About the crystalline structure of vanadates $Ca_{1.5\pm0.1}Mn_{0.5\pm0.1}V_2O_7$ and $Ca_{1.5}Cd_{0.5}V_2O_7$

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The crystal structures of $Ca_{1.5}Mn_{0.5}V_2O_7$ (I) and $Ca_{1.5}Cd_{0.5}V_2O_7$ (II) synthesized by the citrate method and by a conventional solid-state reaction, respectively, were determined using X-ray powder diffraction data. It was found that the compound I has a monoclinic crystal structure $a = 4.88563(9)$ Å, $b = 11.21279(22)$ Å, $c = 5.69643(11$ Å), $\beta = 96.376(7)°$, $V = 310.132(10)$ Å^3 (space group $P2_1/c$), $Z = 2$). Compound I has a narrow homogeneity region $Ca_{1.5\pm0.1}Mn_{0.5\pm0.1}V_2O_7$. The vanadate $Ca_{1.5}Cd_{0.5}V_2O_7$ crystallizes in the triclinic system with the parameters $a = 6.66139(6)$ Å, $b = 6.93019(7)$ Å, $c = 7.02211(6)$ Å, $\alpha = 85.4404(9)°$, $\beta = 63.7505(7)°$, $\gamma = 82.5515(10)°$ и $V = 288.201(5)$ Å^3 (space group $P\bar{1}$, $Z = 2$). It is one of the formulations of the primary solid solution, formed as a result of the substitution of part of the calcium cations for cadmium cations in $Ca_2V_2O_7$. © *2018 International Centre for Diffraction Data.* [doi:10.1017/S0885715618000568]

Key words: vanadates, X-ray powder diffraction, crystal structure, solid solution

I. INTRODUCTION

The interaction between pairs of vanadates $M_2V_2O_7$ with large cations M^{2+} (M = Ba, Sr, Ca, Pb, Cd, Mn) leads to the formation of wide primary solid solutions or double compounds with a cation ratio of 3 : 1 (Zhuravlev and Hodos, 1981; Fotiev *et al*., 1982; Zhuravlev and Velikodnyi, 1990; Murashova *et al*., 1993; Zhuravlev *et al*., 1993, 1994; Surat *et al*., 1996; Zhuravlev and Velikodnyi, 1997). Often the question arises as to whether a compound or solid substitutional solution was obtained as a result of the directed synthesis of a single sample. For example, Sivakumar T. H. Y *et al*., synthesized two-dimensional lead (II) vanadate, $Ba_3PbV_4O_{14}$ (Sivakumar *et al*., 2007). However, earlier in the study of the $Ba_2V_2O_7 - Pb_2V_2O_7$ system (Zhuravlev and Velikodnyi, 1997) it was shown that in the concentration range 0–30 mol. % $Pb_2V_2O_7$ there is a primary solid substitutional solution. A comparison of the crystal structure of $Ba_2V_2O_7$ (Hawthorne and Calvo, 1972) and $Ba_3PbV_4O_{14}$ shows the isostructural nature of compounds.

Often in solid-phase synthesis, the formation of new vanadates proceeds in a narrow temperature range near the solidus of the binary system $M_2V_2O_7 - M^I_2V_2O_7$. If the synthesis temperature is chosen below the optimum and the starting reagents are chemically inert, then instead of the dual vanadate, a mixture of initial vanadates or primary solid solutions will be obtained. Probably, for this reason, the "$Ca_{1.5}Mn_{0.5}V_2O_7$" compound was not obtained in the work (Zhuravlev *et al*., 1993). An erroneous conclusion was drawn that in the system $(1–x)$ $Mn_2V_2O_7$–x $Ca_2V_2O_7$ n the region $x = 60–80$ mol % $Ca_2V_2O_7$ a mixture of limiting compositions of primary solid solutions is formed.

In this work, the results of X-ray identification and the crystallographic characteristics of the double vanadate $Ca_{1.5}Mn_{0.5}V_2O_7$ and of the "compound" $Ca_{1.5}Cd_{0.5}V_2O_7$ as one of the compositions of solid solutions with the structure $Ca_4(V_4O_{14})$ are given.

II. EXPERIMENT

The compound $Ca_{1.5}Mn_{0.5}V_2O_7$ was synthesized by the citrate method. Vanadium pentoxide (99.95%) was dissolved in nitric acid with the addition of citric acid (3 moles $H_3C_6H_5O_7 \cdot H_2O$: 1 mole V_2O_5). An equivalent amount of calcium nitrate and manganese (II) nitrate and 2.2 moles of $H_2N(CH_2)COOH$ for 1 mol of $Ca_{1.5}Mn_{0.5}V_2O_7$ were added to the resulting solution. The solution was heated and evaporated to a viscous state at a temperature of 100–150 °C. After complete removal of the water, the heating temperature was raised to 300 °C. The decomposition of xerogel occurs with the formation of a bulk fine powder of beige color. The monophase samples $Ca_{1.5\pm0.1}Mn_{0.5\pm0.1}V_2O_7$ were obtained after a two-step annealing of the precursor at a temperature of 750 and 900 °C for 10–15 h at each stage of heat treatment and grinding of the intermediate products.

The compound $Ca_{1.5}Cd_{0.5}V_2O_7$ was synthesized from a mixture of $CaCO_3$(99.5%), $CdCO_3$ (99.5%) и V_2O_5 (99.95%) by conventional solid state reaction at 450–900 °C for 75 h in air, with intermediate regrinding.

The purity of the synthesized product was checked using X-ray powder diffraction (XRD) (Figure 1). XRD pattern was collected at room temperature on a STADI P (Stoe) diffractometer in transmission geometry with a linear mini-PSD

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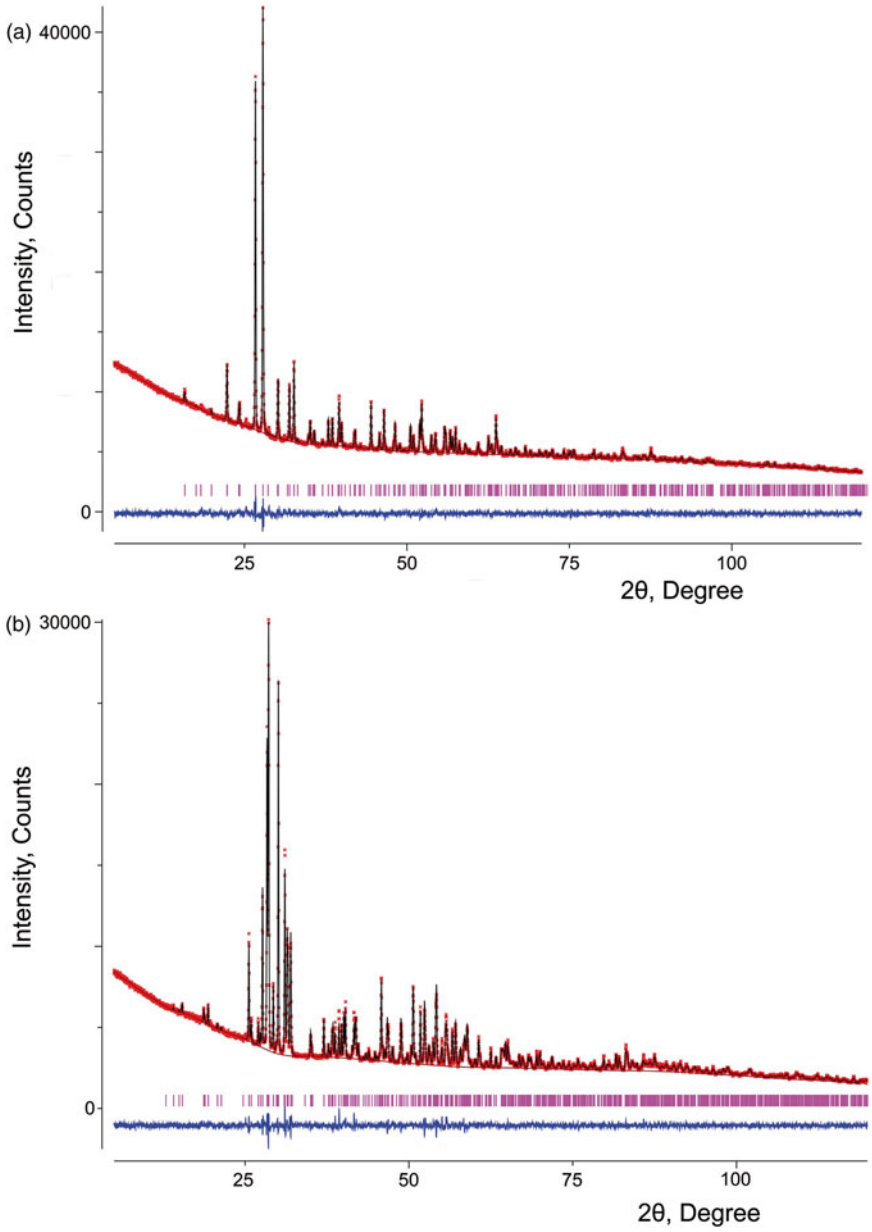


Figure 1. (Color online) Experimental (crosses), calculated (solid line), and difference (bottom line) XRPD patterns of (a) $Ca_{1.5}Mn_{0.5}V_2O_7$ and (b) $Ca_{1.5}Cd_{0.5}V_2O_7$. Series of tick marks correspond to the Bragg reflections.

detector, using Cu$K\alpha_1$ radiation in the 2θ range 5° to 120° with a step of 0.02°. Polycrystalline silicon ($a = 5.43075$ (5) Å) was used as external standard. The possible impurity phases were checked by comparing their XRD patterns with those in the PDF2 database (ICDD, USA, Release 2009). The crystal structure refinement was carried out with the GSAS (Toby, 2001; Larson and Von Dreele, 2004) program suite using the XRD data. The peak profiles were fitted with a pseudo-Voigt function, $I(2\theta) = xL(2\theta) + (1-x)G(2\theta)$ (where L and G are the Lorentzian and Gaussian part, respectively). The angular dependence of the peak width was described by the relation $(FWHM)^2 = Utan^2\theta + Vtan\theta + W$, where FWHM is the full line width at half maximum. A powder sample for XRD data collection in the transmission geometry was applied to a polymer film, the background from which was not smoothly decreasing. The description of such a background by the Chebyshev polynomial of the small order gave large values of the R-factors. The authors carefully checked whether the increase in the order of the polynomial affects the structural parameters, and since they found that it does not affect, 36th-order Chebyshev polynomials were used. It gave perfect fit of the background and low R-factors. The absorption correction function for a flat plate sample in transmission geometry has been applied.

III. DISCUSSION

Up to now, it was known (Zhuravlev *et al.*, 1993) that in the $Mn_2V_2O_7$-$Ca_2V_2O_7$ system there are two primary solid solutions: with a thortveitite structure (100–40 mol. % $Mn_2V_2O_7$) and (80–100 mol. % $Ca_2V_2O_7$. A new double vanadate with a narrow homogeneity region, $Ca_{2-x}Mn_xV_2O_7$, $x =$ 0.4–0.6, (Table I, Figure 1), was obtained because of the use of the citrate method, which gives more chemically active precursors.

The double vanadate of calcium and manganese, unlike vanadates of the type $Pb_2Zn_2(V_4O_{14})$ or Pb_2Mg_2 (V_3O_{10}) (VO_4), can be represented as $Ca_{1.5}Mn_{0.5}V_2O_7$ (Figure 2).

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TABLE I. The calculated and observed values of XRPD data for $Ca_{1.5}Mn_{0.5}V_2O_7$. (Cu$K\alpha_1$, with $\lambda = 1.5406$ Å).

$2\theta_{obs}$ (°)	h	K	l	$2\theta_{cal}$ (°)	$\Delta 2\theta$	I_{obs}	d_{obs} (Å)	d_{cal} (Å)
15.770	0	2	0	15.799	−0.0290	2	5.6151	5.6049
22.302	0	2	1	22.300	0.0015	13	3.9831	3.9833
24.135	−1	1	1	24.108	0.0270	4	3.6846	3.6886
24.228	1	2	0	24.233	−0.0041	5	3.6705	3.6699
26.666	1	1	1	26.668	−0.0017	80	3.3403	3.3401
27.817	−1	2	1	27.816	0.0009	100	3.2046	3.2047
30.155	1	3	0	30.155	−0.0004	13	2.9613	2.9612
31.909	0	4	0	31.908	0.0005	13	2.8024	2.8024
32.605	0	1	2	32.596	0.0095	19	2.7441	2.7449
34.850	−1	0	2	34.840	0.0105	2	2.5723	2.5731
35.098	1	3	1	35.108	−0.0096	5	2.5547	2.5540
35.702	0	4	1	35.720	−0.0178	3	2.5129	2.5116
36.995	1	4	0	37.007	−0.0120	1	2.4279	2.4272
37.890	2	1	0	37.888	0.0011	5	2.3727	2.3727
38.512	1	0	2	38.515	−0.0033	6	2.3357	2.3355
39.539	−1	4	1	39.545	−0.0063	12	2.2774	2.2770
39.914	0	3	2	39.920	−0.0065	6	2.2569	2.2565
41.908	1	2	2	41.869	0.0382	4	2.1540	2.1559
42.004	−2	2	1	42.011	−0.0068	4	2.1493	2.1489
42.850	2	1	1	42.858	−0.0082	1	2.1088	2.1084
44.464	2	3	0	44.467	−0.0033	11	2.0359	2.0358
45.785	1	3	2	45.777	0.0075	4	1.9802	1.9805
46.456	−2	0	2	46.457	−0.0016	9	1.9532	1.9531
47.966	−1	4	2	47.960	0.0062	2	1.8951	1.8953
48.159	1	5	1	48.166	−0.0069	6	1.8880	1.8877
48.866	2	3	1	48.892	−0.0252	2	1.8623	1.8614
50.522	−1	1	3	50.520	0.0019	5	1.8051	1.8051
50.984	−2	4	1	50.973	0.0111	4	1.7898	1.7902
51.975	0	5	2	51.987	−0.0123	6	1.7580	1.7576
52.259	2	0	2	52.246	0.0133	12	1.7491	1.7495
53.733	2	4	1	53.745	−0.0119	4	1.7045	1.7042
54.380	−1	6	1	54.392	−0.0118	4	1.6858	1.6854
55.776	2	5	0	55.767	0.0081	6	1.6468	1.6471
55.909	−1	3	3	55.927	−0.0180	5	1.6432	1.6428
56.640	1	2	3	56.632	0.0074	5	1.6238	1.6240
56.984	−2	5	1	56.996	−0.0124	3	1.6148	1.6144
57.467	−2	4	2	57.466	0.0010	6	1.6023	1.6023
58.040	−3	1	1	58.046	−0.0057	3	1.5879	1.5877
58.953	0	4	3	58.952	0.0003	2	1.5654	1.5655
59.569	2	5	1	59.577	−0.0079	1	1.5507	1.5505
60.965	−2	2	3	60.975	−0.0100	3	1.5185	1.5183
62.534	2	4	2	62.537	−0.0029	4	1.4841	1.4841
63.024	−3	3	1	63.019	0.0042	2	1.4738	1.4739
63.688	3	2	1	63.676	0.0120	9	1.4600	1.4602
63.894	1	7	1	63.876	0.0175	3	1.4558	1.4561
64.498	0	5	3	64.484	0.0135	2	1.4436	1.4439
65.900	0	0	4	65.937	−0.0371	1	1.4162	1.4155
66.685	−1	0	4	66.689	−0.0041	1	1.4015	1.4014
68.196	−3	3	2	68.200	−0.0035	2	1.3740	1.3740
69.008	−1	7	2	69.023	−0.0146	1	1.3598	1.3596
70.367	2	7	0	70.373	−0.0055	1	1.3369	1.3368
71.359	1	7	2	71.356	0.0027	1	1.3207	1.3208
71.936	1	1	4	71.962	−0.0256	1	1.3115	1.3111
72.378	−3	5	1	72.387	−0.0091	2	1.3046	1.3045
74.153	−2	1	4	74.123	0.0295	1	1.2777	1.2781
74.823	−3	2	3	74.797	0.0262	1	1.2679	1.2683
75.654	1	6	3	75.652	0.0011	1	1.2560	1.2561
78.778	4	0	0	78.778	−0.0001	2	1.2139	1.2139
80.940	−1	9	1	80.952	−0.0121	1	1.1868	1.1867
81.903	3	6	1	81.881	0.0220	1	1.1753	1.1755
83.186	3	1	3	83.213	−0.0264	2	1.1604	1.1601
85.179	3	7	0	85.169	0.0102	1	1.1382	1.1384
85.664	−3	7	1	85.645	0.0183	1	1.1330	1.1332
86.330	−3	5	3	86.335	−0.0055	1	1.1260	1.1259
87.516	4	4	0	87.507	0.0096	3	1.1138	1.1139
89.018	1	9	2	88.998	0.0193	1	1.0988	1.0990

Continued

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TABLE I. Continued

$2\theta_{obs}$ (°)	h	K	l	$2\theta_{cal}$ (°)	$\Delta 2\theta$	I_{obs}	d_{obs} (Å)	d_{cal} (Å)
92.274	4	1	2	92.265	0.0095	1	1.0684	1.0685
96.221	3	5	3	96.227	−0.0059	1	1.0347	1.0347
96.585	4	3	2	96.608	−0.0231	1	1.0318	1.0316
99.563	−3	5	4	99.582	−0.0189	1	1.0088	1.0086
101.428	3	2	4	101.420	0.0079	0	0.9952	0.9953
105.447	4	5	2	105.437	0.0107	1	0.9680	0.9681
106.578	1	8	4	106.578	−0.0002	1	0.9609	0.9609
108.690	−5	1	2	108.673	0.0173	0	0.9480	0.9481
110.962	0	9	4	110.929	0.0326	1	0.9349	0.9351

Average delta (2θ) = 0.011°.
Maximum delta (2θ) = 0.038° = 3.5 × average.
Figure of Merit F(30) = 53.6 (0.009, 61).
Durbin–Watson serial correlation = 1.806 (not significant).

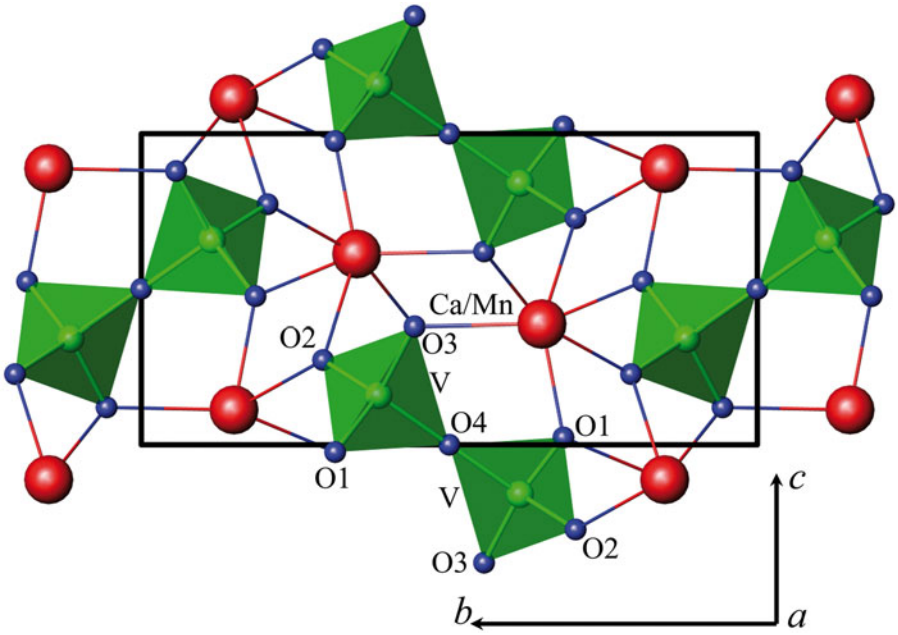


Figure 2. (Color online) Crystalline structure of $Ca_{1.5}Mn_{0.5}V_2O_7$.

TABLE II. Structural data for $Ca_{2-x}Mn_xV_2O_7$.

Formula	$x = 0.4$ $Ca_{1.6}Mn_{0.4}V_2O_7$	$x = 0.5$ $Ca_{1.5}Mn_{0.5}V_2O_7$	$x = 0.6$ $Ca_{1.4}Mn_{0.6}V_2O_7$
Space group, #	$P2_1/c$, 14	$P2_1/c$, 14	$P2_1/c$, 14
The number of formula units, Z	2	2	2
Cell constants:			
a, Å	4.88613(8)	4.88563(9)	4.88495(8)
b, Å	11.24017(20)	11.21279(22)	11.16895(21)
c, Å	5.70751(11)	5.69643(11)	5.68012(10)
β, °	96.3572(8)	96.3703(8)	96.3926(7)
V, Å^3	311.535(10)	310.132(10)	307.979(10)
D_x, g cm^{-3}	3.198	3.228	3.267
D_{ex}, g cm^{-3}	3.20(1)	3.246(5)	3.26(2)
wRp/ Rp, %	1.69/1.16	1.69/1.27	1.39/0.99
χ^2	2.688	1.669	1.878
R(F^2)	10.07	8.55	7.24

The XRD pattern of $Ca_{1.5}Mn_{0.5}V_2O_7$ was indexed in a monoclinic symmetry with unit cell parameter $a = 4.88563$ (9) Å, $b = 11.21279(22)$ Å, $c = 5.69643(11)$ Å, $\beta = 96.3703$ (8)° (space group $P2_1/c$, 14 Z = 2). Crystal structure of $Ca_{1.22}Cd_{0.78}V_2O_7$ (Murashova *et al.*, 1994) was used as the starting model. The calculated and observed 2θ values of XRPD data for $Ca_{1.5}Mn_{0.5}V_2O_7$ are listed in Table I. The crystallographic data for $Ca_{2-x}Mn_xV_2O_7$ and displacement parameters are given in Table II, selected interatomic distances in Tables III–IV.

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TABLE III. Atom coordinates and isotropic thermal parameters $U_{iso} \times 100$ (Å^2) for the $Ca_{2-x}Mn_xV_2O_7$.

Atom	Position	Parameter	$x = 0.4$	$x = 0.5$	$x = 0.6$
Ca/Mn	4*e*	*x/a*	0.3841(8)	0.3842(8)	0.3818(8)
		y/b	0.14902(16)	0.15037(16)	0.15142(15)
		z/c	0.1074(6)	0.1124(6)	0.1104(6)
		$U_{iso} \times 100$	1.95(7)	2.74(8)	2.47(7)
		Fraction	0.8/0.2	0.75/0.25	0.7/0.3
V	4*e*	*x/a*	0.1462(6)	0.1477(6)	0.1464(5)
		y/b	0.61473(17)	0.61476(17)	0.61519(17)
		z/c	−0.1604(5)	−0.1591(5)	−0.1586(5)
		$U_{iso} \times 100$	2.61(8)	3.20(8)	2.26(7)
O(1)	4*e*	*x/a*	0.3936(15)	0.3927(16)	0.3902(16)
		y/b	0.6846(5)	0.6854(5)	0.6868(6)
		z/c	0.0219(12)	0.0236(12)	0.0260(12)
		$U_{iso} \times 100$	1.99(25)	1.84(25)	2.22(25)
O(2)	4*e*	*x/a*	−0.1121(17)	−0.1190(17)	−0.1113(16)
		y/b	0.7020(6)	0.7050(6)	0.7036(5)
		z/c	−0.2801(13)	−0.2727(12)	−0.2745(12)
		$U_{iso} \times 100$	2.50(27)	2.68(26)	1.82(25)
O(3)	4*e*	*x/a*	0.2998(11)	0.3014(11)	0.2890(11)
		y/b	0.5666(5)	0.5564(5)	0.5554(5)
		z/c	−0.3896(13)	−0.3796(14)	−0.3816(14)
		$U_{iso} \times 100$	1.74(20)	1.67(20)	2.94(22)
O(4)	2*c*	*x/a*	0	0	0
		y/b	0	0	0
		z/c	0.5	0.5	0.5
		$U_{iso} \times 100$	5.31(45)	4.33(43)	6.40(50)

The XRD pattern of vanadate $Ca_{1.5}Cd_{0.5}V_2O_7$ was indexed with triclinic unit cell parameters $a = 6.66139(6)$ Å, $b = 6.93019(7)$ Å, $c = 7.02211(6)$ Å, $\alpha = 85.4404(9)°$, $\beta = 63.7505(7)°$, $\gamma = 82.552(1)°$, (space group $P\bar{1}$, 2, Z = 2). The calculated and observed 2θ values of XRPD data for $Ca_{1.5}Cd_{0.5}V_2O_7$ are listed in Table V. Crystal structure data of $Ca_2V_2O_7$ (Trunov *et al.*, 1983) was used as a starting structural model for our refinement. The compound is isostructural to pyrovanadate calcium and, apparently, is part of the solid solutions based on it. In this case, according to Tong *et al.* (2011) it must be described by the formula $Ca_3Cd(V_4O_{14})$ (Figure 3).

TABLE IV. The shortest interatomic distances (d) and angles (°) in the $Ca_{2-x}Mn_xV_2O_7$.

Bond d, Å	$x = 0.4$	$x = 0.5$	$x = 0.6$
Ca/Mn-O(1)	2.304(8)	2.268(8)	2.269(8)
Ca/Mn-O(1)	2.324(7)	2.317(7)	2.302(7)
Ca/Mn-O(2)	2.249(8)	2.290(8)	2.273(8)
Ca/Mn-O(2)	2.415(8)	2.324(8)	2.348(7)
Ca/Mn-O(3)	2.284(7)	2.383(7)	2.427(7)
Ca/Mn-O(3)	2.459(5)	2.355(5)	2.356(6)
Ca/Mn-O[a]	**2.339**	**2.323**	**2.329**
Expected[b]	2.326	2.318	2.309
V-O(1)	1.697(8)	1.693(8)	1.697(8)
V-O(2)	1.682(8)	1.719(8)	1.675(7)
V-O(3)	1.669(7)	1.667(7)	1.652(7)
V-O(4)	1.777(2)	1.773(2)	1.767(2)
V-O[a]	**1.706**	**1.713**	**1.698**
Expected[b]	1.713	1.713	1.713
Angles, °			
O(1)VO(2)	115.5(3)	114.3(2)	114.2(3)
O(1)VO(3)	106.2(4)	107.4(4)	109.7(4)
O(1)VO(4)	108.6(3)	109.0(3)	108.9(2)
O(2)VO(3)	104.6(4)	109.5(4)	107.4(4)
O(2)VO(4)	107.8(3)	106.6(3)	107.5(3)
O(3)VO(4)	114.2(2)	110.1(2)	109.0(2)

[a]The average values are indicated by boldface type.
[b]The sum of the crystal radii according to (Shannon, 1976): Ca^{+2} VI – 1.14 Å, Mn^{+2} VI HS – 0.970 Å, V^{+5} IV – 0.495 Å, O^{-2} III – 1.22 Å, O^{-2} II – 1.21 Å. Ca/Mn - O distances are calculated taking into account fractions of calcium and manganese.

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TABLE V. The calculated and observed values of XRPD data for $Ca_{1.5}Cd_{0.5}V_2O_7$ (Cu$K\alpha_1$, with $\lambda = 1.5406$ Å).

$2\theta_{obs}$ (°)	H	k	l	$2\theta_{cal}$ (°)	$\Delta 2\theta$	I_{obs}	d_{obs} (Å)	d_{cal} (Å)
14.034	0	0	1	14.056	−0.0215	2	6.3054	6.2959
15.353	1	0	1	15.382	−0.0298	2	5.7668	5.7556
18.659	1	1	0	18.669	−0.0099	3	4.7517	4.7492
19.334	0	−1	1	19.346	−0.0122	5	4.5873	4.5845
20.752	−1	1	0	20.762	−0.0095	2	4.2769	4.2749
25.566	1	0	2	25.564	0.0025	26	3.4814	3.4817
25.929	0	2	0	25.919	0.0099	6	3.4335	3.4348
26.977	2	0	1	26.996	−0.0188	6	3.3024	3.3001
27.329	−1	−1	1	27.337	−0.0081	3	3.2608	3.2598
27.647	1	1	2	27.641	0.0064	35	3.2239	3.2246
28.328	0	0	2	28.328	0.0001	75	3.1479	3.1479
28.572	1	2	0	28.585	−0.0134	100	3.1216	3.1202
29.284	0	2	1	29.281	0.0029	15	3.0473	3.0476
30.059	2	0	0	30.062	−0.0026	82	2.9705	2.9702
31.053	2	0	2	31.051	0.0017	48	2.8777	2.8778
31.421	−1	2	0	31.410	0.0116	29	2.8447	2.8458
31.503	2	1	0	31.498	0.0048	25	2.8376	2.8380
31.946	1	−2	1	31.950	−0.0035	26	2.7992	2.7989
34.999	1	2	2	34.980	0.0187	5	2.5617	2.5630
35.119	2	2	1	35.130	−0.0117	3	2.5533	2.5524
37.008	−1	2	1	37.010	−0.0021	9	2.4271	2.4270
37.707	−1	0	2	37.709	−0.0017	3	2.3837	2.3836
37.860	2	2	0	37.857	0.0028	2	2.3744	2.3746
38.303	0	2	2	38.264	0.0386	7	2.3480	2.3503
38.399	1	−2	2	38.401	−0.0016	7	2.3423	2.3422
38.737	−2	0	1	38.734	0.0028	9	2.3227	2.3228
39.324	0	3	0	39.315	0.0094	11	2.2893	2.2899
39.702	−1	−1	2	39.701	0.0009	8	2.2684	2.2685
40.056	1	1	3	40.066	−0.0102	11	2.2492	2.2486
40.314	2	0	3	40.315	−0.0012	14	2.2354	2.2353
41.359	3	0	1	41.354	0.0048	3	2.1813	2.1815
41.592	0	3	1	41.594	−0.0013	11	2.1696	2.1695
41.858	1	−1	3	41.865	−0.0076	10	2.1564	2.1561
41.914	3	0	2	41.922	−0.0079	10	2.1537	2.1533
42.252	3	1	2	42.256	−0.0043	4	2.1372	2.1370
43.434	2	−2	2	43.451	−0.0162	2	2.0817	2.0810
43.861	2	−1	3	43.871	−0.0103	3	2.0625	2.0620
44.818	0	1	3	44.803	0.0148	2	2.0206	2.0213
45.124	3	−1	1	45.119	0.0042	1	2.0077	2.0078
45.783	−1	−2	2	45.785	−0.0021	19	1.9803	1.9802
46.005	2	2	3	45.987	0.0182	4	1.9712	1.9720
46.331	3	1	0	46.316	0.0148	3	1.9581	1.9587
46.714	3	2	2	46.690	0.0239	9	1.9429	1.9439
46.848	−1	2	2	46.865	−0.0162	9	1.9377	1.9371
47.500	2	3	2	47.498	0.0017	4	1.9126	1.9127
48.803	1	−2	3	48.778	0.0250	9	1.8646	1.8655
49.780	0	−3	2	49.785	−0.0051	2	1.8302	1.8300
50.355	0	2	3	50.340	0.0145	4	1.8107	1.8112
50.623	−2	0	2	50.598	0.0246	18	1.8017	1.8025
50.968	3	−1	3	50.962	0.0058	2	1.7903	1.7905
51.754	−2	−1	2	51.744	0.0093	13	1.7650	1.7653
52.386	3	−2	1	52.387	−0.0005	12	1.7451	1.7451
53.057	3	−2	2	53.059	−0.0023	4	1.7247	1.7246
53.267	1	0	4	53.250	0.0174	2	1.7183	1.7188
53.693	1	4	1	53.703	−0.0097	6	1.7057	1.7054
54.121	−1	1	3	54.090	0.0308	14	1.6932	1.6941
54.189	2	−3	2	54.186	0.0035	16	1.6912	1.6913
55.029	0	4	1	55.025	0.0035	6	1.6674	1.6675
55.648	4	0	2	55.657	−0.0086	12	1.6503	1.6501
55.779	0	−4	1	55.792	−0.0129	8	1.6468	1.6464
56.620	3	1	4	56.626	−0.0064	8	1.6243	1.6241
57.104	4	0	1	57.113	−0.0087	10	1.6116	1.6114
57.888	1	−4	1	57.881	0.0067	4	1.5917	1.5918
58.494	1	−3	3	58.470	0.0242	6	1.5766	1.5772
58.879	0	3	3	58.894	−0.0155	9	1.5672	1.5669
59.419	−1	2	3	59.400	0.0188	2	1.5543	1.5547

Continued

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TABLE V. Continued

$2\theta_{obs}$ (°)	H	k	l	$2\theta_{cal}$ (°)	$\Delta 2\theta$	I_{obs}	d_{obs} (Å)	d_{cal} (Å)
60.070	3	2	4	60.089	−0.0192	2	1.5390	1.5385
60.625	0	−1	4	60.639	−0.0140	6	1.5262	1.5259
60.829	−1	4	1	60.843	−0.0144	3	1.5216	1.5213
61.860	4	−1	3	61.868	−0.0081	2	1.4987	1.4985
62.482	4	0	0	62.487	−0.0052	5	1.4852	1.4851
63.299	−3	2	1	63.297	0.0027	3	1.4680	1.4681
64.097	−2	−3	2	64.079	0.0176	5	1.4517	1.4520
64.291	2	−4	1	64.285	0.0060	5	1.4477	1.4479
64.418	4	1	4	64.416	0.0020	5	1.4452	1.4452
64.700	3	4	1	64.677	0.0230	5	1.4396	1.4400
65.089	−2	−4	1	65.072	0.0170	7	1.4319	1.4322
65.886	4	−2	2	65.873	0.0135	2	1.4165	1.4167
66.314	−3	−1	2	66.316	−0.0012	1	1.4084	1.4084
66.830	−1	−3	3	66.831	−0.0010	3	1.3988	1.3988
67.313	4	3	3	67.330	−0.0163	2	1.3899	1.3896
68.257	−3	1	2	68.269	−0.0126	3	1.3730	1.3727
68.519	3	4	3	68.549	−0.0301	2	1.3683	1.3678
69.463	−1	1	4	69.478	−0.0151	3	1.3520	1.3518
69.852	1	1	5	69.848	0.0042	3	1.3455	1.3455
69.998	−3	−2	2	70.002	−0.0044	4	1.3430	1.3429
70.445	0	−5	1	70.458	−0.0128	1	1.3356	1.3354
71.262	−4	0	1	71.275	−0.0129	1	1.3223	1.3220
71.826	−4	2	0	71.816	0.0103	2	1.3133	1.3134
72.886	2	−4	3	72.882	0.0041	1	1.2967	1.2968
73.558	5	2	2	73.530	0.0271	2	1.2866	1.2870
74.443	5	0	1	74.450	−0.0079	1	1.2734	1.2733
75.756	5	−1	3	75.764	−0.0074	2	1.2546	1.2545
76.584	−3	−3	2	76.586	−0.0023	1	1.2431	1.2430
77.768	4	−1	5	77.779	−0.0112	2	1.2271	1.2269
78.291	1	5	3	78.291	−0.0003	2	1.2202	1.2202
79.722	−3	0	3	79.736	−0.0140	3	1.2019	1.2017
80.272	1	3	5	80.245	0.0273	1	1.1950	1.1953
80.538	−4	−3	1	80.532	0.0063	2	1.1917	1.1918
81.612	−2	−1	4	81.595	0.0164	3	1.1787	1.1789
82.052	5	3	1	82.051	0.0008	3	1.1735	1.1735
82.251	2	−4	4	82.256	−0.0054	2	1.1712	1.1711
83.105	−4	0	2	83.095	0.0099	5	1.1613	1.1614
83.307	5	1	5	83.283	0.0243	4	1.1590	1.1593
84.059	−5	1	0	84.069	−0.0092	2	1.1505	1.1504
84.334	1	6	0	84.373	−0.0392	1	1.1475	1.1470
84.768	1	−3	5	84.770	−0.0018	1	1.1427	1.1427
85.796	−4	1	2	85.802	−0.0069	3	1.1316	1.1316
86.128	2	6	1	86.105	0.0238	2	1.1281	1.1284
86.736	0	−6	1	86.761	−0.0248	2	1.1218	1.1215
87.474	1	1	6	87.460	0.0136	4	1.1142	1.1143
88.154	−1	−6	1	88.161	−0.0068	2	1.1073	1.1073
88.631	−1	6	0	88.618	0.0133	1	1.1026	1.1027
89.239	1	−6	1	89.217	0.0215	1	1.0967	1.0969
89.847	6	0	2	89.854	−0.0070	1	1.0908	1.0908
90.382	6	1	4	90.370	0.0123	2	1.0858	1.0859
91.120	−1	2	5	91.144	−0.0240	2	1.0789	1.0787
91.409	−4	2	2	91.383	0.0264	2	1.0762	1.0765
92.321	−4	−3	2	92.317	0.0037	2	1.0680	1.0680
93.580	6	−1	2	93.573	0.0071	1	1.0569	1.0569
94.202	6	0	1	94.249	−0.0477	2	1.0515	1.0511
95.432	0	1	6	95.433	−0.0019	1	1.0412	1.0412
96.401	0	−1	6	96.386	0.0154	2	1.0333	1.0334
97.341	1	3	6	97.355	−0.0136	1	1.0258	1.0257
97.964	3	−4	5	97.978	−0.0144	1	1.0209	1.0208
98.629	0	6	3	98.624	0.0050	2	1.0158	1.0159
102.069	6	−2	4	102.082	−0.0132	2	0.9907	0.9906
107.573	−3	−3	4	107.579	−0.0063	1	0.9547	0.9547
109.102	7	1	4	109.056	0.0462	2	0.9456	0.9459
112.338	−5	−3	2	112.340	−0.0017	1	0.9273	0.9273

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TABLE V. Continued

$2\theta_{obs}$ (°)	H	k	l	$2\theta_{cal}$ (°)	$\Delta 2\theta$	I_{obs}	d_{obs} (Å)	d_{cal} (Å)
113.816	2	−6	4	113.820	−0.0039	1	0.9194	0.9194
115.345	−4	3	3	115.360	−0.0151	1	0.9116	0.9115
117.867	−3	0	5	117.859	0.0078	1	0.8993	0.8993

Average delta (2θ) = 0.012°.
Maximum delta (2θ) = 0.048° = 4.1 × average.
Figure of Merit F(30) = 61.6 (0.009, 54).
Durbin–Watson serial correlation = 1.999 (not significant).

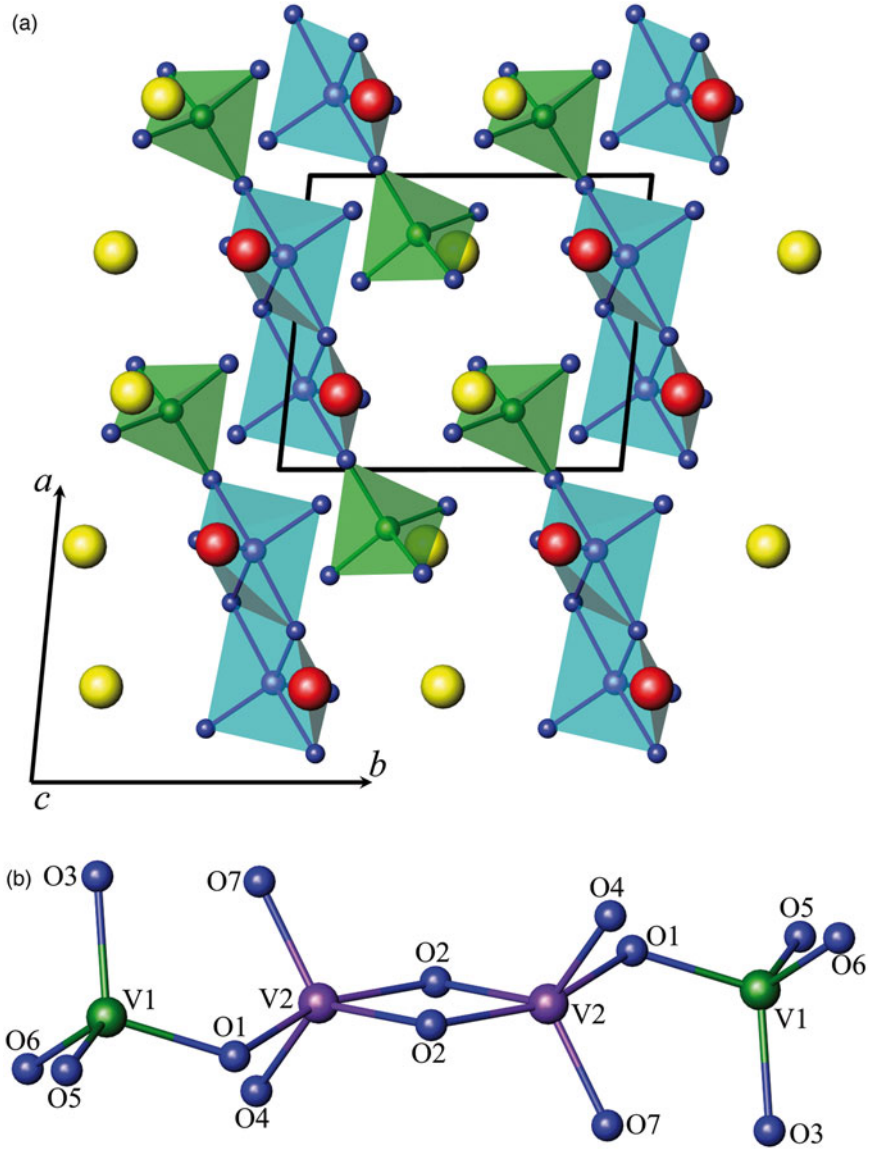


Figure 3. (Color online) Schematic drawing: (a) a view of the $Ca_{1.5}Cd_{0.5}V_2O_7$ structure along *c*-axis and (b) the chain-like $[V_4O_{14}]^{8-}$ anion. Red, yellow, green, violet, and dark blue spheres indicate Ca/Cd (1), Ca/Cd (2), V (1), V (2) and oxygen sites, respectively.

TABLE VI. Structural data for $Ca_{1.5}Cd_{0.5}V_2O_7$ and $Ca_4(V_4O_{14})$.

Parameter Space group, #	$Ca_{1.5}Cd_{0.5}V_2O_7$ $P\bar{1}$, 2	$Ca_2V_2O_7$ $P\bar{1}$, 2
The number of formula units, Z	2	2
Cell constants:		
a, Å	6.66139(6)	6.667(2)
b, Å	6.93019(7)	6.921(1)

Continued

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TABLE VI. Continued

Parameter Space group, #	$Ca_{1.5}Cd_{0.5}V_2O_7$ $P\bar{1}$, 2	$Ca_2V_2O_7$ $P\bar{1}$, 2
c, Å	7.02211(6)	7.018(3)
α, °	85.4404(9)	86.38(2)
β, °	63.7505(7)	63.84(3)
γ, °	82.552(1)	83.64(2)
V, Å^3	288.201(5)	288.8
D_x, g cm^{-3}	3.805	3.381(2)
D_{ex}, g cm^{-3}		
wRp/ Rp, %	2.61/1.89	
χ^2	2.442	
$R(F^2)$	4.26	

TABLE VII. Atomic coordinates and isotropic thermal parameters ($U_{iso} \times 100$, Å^2) for $Ca_{1.5}Cd_{0.5}V_2O_7$.

Atom		*x/a*	*y/b*	*z/c*	Fraction	$U_{iso} \times 100$
V(1)	2*i*	0.7995(5)	0.3349(5)	0.2367(5)	1.0	2.1(1)
V(2)	2*i*	0.2750(6)	0.0490(4)	0.1556(5)	1.0	1.9(1)
Ca/Cd(1)	2*i*	0.2548(5)	0.1577(4)	0.6732(4)	0.802/0.198(4)	1.7(1)
Ca/Cd(2)	2*i*	0.7384(4)	0.4543(4)	0.7399(3)	0.698/0.302(4)	1.8(1)
O1	2*i*	0.034(2)	0.193(1)	0.071(1)	1.0	1.6(1)*
O2	2*i*	0.452(1)	0.099(1)	−0.126(1)	1.0	1.6(1)*
O3	2*i*	0.876(2)	0.503(1)	0.360(1)	1.0	1.6(1)*
O4	2*i*	0.119(2)	−0.135(1)	0.268(1)	1.0	1.6(1)*
O5	2*i*	0.647(2)	0.452(1)	0.100(1)	1.0	1.6(1)*
O6	2*i*	0.640(1)	0.180(1)	0.419(1)	1.0	1.6(1)*
O7	2*i*	0.240(2)	0.217(1)	0.330(1)	1.0	1.6(1)*

*Thermal parameters of oxygen atoms were constrained as a single variable.

TABLE VIII. Selected interatomic distances d(Å) and angles (°) for $Ca_{1.5}Cd_{0.5}V_2O_7$.

Interatomic distances		Interatomic distances		Interatomic distances	
V(1)-O(1)	1.713(9)	Ca(1)-O(1)	2.531(9)	Ca(2)-O(2)	3.140(8)
V(1)-O(3)	1.754(9)	Ca(1)-O(1)	3.211(10)	Ca(2)-O(3)	2.415(9)
V(1)-O(5)	1.773(9)	Ca(1)-O(2)	2.298(8)	Ca(2)-O(3)	2.399(10)
V(1)-O(6)	1.670(9)	Ca(1)-O(3)	2.429(10)	Ca(2)-O(4)	2.289(10)
V(1)-O	**1.728**	Ca(1)-O(4)	2.365(10)	Ca(2)-O(5)	2.323(9)
		Ca(1)-O(5)	3.512(9)	Ca(2)-O(5)	2.324(9)
V(2)-O(1)	2.065(8)	Ca(1)-O(6)	2.408(9)	Ca(2)-O(6)	3.379(9)
V(2)-O(2)	1.834(7)	Ca(1)-O(6)	2.412(8)	Ca(2)-O(7)	3.602(10)
V(2)-O(2)	1.900(8)	Ca(1)-O(7)	2.453(8)	Ca(2)-O(7)	2.301(9)
V(2)-O(4)	1.667(9)	**Ca(1)-O**	**2.624**	**Ca(2)-O**	**2.686**
V(2)-O(7)	1.679(8)				
V(2)-O	**1.847**				

The average values are indicated by boldface type.

The results of the crystal structure refinement and selected interatomic distances for $Ca_{1.5}Cd_{0.5}V_2O_7$ are listed in Tables VI–VIII, respectively. The Crystallographic Information Frameworks (CIF) files are available in the supplementary material. The cadmium replaces calcium with a slight advantage in the second position (Table VII).

IV. CONCLUSION

The new double vanadate, $Ca_{1.5}Mn_{0.5}V_2O_7$, was synthesized and its crystalline structure was described. It has a homogeneity region, $Ca_{2-x}Mn_xV_2O_7$, $x = 0.4$–0.6. The compound $Ca_{1.5}Cd_{0.5}V_2O_7$ is identified as a member of a solid substitution with the structure of calcium pyrovanadate, $Ca_4(V_4O_{14})$.

SUPPLEMENTARY MATERIAL

The supplementary material for this article can be found at https://doi.org/10.1017/S0885715618000568.

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Fotiev, A. A., Zhuravlev, V. D., and Zhukov, V. P. (**1982**). "Diagrams of systems $Sr_2V_2O_7$ – M $_2V_2O_7$ $Ba_2V_2O_7$ – $M_2V_2O_7$, M=Ca, Cd," Zh. Neorg. Khim. **27**, 482–484.

Hawthorne, F. C. and Calvo, C. (**1972**). "The crystal structure of $Ba_2V_2O_7$," J. Solid St. Chem. **4**, 346–356.

Larson, A. C. and Von Dreele, R. B. (**2004**) *General Structure Analysis System* (*GSAS*) (Report LAUR 86-748), Los Alamos, New Mexico: Los Alamos National Laboratory.

Murashova, E. V., Velikodnyi, Yu. A., Ilyukhin, A. V., and Zhuravlev, V. D. (**1993**). "The crystalline structures of $Sr_{1.58}Ca_{0.42}V_2O_7$ and $Sr_{1.5}Cd_2V_2O_7$ and features of their isomorphism," Zh. Neorg. Khim. **38**, 428–431.

Murashova, E. V., Velikodnyi, Yu. A., and Zhuravlev, V. D. (**1994**). "Crystal structure of $Ca_{1.22}Cd_{0.78}V_2O_7$ solid solution," Zh. Neorg. Khim. **39**, 738–739.

Shannon, R. D. (**1976**). "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **32**, 751–767.

Sivakumar, T., Chang, H. Y., and Shiv Halasyamani, P. (**2007**). "Synthesis, structure, and characterization of a new two-dimensional lead (II) vanadate, $Ba_3PbV_4O_{14}$," Solid State Sci. **9**, 370–375.

Surat, L. L., Zhuravlev, V. D., Fotiev, A. A., and Velikodnyi, A.Yu. (**1996**). "Phase relations in systems MO-MIO-V2O5 (M, MI=Cd, Zn, Ni, Mn)," Zh. Neorg. Khim. **41**, 1370–1372.

Toby, B. H. (**2001**). "General structure analysis system (GSAS)," J. Appl. Crystallogr., **34**, 210–213.

Tong, Y.-P., Luo, G.-T., Jin, Z., and Lin, Y.-W. (**2011**). "Synthesis, structure and theoretical investigations of an alkaline earth vanadate oxide compound ($Ca_4V_4O_{14}$): electronic, optical and chemical bond properties," Aust. J. Chem. **64**, 973–977.

Trunov, V. K., Velikodnyi, Y. A., Murasheva, E. V., and Zhuravlev, V. D. (**1983**). "The crystal structure of calcium pyrovanadates," Doklady Akademii Nauk SSSR. **270**, 886–887.

Zhuravlev, V. D. and Hodos, M. Ia. (**1981**) "The phase equilibrium diagram of the system CaO – BaO – V2O5," Zh. Neorg. Khim. **26**, 1066–1069.

Zhuravlev, V. D. and Velikodnyi, Yu. A. (**1990**). "The system SrO – CaO – V2O5," Zh. Neorg. Khim. **35**, 264–2 66.

Zhuravlev, V. D., Velikodnyi, Yu. A., and Surat, L. L. (**1993**). "X-ray study of the systems Mn2V2O7 – M2V2O7, где M=Ba, Sr, Ca, Zn, Cu, Ni," Zh. Neorg. Khim." **38**, 1221–1224.

Zhuravlev, V. D., Surat, L. L., and Velikodnyi, Yu. A. (**1994**). "Diagrams of systems Mn(VO3)2 – M(VO3)2 and Mn2V2O7 – M2V2O7, (M – Sr, Ba)." Neorg. Mater. **30**, 1574–1575.

Zhuravlev, V. D. and Velikodnyi, Yu. A. (**1997**). "The isomorphic substitutions in systems $Pb_2V_2O_7$-$M_2V_2O_7$, when M=Ba, Sr, Ca, Cd," Zh. Neorg. Khim. **42**, 1387–1389.

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