

Electrical, thermal and infrared studies of cadmium metavanadate

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Abstract. Cadmium(II) metavanadate has crystal structure related to brannerite (ThTi_2O_6) structure. The high temperature $\beta\text{-CdV}_2\text{O}_6$ phase is *n*-type semiconductor between 185 and 750 °C. The electrical conduction in the $\beta\text{-CdV}_2\text{O}_6$ occurs due to deviation from oxygen stoichiometric composition of the lattice. The seebeck coefficient (α) of the sample is negative and constant in the entire range of investigation. The mechanism of transport in cadmium metavanadate lattice is via thermally activated hopping of localized electrons on vanadium (V^{5+}) sites of the lattice. The DTA result indicated that CdV_2O_6 undergoes phase transition at 185 °C and not at 670 °C as reported earlier. There is no DTA evidence to show the possibility of $\beta \rightarrow \alpha$ phase reverse transition. The XRD powder patterns of the two modifications are nearly similar indicating brannerite related structures. The infrared absorption band of vanadium–oxygen stretching vibration modes of distorted VO_6 octahedra of $\beta\text{-CdV}_2\text{O}_6$ is exhibited at 855 cm^{-1} .

Keywords. Crystal structure; semiconductor; stoichiometric; phase transition.

1. Introduction

Cadmium metavanadate (CdV_2O_6) was identified in the phase studies of binary oxides of $\text{CdO-V}_2\text{O}_5$ (Tammann and Kelsing 1925; Angenault 1967, 1970; Bouloux and Galy 1969; Bouloux *et al* 1972; Brown 1972). Tammann and Kelsing (1925) and Brown (1972) noticed an eutectic temperature at $650 \pm 15^\circ\text{C}$ during the phase studies of $\text{CdO-V}_2\text{O}_5$. Bouloux and Galy (1969) obtained $\alpha\text{-CdV}_2\text{O}_6$ by heating equimolar amounts of CdO and V_2O_5 at 580°C for 24 h and also prepared $\beta\text{-CdV}_2\text{O}_6$ by either heating $\alpha\text{-CdV}_2\text{O}_6$ for 5–6 h at 750°C or by fusing $\alpha\text{-CdV}_2\text{O}_6$ to molten state and quenching to room temperature. Both modifications of CdV_2O_6 crystallized in the brannerite related crystal structures (Wadsley and Ruh 1966). $\alpha\text{-CdV}_2\text{O}_6$ phase is yellow and changes to brown after phase transition with volume contraction (10%) of the unit cell from 243 \AA^3 to 216 \AA^3 . The crystal structure of $\alpha\text{-CdV}_2\text{O}_6$ is monoclinic (space group: $C2/m$) (Bouloux *et al* 1972), while that of $\beta\text{-CdV}_2\text{O}_6$ is also monoclinic ($C2/m$) (Bouloux and Galy 1969) isostructural with brannerite crystal structure [monoclinic, $C2/m$]. Angenault (1970) did not observe phase transition and could synthesize only $\beta\text{-CdV}_2\text{O}_6$. Brown (1972) prepared a yellow coloured CdV_2O_6 which transformed to high temperature $\beta\text{-CdV}_2\text{O}_6$ phase at $180 \pm 10^\circ\text{C}$ with a distinct colour change (brown). The phase transition observed for CdV_2O_6 is reversible. The CdV_2O_6 phase melts congruently at 800°C . Apart from these, no other information is available in literature.

Vanadates of cations (trivalent/divalent) have extensive industrial applications as phosphors/luminescent materials. As a part of the investigation of $\text{MO-V}_2\text{O}_5$ systems (where M = cation), we are prompted to investigate the electrical, thermal and infrared studies of CdV_2O_6 phase. The results are discussed in the present paper.

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2. Experimental

Cadmium(II) vanadate was obtained by heating an equimolar ratio (1:1) of CdCO_3 and V_2O_5 (both Mathey-Johnson/Baker AR Grade) at 500°C for 36 h adopting conventional solid state ceramic technique. The dc electrical conductivity (σ) of the sample was obtained by measuring the resistance of the sample by current-voltage method using 12 V dc source and standard resistances. The seebeck coefficient (α , $\mu\text{V}/\text{degree}$) was measured by integral method between 185 and 750°C . The sample (18 mm dia., 2 mm thickness) was in the form of sintered pellet of about 85% density. The differential thermal analysis (DTA) of the sample was carried out in the laboratory built unit and was recorded using a sensitive strip chart recorder (ECIL India Pvt. Ltd). The following conditions were maintained during DTA run of the sample: (i) the sample holder, Pt cups, (ii) reference material, ignited anhydrous Al_2O_3 , (iii) heating rate, $8^\circ/\text{min}$, and (iv) atmosphere, static air. The XRD powder patterns of the sample were obtained on a Philips X-ray diffractometer (Ni filter, $\lambda = 1.5418 \text{ \AA}$) using CuK_α radiation. The infrared spectrum of CdV_2O_6 was recorded in nujol mull on a Perkin-Elmer spectrophotometer.

3. Results and discussion

The XRD powder patterns of the samples prepared under different conditions agrees with both α and β phases of CdV_2O_6 (Bouloux and Galy 1969; Bouloux *et al* 1972; Brown 1972; ASTM card file NO 20-189). These phases are isotypic with brannerite (Wadsley and Ruh 1966) related crystal structures such as MgV_2O_6 (Ng and Calvo 1972; Palanna 1979), ZnV_2O_6 (Angenault 1970) and CuV_2O_6 (Lavaud and Galy 1972). Bouloux *et al* (1972) reported that low temperature α - CdV_2O_6 phase is isostructural with CaV_2O_6 (both monoclinic, $C2/m$) and observed similar XRD patterns. In the present investigation, XRD results of the samples of annealed (heated to 600°C for 4-5 h and cooled) and quenched (heated to 750°C and chilled to room temperature) are identical (figure 1) as that observed for β - CdV_2O_6 and the strong 2θ reflection peak of α - CdV_2O_6 corresponding to $d_{201} = 3.52 \text{ \AA}$ is absent (Brown 1972). However, XRD results indicate variations in the intensity of reflections corresponding to $d = 4.40 \text{ \AA}$ ($20\bar{1}$ plane) and $d = 3.10 \text{ \AA}$ (201 plane) of CdV_2O_6 . The DTA result of CdV_2O_6 (figure 2) showed phase transition at 185°C , as was observed by Brown (1972); in contrast to the results of Bouloux and Galy (1969) who noticed the phase transition at 670°C .

Bouloux and Galy (1969) and Brown (1972) have shown that the phase transition in CdV_2O_6 is reversible; however, our results (DTA and XRD) did not indicate any such possibility. Therefore, the structural transition ($\alpha \rightarrow \beta$) is irreversible for CdV_2O_6 . Angenault (1970) could prepare only β - CdV_2O_6 and did not report phase transition. The high temperature XRD powder patterns of the samples is desirable at this stage of investigation to confirm the reversibility of phase transformation process. The phase studies of $\text{CdO}-\text{V}_2\text{O}_5$ system (Tammann and Kelsing 1925; Brown 1972) showed an eutectic (β - CdV_2O_6 -liquid phases) at $650 \pm 15^\circ\text{C}$ in the phase diagram. Therefore, one can clearly understand that the endotherm at 670°C observed by Bouloux and Galy (1969) is not the phase transition temperature for CdV_2O_6 .

Cadmium metavanadate (β - CdV_2O_6) is isostructural with brannerite (ThTi_2O_6) crystal structure (Wadsley and Ruh 1966) with monoclinic symmetry (space group

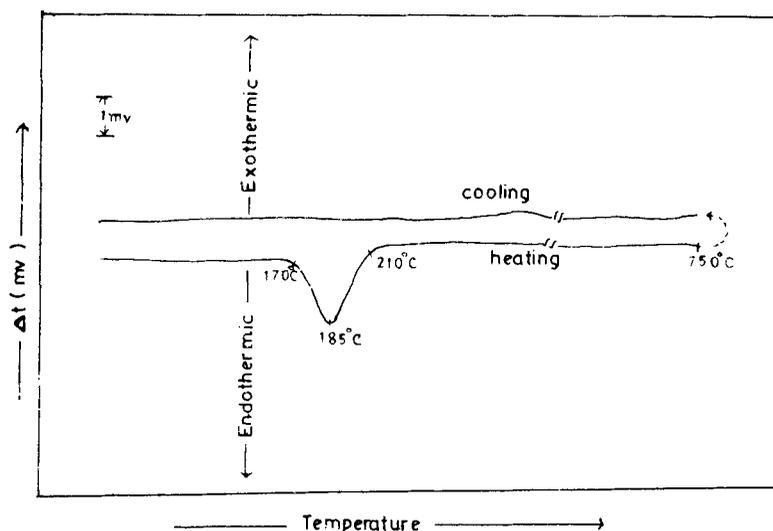


Figure 1. DTA of cadmium metavanadate.

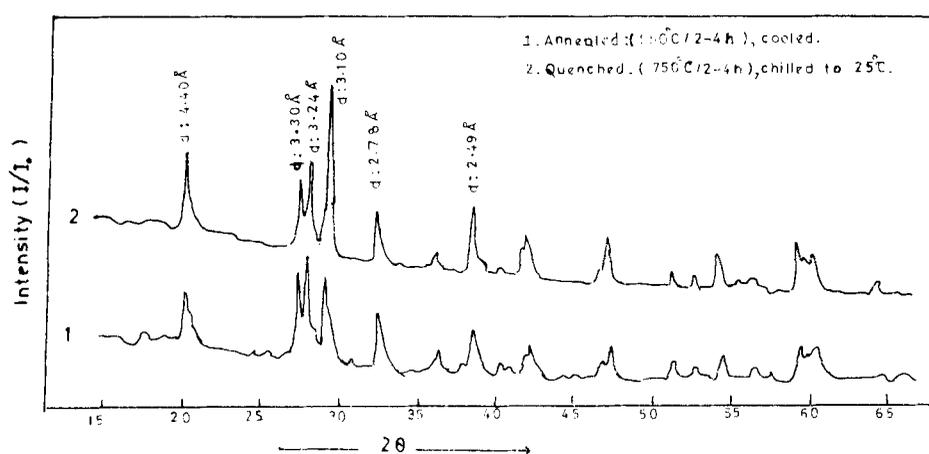


Figure 2. XRD powder patterns of 1. annealed and 2. quenched CdV_2O_6 samples.

$C2/m$). The crystal structure of $\beta\text{-CdV}_2\text{O}_6$ (monoclinic, $C2/m$) is given in figure 3b (Bouloux and Galy 1969), which is also isostructural with MgV_2O_6 (monoclinic $C2/m$) (Ng and Calvo 1972). This class of $\beta\text{-CdV}_2\text{O}_6$ crystal can be described as brannerite type crystal structure, composed of distorted VO_6 octahedra which share opposite corners forming chains parallel to b-axis. VO_6 octahedra in adjacent chains share edges ($\text{O}-\text{O}_3$) on one side of the chain. On the other side chains interleaf such that one VO_6 octahedron shares two edges with two adjacent VO_6 octahedra in a neighbouring chain (b-axis). The vanadium-oxygen bond distances in VO_6 octahedra (figure 3b) of $\beta\text{-CdV}_2\text{O}_6$ crystal varies from 1.69 to 2.46 Å. Cd^{2+} ion lies in the octahedral interstices sharing oxygen atoms with 5 different vanadium ions. CdO_6 octahedra form chains parallel to the b-axis by sharing edges with equivalent CdO_6 groups (Bouloux and Galy 1969).

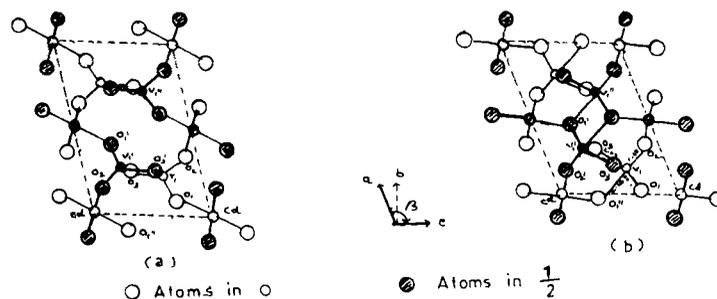


Figure 3. Projection of the structure of (a) α - CdV_2O_6 and (b) β - CdV_2O_6 on the plane a-c.

The crystal structure of α - CdV_2O_6 (monoclinic, $C2/m$) was discussed by Bouloux *et al* (1972) who reported that this crystal structure is isostructural with CaV_2O_6 (monoclinic, $C2/m$). In the brannerite related crystal structure of this type, unlike β - CdV_2O_6 , vanadium has five coordination (C.N-5) of oxygen atoms (trigonal bipyramidal VO_5 group) in α - CdV_2O_6 and the cadmium has octahedral (C.N-6) environment of oxygen atoms (CdO_6 group). Both the VO_5 and CdO_6 groups of CdV_2O_6 form zig zag chains parallel to the b-axis (figure 3a). The vanadium-oxygen bond distances of VO_5 group (trigonal bipyramidal) in α - CdV_2O_6 varies from 1.71 to 1.88 Å. This type of crystal structure could arise in α - CdV_2O_6 (figure 3a) due to loss of the sixth long vanadium-oxygen bond ($\text{V}-\text{O}:3.67$ Å) between the vanadium of VO_5 group and oxygen of the CdO_6 group in the (201) plane of α - CdV_2O_6 with the retention of identical symmetry (monoclinic, $C2/m$), as that observed for β - CdV_2O_6 .

Since there is no change in the crystal symmetry (monoclinic, $C2/m$) of both α and β -phases of CdV_2O_6 during the transformation (Bouloux and Galy 1969; Bouloux *et al* 1972), the XRD powder patterns are expected to be nearly identical; however, a shift in the intensity and XRD 2θ reflections (d_{hkl}) of high temperature phase could arise only if there is small translation or reduction in d_{hkl} in any one of the d_{hkl} planes or due to contraction of the unit cell parameters. A clear indication of the reduction in the interplanar spacings of d_{201} planes of CdV_2O_6 crystal is evident from a shift of XRD 2θ reflection peak from $d_{201} = 3.52$ Å to $d_{201} = 3.10$ Å (Bouloux and Galy 1969) for β - CdV_2O_6 . Therefore, one can attribute the DTA peak at 185°C to structural transformation (identical crystal symmetry) from α - CdV_2O_6 to β - CdV_2O_6 phase for the following reasons: the low temperature, α - CdV_2O_6 phase (monoclinic, $C2/m$), crystallized in the brannerite related crystal structure (figure 3a). A small displacement of oxygen atoms of VO_5 (trigonal bipyramid) group takes place in a-c plane of the crystal during the structural transformation of α - CdV_2O_6 , followed by a minor rotation of ($\sim 8^\circ$) CdO_6 octahedra about b-axis and a consequent displacement of the (201) plane containing oxygen ($\text{O}_{1\cdot}$) to facilitate the sixth coordination of vanadium (V_1) to give ($\text{V}-\text{O} = 2.46$ Å) a distorted VO_6 octahedra (figure 3b). This mode of structural changes from α - CdV_2O_6 to β - CdV_2O_6 (monoclinic, $C2/m$) is followed by a contraction of the unit cell parameters of α - CdV_2O_6 (a volume decrease from 243 Å³ to 216 Å³) and also associated with a marked increase in the unit cell angle, β ($\sim 8^\circ$), as was reported by Bouloux and Galy (1969).

The results of the dc electrical conductivity (σ) (figure 4) indicates that σ follows a relationship of the form

$$\sigma = \frac{\sigma_0}{T} \exp[-\Delta G^*/KT], \quad (1)$$

with activation energy of 1.40 eV.

The seebeck coefficient (α , $\mu\text{V}/\text{degree}$) is described by

$$\alpha = \frac{A}{eT} - \log \frac{V^{5+}}{V^{4+}}, \quad (2)$$

for CdV_2O_6 where all the terms have their usual significance. The term 'A' represents the K.E transported by the migrating electrons. The value of A/eT is small for ionic solids. In (2), V^{5+} (d^0) is the density of sites available for localized electrons, and V^{4+} (d^1) is the density of localized electrons, the concentration of which is very small (x) and is dependent on the extent of oxygen defect lattice of CdV_2O_6 .

The cadmium metavanadate is an insulator in the pure and stoichiometric state. The electrical conductivity (σ) data indicated that $\beta\text{-CdV}_2\text{O}_6$ is n -type semiconductor between 185° and 750°C , which is due to deviation from stoichiometry of oxygen lattice of CdV_2O_6 . The phase of $\beta\text{-CdV}_2\text{O}_6$ is predominantly ionic and the electrons are localized. Therefore the only mode of electron transport is via the thermally activated jumps on equivalent vanadium sites (b-axis) of the CdV_2O_6 lattice.

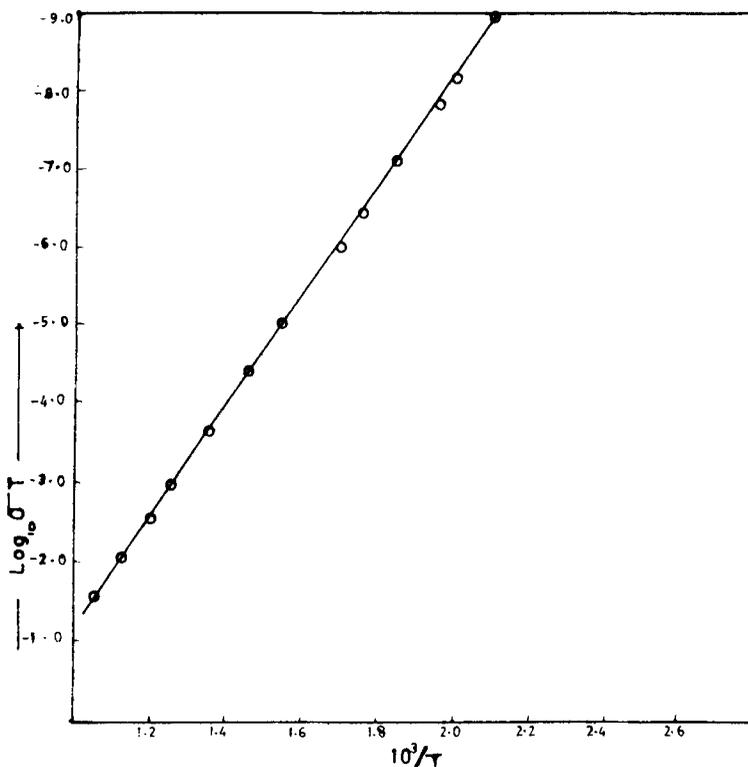
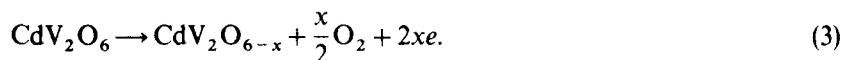


Figure 4. Plot of $\log_{10} \sigma T$ vs $10^3/T$.

A nearly constant number of electrons (for very small value of x) are indicated for the seebeck coefficient (α , $\mu\text{V}/\text{degree}$) of $\beta\text{-CdV}_2\text{O}_6$ and is temperature independent. This behaviour could be attributed to vacant oxygen lattice model of CdV_2O_6 . At the conditions of preparation of the sample, oxygen vacancies (defect structure) occur in CdV_2O_6 lattice leaving behind two electrons per half molecule oxygen resulting in an oxygen deficient lattice.



In other words, CdV_2O_6 can be represented as



Therefore, n -type semiconduction in $\beta\text{-CdV}_2\text{O}_6$ can be explained as follows: both Cd^{2+} (d^{10}) and V^{5+} (d^0) are in their highest oxidation states in cadmium metavanadate. The $\beta\text{-CdV}_2\text{O}_6$ has oxygen deficient lattice structure (4) due to deviation from oxygen stoichiometric composition of the lattice (3). The $2x$ electrons released per $\frac{1}{2}\text{O}_2$ molecule are trapped only on the V^{5+} (d^0) sites as localized electrons for conduction which results in the formation of V^{4+} (d^1) sites in the lattice of $\beta\text{-CdV}_2\text{O}_6$ (figure 3b) of the brannerite structure (Wadsley and Ruh 1966).

A negative and constant value ($-850 \mu\text{V}/\text{degree}$) of seebeck coefficient (α) is observed for the sample and is temperature independent between 185 and 750°C . Therefore, one can attribute that the only mode of transport in such a compound is via thermally activated jumps of localized electrons on vanadium sites of edge shared zig-zag sheets (b-axis) of VO_6 octahedra of the brannerite related $\beta\text{-CdV}_2\text{O}_6$ structure (figure 3b). This n -type semiconduction (V^{4+} : localized electrons in V^{5+} lattice) of CdV_2O_6 is reminiscent of n -type semiconduction which is well established for many metavanadates of the general formula MV_2O_6 (where $\text{M} = \text{Zn}^{2+}, \text{Mg}^{2+}, \text{Cu}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}$ etc) under normal and PO_2 conditions (Palanna 1976). However, evidences for the oxygen stoichiometry could be ascertained only from detailed studies of $p_0 - \Delta w$ (weight change)– T , and $p_0 - \sigma - T$ of $\beta\text{-CdV}_2\text{O}_6$ sample, which is desirable to confirm the above results. The infrared spectra observed for a few vanadates (figure 5) revealed that they are related to stretching vibration modes of vanadium–oxygen bond (and their force constant) of the VO_6 octahedra (or VO_5 , trigonal bipyramid) of the brannerite related (Wadsley and Ruh 1966) crystal structure. The $\beta\text{-CdV}_2\text{O}_6$ (monoclinic, $C2/m$) sample exhibited V–O stretching vibration modes at 855 cm^{-1} which is similar to that observed at 860 cm^{-1} for isostructural MgV_2O_6 (monoclinic, $C2/m$) with identical V^{5+} ion site symmetry. The observed infrared absorption band at 855 cm^{-1} is due to stretching vibration modes of various vanadium–oxygen bond distances (figure 3b) of distorted VO_6 octahedra (b-axis) of $\beta\text{-CdV}_2\text{O}_6$. The $\alpha\text{-CdV}_2\text{O}_6$ phase has V–O bond distances as given in figure 3a and has VO_5 (trigonal bipyramidal) group along the b-axis in the crystal structure. The stretching vibration modes of VO_5 groups should be similar to the one observed ($\sim 940 \text{ cm}^{-1}$) for the IR spectrum of the VO_5 groups of the isostructural CaV_2O_6 (monoclinic, $C2/m$) (Fredrickson and Hausen 1963) as shown in figure 5, which is due to higher force constants of the V–O bonds of VO_5 group than the VO_6 octahedra of $\beta\text{-CdV}_2\text{O}_6$; while the IR band characteristics of the isotypic crystal structure of less symmetric compound MgV_2O_6 (monoclinic, space group, $C2$) and ZnV_2O_6 (monoclinic, $C2$) are observed at about $860\text{--}870 \text{ cm}^{-1}$ (for VO_5 , tetragonal base pyramid).

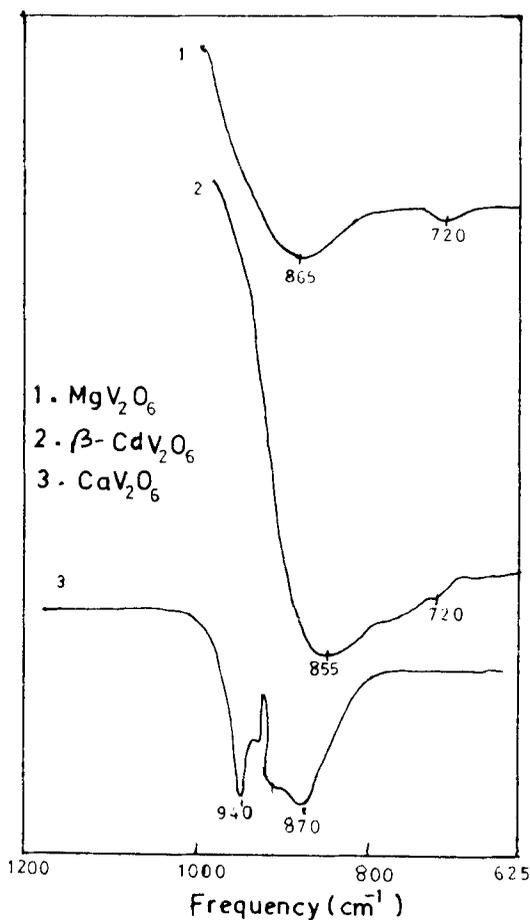


Figure 5. IR spectra of metavanadates.

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References

- Angenault J 1967 *C. R. Acad. Sci. Ser. C* **264** 435
 Angenault J 1970 *Revue de Chimie Mineral.* **17** 657
 ASTM Card file No. 20-189
 Bouloux J C and Galy J 1969 *Bull. Soc. Chem. Fr* **3** 736
 Bouloux J C, Perez G and Galy J 1972 *Bull. Soc. Fr. Mineral. Crystallogr.* **95** 130
 Brown J 1972 *J. Am. Ceram. Soc.* **55** 500
 Fredrickson L and Hausen D M 1963 *Anal. Chem.* **35** 818

- Lavaud D and Galy J 1972 *Bull. Soc. Fr. Mineral. Crystallogr.* **95** 134
Ng H N and Calvo C 1972 *Canadian J. Chem.* **50** 3619
Palanna O G 1975 *Studies on some mixed oxide systems of vanadium*, Ph. D Thesis, IIT, Bombay
Palanna O G 1979 *Proc. Indian Acad. Sci.* **A88** 19
Wadsley A D and Ruh R 1966 *Acta Crystallogr.* **21** 974
Tammann G and Kelsing H 1925 *Z. Anorg. Chem.* **t149** 21