

Phase transition in magnesium metavanadate

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Abstract. A new MgV_2O_6 phase having brannerite ($ThTiO_6$) related structure is obtained by solid state reaction and its x-ray powder diffraction and thermal studies are discussed. These studies confirm a structural transition at 833 K for non-stoichiometric magnesium metavanadate. The phase transition is reversible and the two forms of MgV_2O_6 have a closely related crystal structure.

Keywords. Nonstoichiometry; structural transition; crystal structure; magnesium metavanadate.

1. Introduction

A number of phase composition studies have been carried out on $MgO-V_2O_5$ (Pollard 1964; Galy and Pouchard 1967; Wollast *et al* 1969; Matveevicheva *et al* 1969; Eke and Brett 1973; Clark and Pick 1975). However, some contradictions are apparent on the true composition of magnesium vanadates. The results of the earlier studies indicated the following stable phases: the metavanadate, MgV_2O_6 ; the pyrovanadate, $Mg_2V_2O_7$ and the orthovanadate, $Mg_3V_2O_8$. Kerby and Wilson (1973) have identified a new phase of composition $2MgO \cdot 3V_2O_5$ which appears to be the stoichiometric equivalent of the oxygen deficient compound $\alpha-MgV_3O_8$ or $2MgO \cdot V_2O_4 \cdot 2V_2O_5$ prepared by Galy and Pouchard (1967) under reducing conditions. The investigations of Speranskay (1971) and King and Suber (1955) on the system deny the appearance of MgV_2O_6 but claims to have obtained $Mg_3V_4O_{13}$ or $3MgO \cdot 2V_2O_5$.

At normal pressure, the phases MV_2O_6 (where M = Mg, Co, Zn, Cu, Cd and Hg) have the brannerite ($ThTiO_6$) related structure (Wadsely and Ruh 1966). Some of these like ZnV_2O_6 (Angnault and Rimsky 1968; Angnault 1970) and CuV_2O_6 (Galy and Lavaud 1972) have been refined in space group C2 and others such as $\beta-CdV_2O_6$ (Galy and Bouloux 1969), CoV_2O_6 (Sauerbrei 1972) in centrosymmetric space group C2/m. CaV_2O_6 and $\alpha-CdV_2O_6$ (Bouloux *et al* 1972) have a slightly different structure as a result of a lost sixth v-o interaction.

A recent report (Shannon *et al* 1974) indicates that a series of MV_2O_6 compounds (where M = Mg, Mn, Co, Ni, Zn, Cu and Cd having orthorhombic-columbite type structure) have been synthesised at pressures of 50-80 Kbars and

temperatures of 800–1200° C. This is a series of brannerite–columbite transitions involving an increase in V^{5+} coordination and rearrangement of octahedra similar to the rutile α - PbO_2 transitions.

Although, the crystal structures of brannerite related series of MV_2O_6 (where $M = Mg, Co, Zn, Ca, Cu, Cd$ and Hg phases) are reported, only Cd and Hg are dimorphous. The crystal structures of α - CdV_2O_6 (Bouloux *et al* 1972) and β - CdV_2O_6 (Galy and Bouloux 1969) are well established. CuV_2O_6 has been reported to exist in two structures at normal pressure, both closely related to brannerite structures (Calvo and Monolescu 1973; Galy and Lavaud 1972). Apart from these studies no other information is available on the true composition and structural behaviour of MV_2O_6 phase at normal pressure as well as at different temperatures. This has prompted to investigate the x-ray diffraction and thermal effects of MgV_2O_6 phase synthesised under slightly reducing atmosphere and an attempt is made to elucidate the structural transition of the phase.

2. Experimental

2.1. Preparation of the sample

Analytically pure V_2O_5 and MgO were mixed in desired proportion (1 : 1) and the homogenised mixture was kept in a platinum boat inside a tubular furnace maintained at 900 K for 2–3 days under controlled atmosphere of hydrogen/argon gas mixture (H_2 gas at 1–2 l/hr). The final heating of the sample was done at 1000 K for 48 hr in an inert atmosphere and cooled to room temperature avoiding quenching of the sample.

2.2. X-ray diffraction studies

The compound synthesised by solid state reaction was characterised by x-ray powder diffraction technique using CuK_α radiation ($\lambda = 1.541 \text{ \AA}$; Ni filter). The high temperature x-ray diffraction studies were made on an MRC attachment to a Philips PW1051 diffractometer using CuK_α radiation. The sample was maintained at each temperature for about 15–20 min. A Pt–Pt/13% Rh thermocouple was used for the measurement of the sample temperature.

2.3. Differential thermal analysis (DTA)

This investigation was carried out using an apparatus fabricated in this laboratory and was recorded on an x-y potentiometric strip chart recorder (sensitivity : 1 mv/10 in.). The following conditions were maintained during the DTA run of the sample: sample holder—Pt cups; Reference material— Al_2O_3 (calcined at 1200° C); heating rate—8°/min; atmosphere—static air; amount of the sample taken—0.846 g.

3. Results and discussion

The x-ray powder diffraction data (table 1) of the compound do not match with any of the following known phases: $Mg_3V_4O_{13}$ (Speranskay 1971); MgV_3O_8 — α

Table 1. X-ray powder diffraction data for MgV_2O_6

Galy and Pouchard (1967)		Matveevicheva <i>et al</i> (1969)		Present work			
MgV_2O_6		MgV_2O_6		$\alpha\text{-MgV}_2\text{O}_6$		$\beta\text{-MgV}_2\text{O}_6$	
dÅ	I/I ₀	dÅ	I/I ₀	dÅ	I/I ₀	dÅ	I/I ₀
6.19	30	6.10	10	6.19	40	6.19	5
..	5.37	20
..	..	4.77	5	4.77	60	4.74	100
4.29	85	4.30	100	4.31	20	4.33	30
..	4.13	80
..	3.78	15
3.36	12	3.30	50	3.36	20
3.22	11	3.23	10	3.24	20	3.24	10
3.12	45	3.14	50	3.14	60	3.09	30
3.04	100	3.05	80	3.05	100	3.07	40
2.91	4	2.97	25	2.91	50
..	2.84	45
2.71	17	2.71	15	2.72	25	2.72	10
..	2.63	10
..	..	2.53	10	2.53	10
..	2.47	15	2.38	25
2.31	8	2.31	25	2.36	15
2.18	15	2.18	25	2.18	25
2.16	12	2.15	15	2.10	15	2.11	10
2.07	8	2.08	10	2.08	20	2.06	10
..	2.01	10
1.91	4	1.92	30	1.87	20
1.88	5	1.88	5	1.89	10	1.83	40
1.74	5	1.74	6	1.75	10	1.79	20
1.60	4	1.65	25
1.52	13	1.54	15	1.48	20
..	..	1.43	35	1.45	15

or $\text{Mg}_{1+x}(\text{V}_3\text{O}_8)_2$ (Galy and Pouchard 1967); MgV_2O_6 —II (Shannon *et al* 1974); MgV_2O_4 or MgVO_3 (Reuter *et al* 1947). However, it is observed that the x-ray diffraction data are similar to MgV_2O_6 phase reported by Galy and Pouchard (1967) and Matveevicheva *et al* (1969), except for few additional intensity peaks which appeared in the diffraction pattern of MgV_2O_6 phase matched with none of the strongest peaks of the component oxides. The compound synthesised thus is monophasic with a defect crystal structure of the type $\text{Mg}^{2+}\text{V}_{2-x}^{5+}\text{V}_{2x}^{4+}\text{O}_{6-x}$ where x is small under the conditions of its synthesis and is a structural analogue of MgV_2O_6 phase obtained by Calvo and Ng (1972). Direct evidence for the V^{4+} centres is obtained from the electron spin resonance measurement of this phase which gave a single absorption signal centred at $g = 1.96$ (not shown in the figure).

The x-ray diffraction of the sample was recorded at different temperatures between 300 and 1000 K. A good representative of the compound is given in table 1 for temperatures above and below the transition temperature. This shows that there is a stable high temperature phase above the transition temperature. The additional intensity peaks observed for the low temperature phase disappear for the high temperature phase. Further investigation of the compound revealed that the two polymorphs are reversible.

The DTA results of the magnesium metavanadate confirms the observation of the x-ray diffraction studies. The DTA curve (figure 1a) of the compound recorded under an atmosphere of static air showed two endothermic peaks at 833 K and 920 K respectively. The DTA peak observed at 833 K corresponds to the transition temperature of MgV_2O_6 which agrees with the x-ray diffraction results. The second peak at 920 K matches with the temperature reported by Pollard (1964) and Speranskay (1971). The endothermic peak at 833 K is small ($\Delta H = 3.15$ kcal/mole) and rather sharp indicating that the transition process is faster with low energy barrier and takes place with ease at the temperature. The thermal cycling of the DTA of the compound carried below 1000 K confirms that the two phases are reversible (figures 1a and 1b).

From these results it appears that the low and high temperature phases have a closely related crystal symmetry such that the crystal structure may change rapidly from one structural type to the other with an absorption of a small amount of energy ($\Delta H = 3.15$ kcal/mole). In this case, the crystal symmetry may remain unchanged and even the volume change during the structural transition may also be very small as observed in the case of cadmium analogue (Galy and Bouloux 1969).

If the crystal structure of the low temperature of MgV_2O_6 and CuV_2O_6 phases are isotopic (C2), then it is found from the x-ray diffraction studies that the structural characteristics are intermediate between the α - and β -phases of CdV_2O_6 (Bouloux *et al* 1972) in which coordination changes in two structures: a trigonal bipyramidal (α - CdV_2O_6 ; C2/m) and the other distorted octahedra (β - CdV_2O_6 ; C2/m).

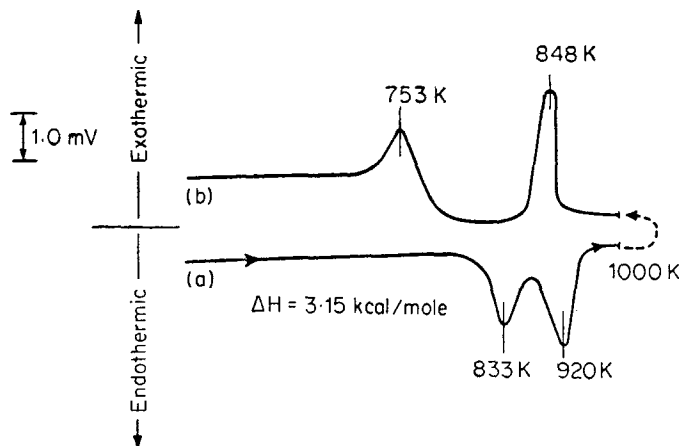


Figure 1. Differential thermal analysis curves for MgV_2O_6 in air on a. heating and b. cooling.

The structural transition occurs between brannerite related crystal structures as a result of the passage of one structural type to the other resulting in a small displacement of the atoms followed by a little rotation of $(V_2O_6)_n^{2n-}$ chains. The coordination is trigonal-bipyramidal in the former case and tetragonal base pyramid for the latter. The third type results only when MgO_6 group rotates and displaces about the b -axis giving an octahedral coordination resulting in a stronger $v-o$ interaction with an increase in the coordination of vanadium (6-fold). This mode of passage during transition is followed by a contraction in the unit cell volume and a decrease in the value of the cell parameters and a marked increase in the angle β .

The experimental data indicate that the low temperature α - MgV_2O_6 phase has space group C2 (tetragonal base pyramid) and the high temperature phase, β - MgV_2O_6 , is C2/m of monoclinic symmetry of the brannerite related structure. However, the proper symmetry and space group of the phases of MgV_2O_6 could only be assigned after a detailed single crystal investigation of each phase which is desirable at this stage to confirm the experimental results.

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