

Phase transition in copper(II) pyrovanadate

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Abstract. A new phase $\text{Cu}_2\text{V}_2\text{O}_7$ synthesized, exhibits phase transitions between 475°C and 500°C. These phase transitions are reversible with ease in contrast to $\alpha \rightarrow \beta$ phase transition at 712°C of $\text{Cu}_2\text{V}_2\text{O}_7$ phase reported earlier. These phase transitions are identified by DTA technique and characterized by detailed XRD investigations at different temperatures. The crystal structures of these $\text{Cu}_2\text{V}_2\text{O}_7$ phases are related to either thortveitite ($\text{Sc}_2\text{Si}_2\text{O}_7$) type or a modification of it.

Keywords. Copper(II) pyrovanadate; phase transition; crystal structure.

1. Introduction

A considerable interest has been generated to study the crystal chemistry of the type $\text{M}_2\text{V}_2\text{O}_7$ where M is divalent cation since the structures of these types are governed by the rules based on their relative dimensions, M/o and V/o. These compounds can be related to either thortveitite structure (Cruickshank *et al* 1962) (figure 1) or a modification of it. Structural studies of metal pyrovanadates show a variety of new structural modifications: thortveitite structure for $\text{Mn}_2\text{V}_2\text{O}_7$ (Dorm and Mariander 1967), $\text{Cd}_2\text{V}_2\text{O}_7$ (Calvo and Au 1967), $\text{Cu}_2\text{V}_2\text{O}_7$ (Ayamonino *et al* 1973), and related structures in $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$ (Gopal and Calvo 1973; Angenault 1970), $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ (Mercurio *et al* 1973b), $\text{Mg}_2\text{V}_2\text{O}_7$ (Gopal and Calvo 1974), $\beta\text{-Sr}_2\text{V}_2\text{O}_7$ (Baglio and Dann 1971); $\text{Ca}_2\text{V}_2\text{O}_7$ (Monelescu 1974), $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ (Mercurio *et al* 1973a; Calvo and Faggiani 1975) and $\text{Mn}_2\text{V}_2\text{O}_7$ (Ziolkowski and Deimbaj 1978).

The investigations of copper(II) ion in vanadates are curious ones since Cu^{2+} (d^9) could induce Jahn – Teller distortion of metal-oxygen polyhedra in $\text{Cu}_2\text{V}_2\text{O}_7$ lattice and also in crystal structures of the type $\text{M}_2\text{V}_2\text{O}_7$ (where $\text{M} = \text{Cu}^{2+}$, Zn^{2+} etc) having the crystal symmetry other than monoclinic C^2/m , phase transition could be predicted at higher temperatures.

The $\alpha \rightarrow \beta$ phase transition of $\text{Cu}_2\text{V}_2\text{O}_7$ was observed (Fluery *et al* 1969), but

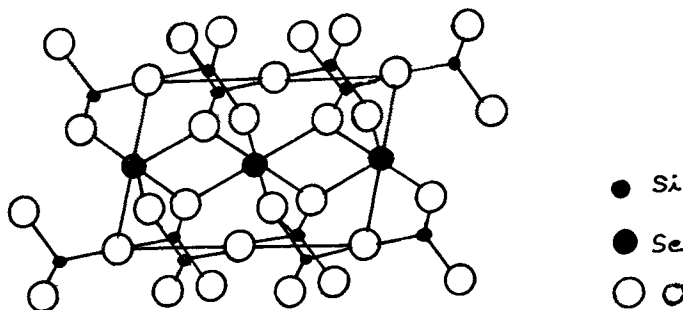


Figure 1. Structure of thortveitite ($\text{Sc}_2\text{Si}_2\text{O}_7$) projected on b-face.

ambiguity still persists regarding the identification of structural phases in the above phase transformations at 712°C. However, many structural types of $\text{Cu}_2\text{V}_2\text{O}_7$ related to thortveitite family were reported (Riassento 1958; ASTM card file No. 16-417), orthorhombic Fdd2 (Mercurio *et al* 1973a; Calvo and Faggiani 1975) and monoclinic C2/m (Fluery *et al* 1969; Ayamonino *et al* 1973). Therefore, a detailed investigation of DTA and high temperature XRD characterization of $\text{Cu}_2\text{V}_2\text{O}_7$ was carried out to study the $\alpha \rightarrow \beta$ phase transition and to identify and index the possible structural modifications.

2. Experimental

2.1 Preparation of $\text{Cu}_2\text{V}_2\text{O}_7$ sample

The copper(II) pyrovanadate was synthesized by a conventional solid state technique by heating in air an intimate mixture of $2\text{CuO}:\text{V}_2\text{O}_5$ (both of high purity grade at 600°C for 24 h) in a Pt crucible which was then melted in air. The sample was then annealed (10/min) slowly in air to room temperature (sample I). Another batch of $\text{Cu}_2\text{V}_2\text{O}_7$ was synthesized as above, annealed slowly to room temperature; again heated to 550°C for 15 min and quenched to liquid N_2 temperature (80 K) (sample II).

2.2 X-ray diffraction studies

The $\text{Cu}_2\text{V}_2\text{O}_7$ samples synthesized above were characterized by X-ray powder diffraction technique using CuK_α radiation ($\lambda = 1.541 \text{ \AA}$, Ni filter).

The high temperature XRD studies were made on an MRC attachment to a Philips PW 1051 diffractometer using CuK_α radiation. The sample was maintained at each temperature for about 15 min.

A Pt-Pt 13% Rh thermocouple was used for measuring the temperature of the sample.

2.3 Differential thermal analysis

The differential thermal analysis (DTA) was carried out using a fabricated unit and was recorded on a strip chart recorder (sensitivity: 1 mV/10 inches). The following conditions were maintained during DTA run of the samples: (1) sample holder – Pt cups, reference material – Al_2O_3 , heating rate – 8/min, atmosphere – static air, standard material – $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$.

3. Results and discussion

The DTA of $\text{Cu}_2\text{V}_2\text{O}_7$ (sample I) phase obtained as above is shown in figure 2. The new $\text{Cu}_2\text{V}_2\text{O}_7$ phase exhibits endothermic peak at 475°C and a knee at 500°C indicating phase transformations (curve 1) (m.p. 780°C). On cooling the DTA sample in air in DTA unit, two distinct exotherms (curve 2) at 485°C and 435°C were obtained showing the reversibility of the process. A lower temperature (712°C) phase transition for $\text{Cu}_2\text{V}_2\text{O}_7$ has not been reported to date. The DTA run of the above sample

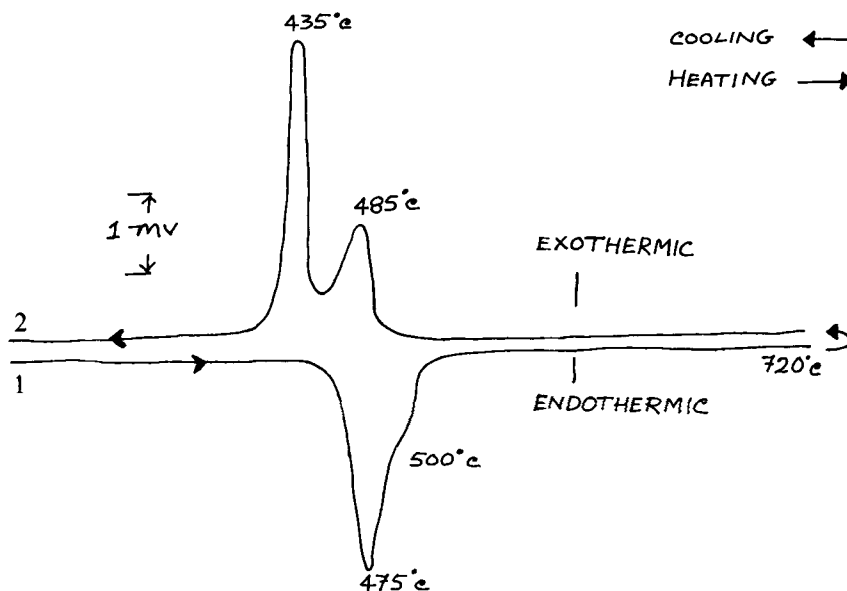


Figure 2. DTA of $\text{Cu}_2\text{V}_2\text{O}_7$ in static air (sample-I).

under a set of above conditions were repeated several times to confirm this and the DTA results were reproducible and reversible.

The sample I thus prepared was characterized by X-ray powder diffraction studies and identified as $\text{Cu}_2\text{V}_2\text{O}_7$ (Riassento 1958; ASTM card file No 16-417) (figure 3(I)) and was isostructural to $\text{Cu}_2\text{V}_2\text{O}_7$ phase obtained by Mercurio *et al* (1973a) and Calvo and Faggiani (1975) which they called $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$. This confirms therefore that the $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ (sample I) could only be obtained from a melt of the phase obtained from $2\text{CuO}:\text{V}_2\text{O}_5$ by solid state reaction in air atmosphere which was as described earlier.

To confirm the predicted structural modifications at high temperature, we have quenched sample I from 550°C to liquid nitrogen temperature (80 K) to stabilize the possible high temperature modification (sample II). The XRD pattern of this $\text{Cu}_2\text{V}_2\text{O}_7$ phase is shown in figure 3(II).

A new XRD 2θ -intensity spectrum was obtained (e.g. reflections as $d\text{\AA}$: 3.60 \AA , 3.09 \AA and 3.06 \AA) indicating a new high temperature $\text{Cu}_2\text{V}_2\text{O}_7$ phase. The strongest intensity reflection of the phase (sample I) positioned at 3.27 \AA disappeared and a new strongest reflection peak appeared at 3.60 \AA . Other peaks appeared at 3.09 \AA , 3.06 \AA , 2.11 \AA , etc. Incidentally, the entire XRD 2θ -intensity reflections of the high temperature form (quenched sample II) match exactly with the XRD data presented by Mercurio *et al* (1973b) known as $\beta\text{-Cu}_2\text{V}_2\text{O}_7$.

This new XRD 2θ -intensity reflections of quenched sample of $\text{Cu}_2\text{V}_2\text{O}_7$ prompted us to reinvestigate, to trace the possible structural modifications at high temperature and to identify the phases at low and high temperatures and their structural relationship based on this biography of the sample.

The high temperature X-ray diffractograms of the sample $\text{Cu}_2\text{V}_2\text{O}_7$ (sample I) were taken between 25°C and 625°C at an interval of about 50°C . The X-ray diffractograms were recorded only after the sample was maintained at equilibrium temperature for

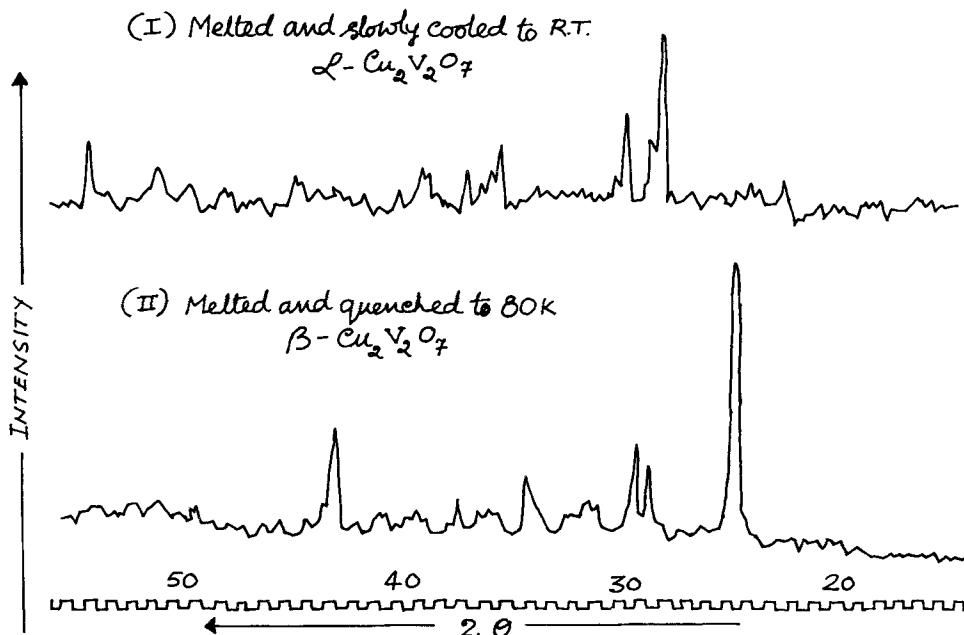
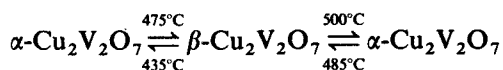


Figure 3. XRD patterns of $\text{Cu}_2\text{V}_2\text{O}_7$ samples (I) and (II).

proper nucleation and growth of the phase during heating and cooling cycles. A representative portion of the high temperature XRD of this sample I that was recorded at 25°C, 478°C and 528°C is shown in figure 4. The XRD patterns clearly showed phase transformations at high temperature. The XRD reflections recorded during the cooling cycle of $\text{Cu}_2\text{V}_2\text{O}_7$ also confirmed the reversibility of the phases. These observations (both DTA and XRD) were in contrast to the $\alpha \rightarrow \beta$ transformation observed at 712°C by Fluery *et al* (1969) where $\beta \rightarrow \alpha$ transition was sluggish.

As is evident from figure 4 the XRD reflections of $\text{Cu}_2\text{V}_2\text{O}_7$ (sample I) at 3.26 Å was the strongest at 25°C and fell gradually in intensity with temperature and disappeared altogether above 478°C. Curiously enough, the same reflection ($d: 3.27$ Å) appeared above 525°C. The decreasing intensity of reflection at 3.27 Å was accompanied by the growth characteristic of $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ phase (i.e. 3.60 Å, 3.09 Å, 3.06 Å etc). It was noticed that when the $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ was heated to a temperature above 525°C the strongest reflection was observed (3.60 Å) and few others disappeared. The entire XRD data obtained above 525°C was similar to the XRD data $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ taken at 25°C. This points out that the phase existing above 525°C is also isostructural to $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ (or a closely related thortveitite structure, figure 1). Thus high temperature XRD confirmed and corroborated our DTA results.

The DTA and XRD of $\text{Cu}_2\text{V}_2\text{O}_7$ (sample I) can be summarized as below:



All the three phases of $\text{Cu}_2\text{V}_2\text{O}_7$ were identified, characterized and indexed. The XRD data of these crystal phases are given in table 1.

The room temperature phase of $\text{Cu}_2\text{V}_2\text{O}_7$ is identified as $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ which is

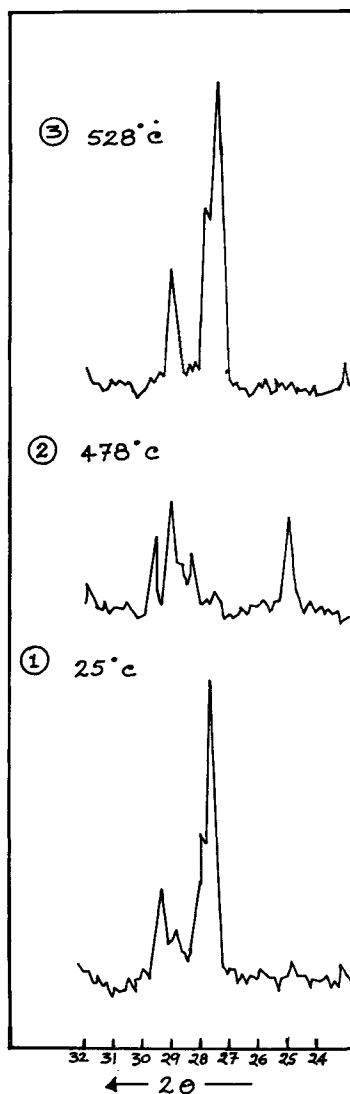


Figure 4. XRD for $\text{Cu}_2\text{V}_2\text{O}_7$ at 25°C (1), 478°C (2) and 528°C (3) respectively.

isotypic to the phase reported by Mercurio *et al* (1973a) and Calvo and Faggiani (1975). This $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ has crystal symmetry orthorhombic $Fdd2$; while the $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ phase observed at 478°C is also isostructural to the phase reported by Mercurio *et al* (1973b) with crystal symmetry monoclinic $C2/c$. In contrast, Ayamonino *et al* (1972) and Fluery *et al* (1969) reported a different $\text{Cu}_2\text{V}_2\text{O}_7$ phase with thortveitite structure with the crystal symmetry monoclinic $C2/m$ (which they obtained only on heating $2\text{CuO}\cdot\text{V}_2\text{O}_5$ at 600°C for 80 h in air). Interestingly, the $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ phase is unstable above 525°C and reverts to $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ structure. Since this high temperature $\text{Cu}_2\text{V}_2\text{O}_7$ phase is isotypic to $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$, the crystal symmetry of this high temperature phase is orthorhombic $Fdd2$ (or a closely related structure).

Table 1. XRD data for $\text{Cu}_2\text{V}_2\text{O}_7$ at 25°C, 478°C and 528°C.

$\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ at 25°C			$\beta\text{-Cu}_2\text{V}_2\text{O}_7$ at 478°C			$\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ at 528°C		
$d\text{\AA}_{\text{obs}}$	I/I_0	hkl	$d\text{\AA}_{\text{obs}}$	I/I_0	hkl	$d\text{\AA}_{\text{obs}}$	I/I_0	hkl
5.170	10	400	5.340	15	110	5.160	15	400
4.970	8	111	4.200	15	111	4.970	8	111
4.100	15	311	4.100	10	112	4.100	20	311
3.896	8	220	3.980	15	020	3.890	15	220
3.266	100	420	3.680	5	027	3.250	100	420
3.225	30	511	3.600	100	200	3.210	70	511
3.070	40	202	3.160	40	112	3.070	45	202
3.050	40	—	3.090	100	113	3.040	10	—
2.585	15	800	3.040	75	022	2.580	20	800
2.560	20	022	2.771	10	221	2.558	25	022
2.487	30	222	2.640	60	222	2.480	30	222
2.407	10	331	2.490	10	131	—	—	—
2.354	10	602	2.460	20	113	—	—	—
2.292	10	422	2.360	5	004	2.292	15	422
2.203	20	802	2.350	20	131	2.203	10	802
2.183	25	521	2.300	15	310	2.180	10	531
2.102	20	040	2.111	40	222	2.099	5	040
2.096	20	911	2.080	45	133	2.090	30	911
—	—	—	2.057	30	224	2.072	20	113
2.054	30	622	1.950	20	041	2.048	20	622
1.945	6	440	1.850	15	133	1.945	20	440
—	—	—	1.824	5	223	1.940	10	731
—	—	—	1.778	20	225	1.734	10	242
1.712	30	931	1.693	10	423	1.710	40	931
1.700	20	133	1.674	10	206	1.700	20	133
1.631	10	840	1.606	15	135	1.630	30	840
1.611	20	004	1.564	10	150	1.611	20	004
1.576	15	533	1.560	10	151	—	—	—

These structures can be considered as members of the thortveitite type with nearly staggered $(\text{V}_2\text{O}_7)^{4-}$ groups. These pyrovanadate groups lie in paralleled sheets bonded by Cu^{2+} (d^9) cation. Each copper atom is surrounded by five oxygen atoms forming a distorted trigonal bipyramid.

It is remarkable that when $\text{Cu}_2\text{V}_2\text{O}_7$ phase is melted and annealed (or quenched) oxygen vacancies or depletion of oxygen to a smaller extent could be expected in the copper-vanadium-oxygen lattice. On oxygen depletion either by annealing or by quenching from high temperatures, the linear chains may be disrupted and the oxygen atoms rearranged in the lattice. It was interesting to observe that the superconducting cuprate perovskites were found to be structurally sensitive to the oxygen content (Cava *et al* 1987; Jorgensen *et al* 1987). It was observed in $\text{YBa}_2\text{Cu}_3\text{O}_x$ systems that the superconducting orthorhombic phase stabilized at room temperature for an oxygen content $6.5 < x < 7$ (Jorgenson *et al* 1987). Below $x = 6.5$, the high temperature tetragonal semiconducting phase stabilized and the stabilities of such phases based on oxygen stoichiometry appeared to depend on the biography of the samples synthesized. Thus $\text{Cu}_2\text{V}_2\text{O}_7$ phase obtained was stabilized under the above conditions of preparation with a oxygen deficient lattice. The $\text{Cu}_2\text{V}_2\text{O}_7$ phase structure appeared

to be sensitive and prone to transformation at high temperature due to Cu^{2+} (d^9) in oxygen lattice and/or vacancy disordered oxygen lattice. *n*-Type semiconductivity was observed for $\text{Cu}_2\text{V}_2\text{O}_7$ (Palanna 1975) which confirmed the oxygen deficient lattice of $\text{Cu}_2\text{V}_2\text{O}_7$. But for this behaviour, $\text{Cu}_2\text{V}_2\text{O}_7$ phase would have been an insulator.

In conclusion, we would attribute that molten $\text{Cu}_2\text{V}_2\text{O}_7$ when annealed (or quenched) to room temperature has an oxygen deficient/vacancy disordered structure. This stabilized crystal structure at room temperature has XRD data similar to $\text{Cu}_2\text{V}_2\text{O}_7$ XRD of Riassento (1958) (ASTM card File No 16-417) obtained below the melting point of $\text{Cu}_2\text{V}_2\text{O}_7$. Both the samples obtained above and below the melting point (780°C) of $\text{Cu}_2\text{V}_2\text{O}_7$ have identical XRD pattern indicating that they have the same basic structure; but as was evident from our investigation, the thermal behaviour (DTA) was different for the former exhibiting temperature phase transition and that too, at a temperature much lower than 712°C as reported earlier (Fluery *et al* 1969).

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