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Structural Modification of $Mn_2V_2O_7$: Thermal Expansion and Solid Solutions

T. I. Krasnenko and M. V. Rotermel

*Institute of Solid State Chemistry, Urals Branch, Russian Academy of Sciences,
ul. Pervomaiskaya 91, Yekaterinburg, 620990 Russia
e-mail: Krasnenko@ihim.uran.ru*

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Abstract—Thermally activated structural change of $Mn_2V_2O_7$ has been studied at –180 to 1000°C. The patterns of the solid solutions based on magnesium pyrovanadate stability upon isovalence substitution have been induced.

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The interest to manganese pyrovanadate $Mn_2V_2O_7$ is due to its remarkable set of properties. At room temperature, manganese pyrovanadate is an antiferromagnetic material [1] with low coercive force and remanent magnetization, characterized by sharp anisotropy of properties [2–5]. $Mn_2V_2O_7$ is also considered a promising thermistor material with negative temperature coefficient of conductivity [6]. Furthermore, $Mn_2V_2O_7$ is a unique dark pigment with high reflectance in the infrared spectral range, capable of reducing the IR-induced heat accumulation. Thus, materials based on manganese pyrovanadate will minimally absorb near-infrared radiation which is applicable in developing paints and coatings for automotive, aerospace, and building industries [7].

Thermal behavior of $Mn_2V_2O_7$ has been reported in a number of papers. $Mn_2V_2O_7$ may exist in two modifications with phase transition occurring about the room temperature; it melts congruently at 1080°C [1, 2, 8]. The polymorphic transition is endothermic upon heating ($T_{\max}$ = 28°C, ΔH = 3.43 kJ mol^{-1}) and exothermic upon cooling ($T_{\max}$ = 17°C, ΔH = –4.0 kJ mol^{-1}). Noteworthy, the first order phase transition close to room temperature is a drawback for practical use of any type of material (monocrystal, ceramics, $Mn_2V_2O_7$-based composites) at 20–60°C, as the material will be disrupt during temperature cycling. Phase transition temperature may be changed upon formation of $Mn_2V_2O_7$-based solid solutions.

Below room temperature, α-$Mn_2V_2O_7$ crystallizes in triclinic system ($P\bar{1}$ space group) with the following parameters at 20°C: a = 6.868(2), b = 7.976(2), and c = 10.927(2) Å; α = 87.81(1), β = 72.14(1), and γ = 83.08(1)°; V = 564.5(5) Å^3; Z = 4. At 50°C, β-$Mn_2V_2O_7$ crystallizes in the thortveitite structure (monoclinic system, $C\,2/m$ space group; a = 6.7129(6), b = 8.7245(5), and c = 4.9693(4) Å; β = 103.591(8)°; V = 282.88(4) Å^3; Z = 2 [2]. Crystal structure of both manganese pyrovanadate modifications consists of honeycomb layers of Mn^{2+} ions separated with [VO_4] groups, pairwise bound by bridging oxygen. Layered arrangement of the manganese ions stipulates the $Mn_2V_2O_7$ magnetic properties anisotropy [2–5]. The conformation of vanadium-oxygen groups is different in the cases of α-$Mn_2V_2O_7$ and β-$Mn_2V_2O_7$: the VOV angles are less than 180° in the α-modification, being flat in the β-modification (Fig. 1).

The study of the samples annealed at 950°C has revealed [9] that another polymorphic transition of $Mn_2V_2O_7$ occurs above 700°C, never mentioned previously. The existence of the third polymorphic modification has been supported in [6], reporting monoclinic γ-$Mn_2V_2O_7$ with the following unit cell parameters: a = 7.73091, b = 6.640788, and c = 6.70779 Å; β = 98.7086°; V = 340.40(3) Å^3. However, the temperature range of the modification stability and the β > γ-$Mn_2V_2O_7$ phase transition enthalpy has not been reported, the possibility of the reverse transition has not been discussed either. The information on manganese pyrovanadate isomorphic capacity (with the accuracy of ±5 mol %) can be found in [10, 11]. For the $Mn_2V_2O_7$–$M_2V_2O_7$ systems (with M being Co, Ni, Mg, Cu, or Zn), at room temperature the intermediate compounds are absent, and the solid

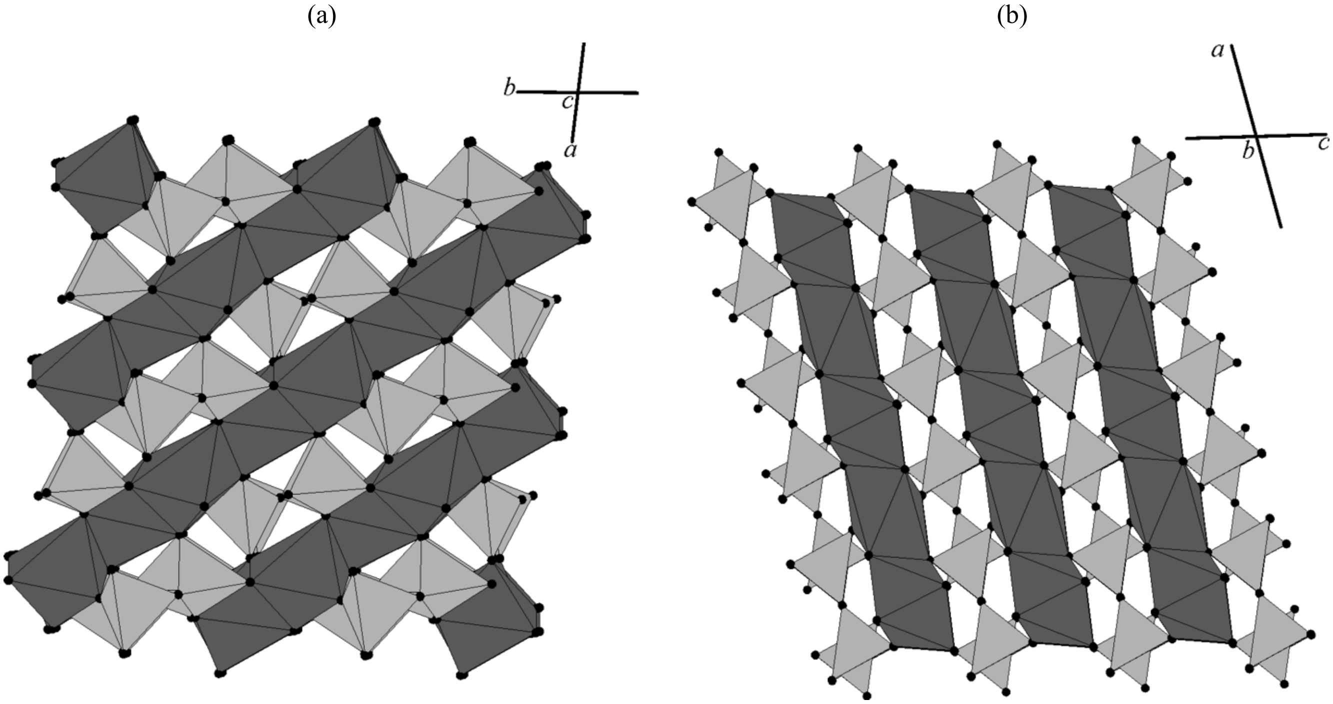

Fig. 1. Crystal structures projections of α-$Mn_2V_2O_7$ (a) and β-$Mn_2V_2O_7$ (b) onto the (*ab*) and (*ac*) planes, respectively.

solutions are formed by the α-modification. Consequently, the manganese ions substitution with smaller cations has decreased the temperature of phase transition from less symmetric ($P\bar{1}$ space group) to more symmetric ($C\,2/m$ space group) modification.

The solid solution based on α-$Mn_{2-2x}M_{2x}V_2O_7$ may contain up to 30 mol % of $Co_2V_2O_7$, 20 mol % of $Ni_2V_2O_7$, 25 mol % of $Mg_2V_2O_7$, 10 mol % of $Cu_2V_2O_7$, and 35 mol % of $Zn_2V_2O_7$. Upon manganese ions substitution with larger calcium ions the thortveitite structure has been preserved with up to 60 mol % of $Ca_2V_2O_7$, the perfect isomorphism has been observed in the case of manganese substitution with cadmium ion.

To sum up, the references analysis has shown that the information on thermal and chemical transformations of manganese pyrovanadate is not complete: the reliable crystal-chemical validation of γ-$Mn_2V_2O_7$ is still needed, the data on the range of solid solutions based on α-$Mn_2V_2O_7$ have to be refined, and the information on thermal expansion coefficient of $Mn_2V_2O_7$ structural modifications is absent. To fill in the gap, this work aimed at study of thermally activated $Mn_2V_2O_7$ structural deformation in the range of –180 to 1000°C, and at determination of stability of the solid solutions based on magnesium pyrovanadate upon isovalence substitution.

Thermal behavior of $Mn_2V_2O_7$. In the X-ray diffraction patterns recorded in the temperature range of –180 to 1000°C, no diffraction maxima other than assigned to α-$Mn_2V_2O_7$ or β-$Mn_2V_2O_7$ were observed. In the view of that, the results reported in [6] were carefully revised. Firstly, in should be noted that the γ-modification of manganese pyrovanadate described in [6] was prepared from Mn_2O_3 and VO_2 taken in the 9:1 (w/w) ratio. At that ratio, the interaction could result in a mixture of phases, either ($Mn_2V_2O_7$ + Mn_2O_3) or ($Mn_3V_2O_8$ + Mn_2O_3), with significant excess of Mn_2O_3 (1 mol of $Mn_2V_2O_7$ corresponded to 9 moles of Mn_2O_3). Indeed, the comparison of the X-ray diffraction pattern assigned to γ-$Mn_2V_2O_7$ in [6] with similar data for α-$Mn_2V_2O_7$, β-$Mn_2V_2O_7$ [2], Mn_2O_3 [11], and $Mn_3V_2O_8$ [12] demonstrated that "γ-$Mn_2V_2O_7$" was in fact the mixture of β-$Mn_2V_2O_7$ and Mn_2O_3 (bixbyite) phases. Furthermore, results of X-ray diffraction study of the annealed mixtures of Mn_2O_3 and VO_2 with increasing VO_2 ratio [6] pointed at increasing the content of the reaction product, β-$Mn_2V_2O_7$, up to practically single-phase β-$Mn_2V_2O_7$ at 1:1 (w/w) Mn_2O_3 and VO_2 ratio (note that the single-phase $Mn_2V_2O_7$ could be obtained at the molar ratio of Mn_2O_3 and VO_2 equal to 1:2). We performed the experiment described in [6] and showed that "γ-$Mn_2V_2O_7$" was a mixture of β-$Mn_2V_2O_7$ and Mn_2O_3

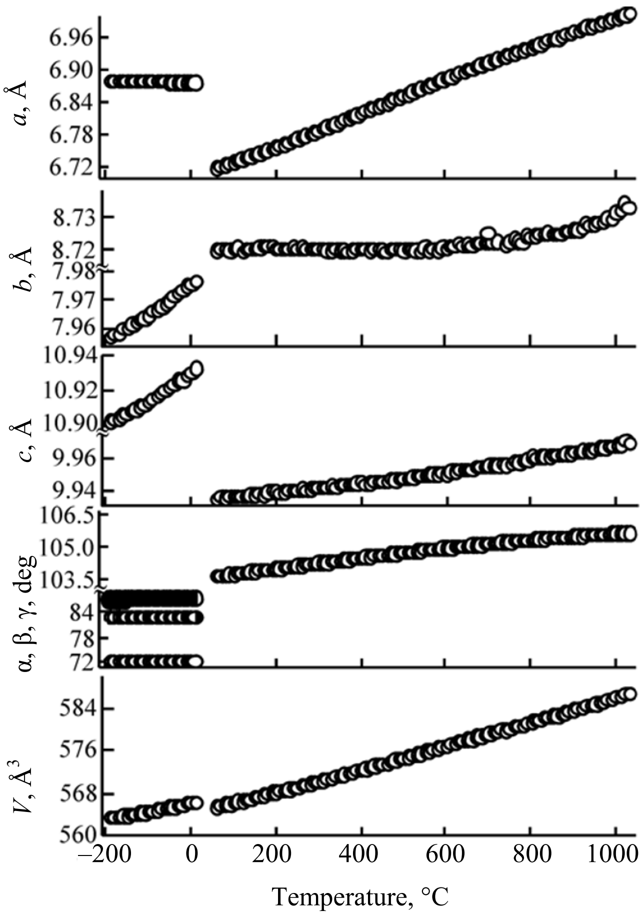

Fig. 2. $Mn_2V_2O_7$ unit cell parameters as functions of temperature.

phases. Thus, our results and the references analysis proved that under normal atmospheric pressure $Mn_2V_2O_7$ could only crystallize in two polymorphic modifications: triclinic α-$Mn_2V_2O_7$ and monoclinic β-$Mn_2V_2O_7$.

Thermal expansion of $Mn_2V_2O_7$. The unit cell parameters of manganese pyrovanadate were determined in the temperature range of –180 to 1000°C (Fig. 2). With thermal expansion coefficients (upon heating from –180 to 20°C) being of 1.26×10^{-5} and 1.38×10^{-5} deg^{-1}, respectively, heat-induced deformation of the α-$Mn_2V_2O_7$unit cell was the most pronounced along the *b* and *c* axes. The highest thermal expansion coefficient was found in the case of α angle ($\alpha_\alpha = 1.42\times10^{-5}$ deg^{-1}). The changes of *a*, β, and γ were not significant: $\alpha_a = -0.20\times10^{-5}$, $\alpha_\beta = -0.50\times10^{-5}$, and $\alpha_\gamma = -0.12\times10^{-5}$ deg^{-1}. The unit cell volume linearly increased with temperature, the volume thermal expansion coefficient being of $\alpha_V = 2.57\times10^{-5}$ deg^{-1}.

At 25±5°C, the polymorphic transformation occurred, accompanied with the stepwise decrease of the unit cell volume. In the case of β-$Mn_2V_2O_7$, the monoclinic plane (*ac*) deformation determined the temperature-induced changes: the parameters *a*, *c*, and β increased, while *b* was constant up to about 600°C. The thermal expansion coefficients in the temperature range of 50–1000°C were as follows: $\alpha_a = 4.35\times10^{-5}$ deg^{-1}, α_c changed from 0.30×10^{-5} to 0.44×10^{-5} deg^{-1}, α_β changed from 3.10×10^{-5} to 1.64×10^{-5} deg^{-1}, $\alpha_V = 4.25\times10^{-5}$ deg^{-1}. Thermal expansion along *b* axis was negligible at 50 to 600°C; at higher temperatures expansion in that direction started, and at 900–1000°C the respective thermal expansion coefficient was 0.55×10^{-5} deg^{-1}.

Thermal expansion anisotropy was due to layered structure of both $Mn_2V_2O_7$ modifications. The most prominent thermally induced changes occurred along the planes containing the $[MnO_6]$ polyhedra, being much smaller along the direction perpendicular to those layers. In α-$Mn_2V_2O_7$, the (*bc*) plane was the most deformed upon temperature change, whereas in the case of β-$Mn_2V_2O_7$ the changes were most significant along the (*ac*) plane (Fig. 1).

Solid solutions based on $Mn_2V_2O_7$. According to the X-ray powder diffraction data, the ranges of the α-$Mn_{2-2x}M_{2x}V_2O_7$ solid solution stability were 40±2 mol % of $Co_2V_2O_7$, 27±2 mol % of $Ni_2V_2O_7$, 25±2 mol % of $Mg_2V_2O_7$, 10±2 mol % of $Cu_2V_2O_7$, and 5±2 mol % of $Zn_2V_2O_7$. Studies of the $Mn_2V_2O_7$–$Cd_2V_2O_7$ and $Mn_2V_2O_7$–$Ca_2V_2O_7$ systems revealed that those manganese pyrovanadate solid solutions crystallized in the β-$Mn_2V_2O_7$ structure. Similarly to found in [9–11], manganese ions could be completely substituted with cadmium ions, whereas the $Mn_{2-2x}Ca_{2x}V_2O_7$ solid solutions were formed with up to 64±2 mol % of $Ca_2V_2O_7$.

The manganese ions substitution with larger cadmium or calcium ions led to structural changes similar to the heating-induced ones: the high-temperature β-modification was stabilized, the unit cell volume *V* was increasing. The monoclinic plane was deformed primarily due to *a* change, whereas *c* and β changes were negligible. Upon Mn^{2+} substitution with ions of cobalt, nickel, magnesium, copper, or zinc, the low-temperature α-modification was observed at room temperature, and the unit cell volume of the solid solution was decreasing with the dopant concentration, due to decrease of *a* and *c*. The angular parameters as well as *b* were almost constant with the substituting ion concentration, and did not depend on the ion nature. Noteworthy, the manganese ions substitution with smaller ions of cobalt, nickel, magnesium, copper, and zinc led to the increase of α–β phase transition temperature; the effect of substitution with the larger ions was the opposite. For example, in the case of $Mn_{1.50}Mg_{0.50}V_2O_7$ (25 mol % of $Mg_2V_2O_7$), the phase transition temperature was of (190±10)°C [8].

The area of manganese pyrovanadate solid solutions stability was determined by the relative volume difference of the substituted (MnO) and substituting (MO) metal-oxygen polyhedra. The (MO) volumes were calculated taking into account the data on the structures of $M_2V_2O_7$ (M = Ni, Co, Mg, Cu, Zn, Cd, and Ca) [13–16]. The volume difference relative to the (MnO) polyhedron volume was in line with the range of the respective homogeneous solid solution stability: with lower $\Delta V/V_{MnO}$ the $Mn_{2-2x}M_{2x}V_2O_7$ solution stability range was wider (see table and Fig. 3).

The deduced relationship was used to estimate the conditions of the solid solutions stability upon double isovalence cation substitution. Having known the crystal lattice parameters at a given concentration of the first substituting ion M^1, we could calculate the mean size of the $[Mn(M^1)O]$ polyhedron as well as the relative difference of the $[Mn(M^1)O]$ and $[(M^2)O]$ polyhedra volume; then, the range of the solution stability was estimated graphically.

EXPERIMENTAL

Manganese pyrovanadate $Mn_2V_2O_7$ was prepared via the solid-phase synthesis from Mn_2O_3 and V_2O_5 (both of extra pure grade), taken in the desired ratio. Equilibrated samples of the $Mn_{2-2x}M_{2x}V_2O_7$ systems (M = Co, Ni, Cu, or Zn) were obtained via the solid-phase synthesis from $Mn_2V_2O_7$ and the respective pyrovanadate (prepared in turn from the oxides similarly to $Mn_2V_2O_7$).

X-ray diffraction studies at low and high temperatures were performed *in situ* at air using the D8 ADVANCE diffractometer (CuK_α-radiation, β-filter, position-sensitive detector VANTEC) in the temperature range from –180 to 1000°C. The sample was heated with 10° steps at a rate of 0.5 deg s^{-1}. The diffraction patterns were taken at the 30 s point. The phase analysis of the solid solutions was performed using STADI-P autodiffractometer, the samples homogeneity was checked by comparison of the diffraction patterns with the data on all structural modifications of $Co_2V_2O_7$, $Ni_2V_2O_7$, $Cu_2V_2O_7$, $Zn_2V_2O_7$, and $Mn_2V_2O_7$ [13].

Crystal-chemical properties of $M_2V_2O_7$ (M = Ni, Co, Mg, Cu, Zn, Cd, Ca, Mn) and $Mn_{2-2x}M_{2x}V_2O_7$ solid solutions

$M_2V_2O_7$	r_M^{2+}, Å [17]	V_{MO}, Å^3	$\Delta V_{MnO-MO}/$ $/V_{MnO}\times10^{-2}$	x, mol %
$Ni_2V_2O_7$	0.69	11.3	5.0	27
$Co_2V_2O_7$	0.75	11.4	4.0	40
MgV_2O_7	0.72	12.6	5.8	25
$Cu_2V_2O_7$	0.73	12.8	7.6	10
$Zn_2V_2O_7$	0.88	13.4	12.5	5
$Cd_2V_2O_7$	0.95	14.8	1.4	100
$Ca_2V_2O_7$	1.00	15.0	2.7	65
α-$Mn_2V_2O_7$	0.83	11.9	1	100
β-$Mn_2V_2O_7$	0.83	14.6	1	100

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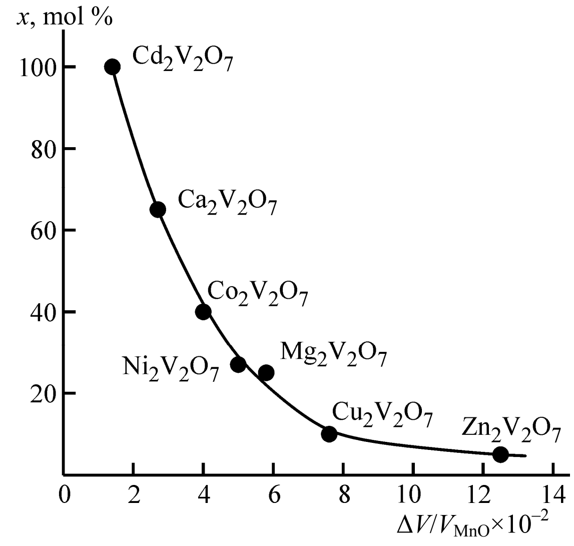

Fig. 3. Solid solutions stability range for $Mn_{2-2x}M_{2x}V_2O_7$ as a function of relative volume difference of metal-oxygen polyhedra.

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