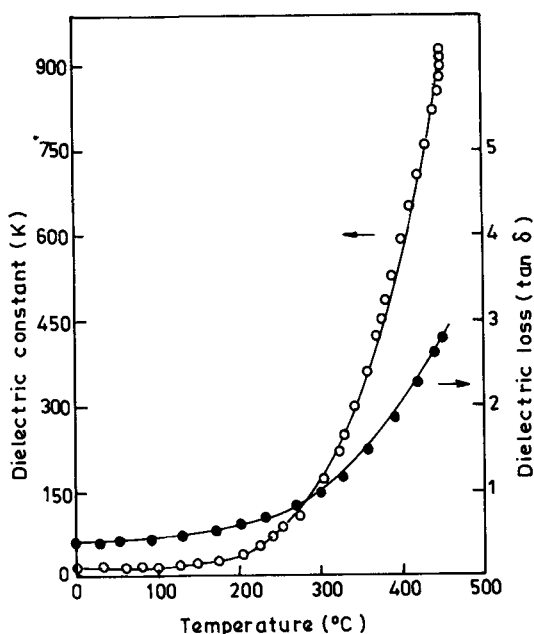


Figure 4. Temperature dependence of dielectric constant and dielectric loss of KVO_3 .

As shown in table 2 and figures 2 and 3 there are eight Raman and seven IR bands up to wave number 500 cm^{-1} of which the coupling of C_{2v} with unit cell yield 4 Raman and 3 IR peaks. Others are originated from V_2O_6 chain.

Figure 4 shows the variation of K and $\tan \delta$ of KVO_3 with temperature at a frequency of 10 kHz. The room temperature K was 15 which remained constant up to 150°C and then increases faster to a value around 900 at 420°C . Within this temperature range no dielectric anomaly was observed. The slow increase at low temperature is due to lattice ionic polarizability and the faster increase in high temperature region is due to space charge polarization. Further no hysteresis loop has been observed at room temperature.

Our results of systematic structural, dielectric, hysteresis loop, spectroscopic studies clearly support the reported centrosymmetric space group.

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