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The Structures of the Solid Solutions Formed in the System $(Cr_xFe_{1-x})VO_4$

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Solid solutions $(Cr_xFe_{1-x})VO_4$ can be prepared over a wide composition range and are thermally stable to above 900°C. They are isomorphous with α-$MnMoO_4$ rather than adopting the $CrVO_4$ or $FeVO_4$ structures. At 3000 atm pressure, a reversible transformation to a $CrVO_4$ type polymorph takes place. substitution of small amounts of phosphate into $CrVO_4$ also produces an α-$MnMoO_4$ isomorph.

Introduction

Although Cr^{3+} and high spin Fe^{3+} have similar ionic radii (*1*), the MXO_4 compounds of the two ions often adopt very different crystal structures due to their different electronic configurations. The high spin $3d^5$ Fe^{3+} ion gains no ligand field stabilization energy (LFSE) from any particular coordination geometry and so occupies tetrahedral sites in $FePO_4$ (*2*), distorted trigonal bipyramidal sites in $FeAsO_4$ (*3*), and both 5- and 6-coordinate sites in $FeVO_4$ (*4*). $3d^3$ Cr^{3+} gains maximum LFSE from a regular octahedral environment and displays this geometry in the chromium analogs of all the above iron compounds (*5–7*).

Harrison (*8*) has recently indicated that solid solutions can be prepared in the system $(Cr_xFe_{1-x})VO_4$. The X-ray powder diffraction patterns of these materials could not be indexed and bore no resemblance to those of $FeVO_4$ or $CrVO_4$. We have determined the structures of the solid solutions formed at ambient and 3000 atm pressure. The same structures are adopted by $CrVO_4$ substituted with a few percent phosphate.

Experimental

Preparation and Analysis of Powder Samples

Polycrystalline samples were prepared from solution residues to facilitate mixing of the oxides before sintering. Appropriate quantities of $Cr(NO_3)_3 \cdot 9H_2O$ (Fisher, certified), $Fe(NO_3)_3 \cdot 9H_2O$ (J. T. Baker, Baker analyzed), NH_4VO_3 (Fisher, purified), and $(NH_4)_2HPO_4$ (Fisher, Certified A.C.S.) to make 5 g product were added to 50 ml distilled water and the resulting mixture was heated to dryness, giving a brown residue. The residues were sintered at temperatures between 800 and 850°C and then quenched

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to room temperature in air. Electron microscopy was performed using a Vacuum Generators HB501 Scanning Transmission Electron Microscope, and differential thermal analyses were obtained from a Du Pont Instruments 990 Thermal Analyzer with alumina as the reference material.

Hydrothermal preparations were carried out by heating 3 g solution residue sealed in a gold tube ($\frac{3}{8}$-in. diameter, 6 in. long) with 4 ml distilled water under 3000 atm supporting nitrogen pressure in an autoclave.

X-Ray powder diffraction patterns were recorded at 25°C using an automated Philips APD3600-02 diffractometer, with graphite monochromated Cu$K\alpha$ radiation, and a Guinier–Hagg type focusing camera (r = 40 mm), using monochromatic Cu$K\alpha_1$ radiation. Absorbance data were collected from the Guinier film with an Optronics P-1700 photomation instrument. A silicon internal standard (a = 5.43088(4) Å) was used to obtain corrected peak positions.

Single Crystal Growth and Data Collection

Single crystals of $(Cr_{0.2}Fe_{0.8})VO_4$ were grown by a standard melt technique. Equal masses of V_2O_5 (Cerac, 99.9% pure) and a solution residue of the required composition were placed in a covered platinum crucible and heated for 9 hr at 1000°C in a muffle furnace in air and then cooled to room temperature at 10°C hr^{-1}. Small, black rod-shaped crystals were extracted from the mixture after washing with hot dilute nitric acid.

A crystal of dimensions ~0.4 × 0.1 × 0.15 mm was sealed in a glass capillary in air. Axial photographs taken on an Enraf–Nonius CAD4 diffractometer using monochromated Mo$K\alpha$ radiation (λ = 0.71069 Å) showed the unit cell to be monoclinic. The orientation matrix and the unit cell parameters were determined from a least-squares refinement of the positions of 25 reflections giving the values a = 9.902(7) Å, b = 8.969(9) Å, c = 6.848(1) Å, and β = 107.58(3)° (esd's in parentheses).

The intensities at 915 independent reflection positions were collected in ω-scan mode up to a maximum 2θ value of 55° (maximum h, k, l values = 11, 10, 7) with a $(2.0 + 0.35 \tan \theta)°$ scan range at 2° min^{-1}. No radiation damage was evident during data collection. The reflection condition $h + k = 2n$ assigned the space group as $C2$, Cm, or $C2/m$. The data were corrected for Lorentz and polarization effects and, after an $I \geq 3\sigma(I)$ cutoff, 556 independent reflection intensities remained. No absorption correction was applied to the data.

Results

Polycrystalline Materials

$(Cr_xFe_{1-x})VO_4$ samples were prepared at 800°C in the range x = 0.05 to 0.80. The unknown structure type reported by Harrison (*8*) was observed in all the samples. Shifts in the X-ray diffraction peak positions with composition signaled the formation of solid solutions in this system; however traces of $FeVO_4$ and $CrVO_4$ were observed in samples with bulk compositions $x < 0.15$ and $x > 0.20$, respectively. This inhomogeneity could not be eliminated by prolonged reheating and regrinding of the samples.

The distribution of composition was investigated by analytical electron microscopy. A sample of $FeVO_4$ was used to calibrate the ratio of the intensities of the V$K\alpha$ and Fe$K\alpha$ peaks, enabling the composition of individual microcrystallites to be calculated in the samples of interest. Sample inhomogeneity was observed, but the mean value of x for the 20 to 30 microcrystallites analyzed in each sample corresponded to the bulk value, within limits of experimental error, showing that little $FeVO_4$ or $CrVO_4$ was present. The composition limits of the solid solution under the conditions of preparation are $0.10 < x < 0.85$.

X-Ray powder diffraction patterns of three compositions were indexed with knowledge of the unit cell parameters of the single crystal; a representative pattern is given in Table I. A least-squares procedure was used to obtain the cell parameters presented in Table II.

Differential thermal analyses of these materials showed no peaks below the endothermic decomposition temperatures given in Table II. The decomposition products were Cr_2O_3, V_2O_5, and $FeVO_4$. A residue with bulk composition $Cr(P_{0.05}V_{0.95})O_4$ was fired at 850°C, and powder X-ray diffraction analysis of the resulting sample showed that Cr_2O_3, $CrVO_4$, and a material isostructural with the $(Cr_xFe_{1-x})VO_4$ phases were present. Samples containing up to 20% phosphate were also prepared, but these gave complex mixtures of the above compounds and other unidentified phases.

TABLE I

THE X-RAY POWDER DIFFRACTION PATTERN OF α-$MnMoO_4$ TYPE $(Cr_{0.5}Fe_{0.5})VO_4$

d_{obs}	I/I_{max}	d_{calcd}	$h\ k\ l$
6.476	9	6.461	−1 1 0
3.261	42	3.261	0 0 2
3.231	100	3.230	−2 2 0
3.193	42	3.192	−1 1 2
3.037	13	3.036	−3 1 1
2.694	22	2.694	1 1 2
2.628	8	2.631	0 2 2
2.584	19	2.589	−3 1 2
		2.581	−2 2 2
2.345	7	2.347	4 0 0
2.225	7	2.227	0 4 0
2.174	12	2.174	0 0 3
2.153	37	2.154	−3 3 0
		2.152	−4 2 1
2.086	4	2.087	2 2 2
2.011	8	2.014	−4 2 2
		2.012	2 4 0
		2.009	−2 2 3
1.855	6	1.855	2 4 1
		1.853	−5 1 2
1.838	9	1.840	4 2 1
		1.839	0 4 2
		1.837	5 1 0
1.803	1	1.806	−1 3 3
1.748	2	1.750	1 5 0
1.720	10	1.720	−3 3 3
1.709	27	1.710	−2 0 4
1.615	10	1.615	−4 4 0
		1.615	−6 0 2
1.597	11	1.597	−5 3 2
		1.596	−2 2 4
1.571	2	1.570	4 2 2
1.560	5	1.560	−3 5 1
1.532	13	1.531	0 2 4
1.517	3	1.518	−6 2 2
1.507	5	1.508	1 1 4
		1.507	1 5 2
		1.505	−6 0 3
1.492	14	1.492	−4 2 4
1.485	11	1.484	0 6 0
1.458	4	1.458	5 3 1
		1.458	3 5 1
1.446	5	1.447	0 6 1
1.425	5	1.426	6 0 1
		1.426	−6 2 3
1.409	6	1.410	−2 6 1
1.391	13	1.391	3 3 3
1.389	12	1.389	2 4 3
1.383	7	1.383	−7 1 1

The $(Cr_{0.5}Fe_{0.5})VO_4$ residue was heated at 350°C for 12 hr under hydrothermal conditions, and was then cooled to room temperature over 12 hr. The product was a dark brown, homogeneous powder which was shown to be isostructural with $CrVO_4$ by X-ray diffraction. A differential thermal analysis of this $(Cr_{0.5}Fe_{0.5})VO_4$-II phase revealed a sharp endotherm at 670°C, due to the transition to the thermodynamically stable polymorph formed in the experiments at ambient pressure. After 8 hr hydrothermal treatment at 700°C, followed by 10°C hr^{-1} cooling to room temperature, a $Cr(P_{0.2}V_{0.8})O_4$ residue also produced a $CrVO_4$ type material. This undergoes an exothermic transition at 320°C to a complex mixture of

TABLE II

CELL PARAMETERS AND DECOMPOSITION TEMPERATURES OF POLYCRYSTALLINE α-$MnMoO_4$ TYPE $(Cr_xFe_{1-x})VO_4$ COMPOUNDS AND $Cr(P_yV_{1-y})O_4$ ($y < 0.05$)

	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)	T_{decomp} (°C)
$(Cr_xFe_{1-x})VO_4$						
$x = 0.25$	9.892(3)	8.947(2)	6.853(2)	107.61(2)	578.1(2)	917(5)
$x = 0.50$	9.852(3)	8.906(3)	6.846(2)	107.69(3)	572.3(2)	927(5)
$x = 0.80$	9.812(5)	8.857(4)	6.839(4)	107.75(6)	566.0(4)	965(5)
$Cr(P_yV_{1-y})O_4$	9.788(2)	8.833(1)	6.836(1)	107.65(2)	563.3(1)	

Note. Estimated standard deviations are in parentheses.

products, including the $(Cr_xFe_{1-x}VO_4$ type. However, a sample of $FeVO_4$ treated under the same hydrothermal conditions did not undergo any structural transformation, although a high-pressure $CrVO_4$ type polymorph of this compound is known (*9*). The indexed powder patterns of these two high-pressure $CrVO_4$ type polymorphs and their refined unit cell parameters are given in Tables III and IV.

TABLE III

THE DIFFRACTION PATTERNS OF THE $CrVO_4$ TYPE SOLID SOLUTIONS FORMED UNDER HYDROTHERMAL CONDITIONS

$(Cr_{0.5}Fe_{0.5})VO_4$–II			$Cr(P_{0.2}V_{0.8})O_4$			
d_{calcd}	d_{obs}	I/I_{max}	d_{calcd}	d_{obs}	I/I_{max}	$h\ k\ l$
4.6421	4.6378	46	4.6053	4.6076	26	1 1 0
4.1312	4.1321	33	4.1054	4.1090	23	0 2 0
3.6872	3.6860	100	3.6539	3.6548	72	1 1 1
3.4151	3.4162	67	3.3887	3.3900	55	0 2 1
2.8057	2.8051	72	2.7813	2.7798	36	2 0 0
2.5400	2.5396	96	2.5145	2.5138	100	1 1 2
2.4724	2.4736	76	2.4558	2.4565	46	1 3 0
			2.2729	2.2742	8	1 3 1
2.1679	2.1683	26	2.1499	2.1496	17	2 2 1
2.0656	2.0664	13	2.0527	2.0528	11	0 4 0
2.0601	2.0607	16	2.0401	2.0401	21	2 0 2
			1.8352	1.8369	6	1 1 3
1.8436	1.8438	29	1.8269	1.8265	24	2 2 2
1.8169	1.8168	17	1.7987	1.7986	17	0 2 3
1.7471	1.7470	20	1.7318	1.7314	9	3 1 1
1.7075	1.7079	30	1.6943	1.6943	23	0 4 2
1.5852	1.5848	16	1.5750	1.5739	10	1 5 0
1.5635	1.5635	38	1.5491	1.5496	24	3 1 2
1.5474	1.5473	22	1.5351	1.5338	12	3 3 0
1.5337	1.5332	15	1.5234	1.5239	10	1 5 1
			1.5104	1.5109	12	2 2 3
1.5173	1.5169	21	1.5007	1.5007	29	0 0 4
1.4587	1.4585	65	1.4470	1.4472	43	2 4 2
			1.4269	1.4261	2	1 1 4
			1.4095	1.4102	8	0 2 4
1.4029	1.4029	24				4 0 0
			1.3207	1.3202	15	2 0 4
			1.2865	1.2872	3	4 2 1
1.2932	1.2934	24	1.2805	1.2803	26	1 3 4

Single Crystal Structure Refinement

The similarity of the *a*/*b* and *c*/*b* ratios and the value of β of $(Cr_{0.2}Fe_{0.8})VO_4$ to those of molybdates with the α-$MnMoO_4$ structure (*10*) (for α-$MnMoO_4$; a = 10.498 Å, b = 9.532 Å, c = 7.156 Å, β = 106.17°, Z = 8, space group $C2/m$) led us to use the coordinates of α-$MnMoO_4$ (*11*) as a starting model for a full-matrix, least-squares refinement with the data. Neutral atom scattering factors (*12*) were used for the vanadium, oxygen, and weighted average *M*

TABLE IV

REFINED CELL PARAMETERS OF THE $CrVO_4$ ISOMORPHS $Cr_{0.5}Fe_{0.5}VO_4$–II AND $CrP_{0.2}V_{0.8}O_4$ (esd's IN PARENTHESES)

Compound	a (Å)	b (Å)	c (Å)	V (Å^3)
$Cr_{0.5}Fe_{0.5}VO_4$–II	5.6115(6)	8.2624(9)	6.0691(7)	281.39(4)
$CrP_{0.2}V_{0.8}O_4$	5.563(1)	8.211(2)	6.003(1)	274.17(7)
$FeVO_4$–II[a]	5.646(4)	8.303(5)	6.134(4)	287.6(6)
$CrVO_4$[b]	5.5806(4)	8.2371(6)	5.9955(4)	275.60(3)
β-$CrPO_4$[c]	5.1710(4)	7.7573(2)	6.1183(2)	245.42(3)

Note. The values for $FeVO_4$–II, $CrVO_4$, and β-$CrPO_4$ are given for comparison.

[a] Ref. (*9*).

[b] These cell parameters were refined from Guinier data collected from a standard sample of $CrVO_4$.

[c] Ref. (*5*).

atoms ($M = \frac{1}{5}$Cr + $\frac{4}{5}$Fe). The Mn and Mo sites were used for the M and V atom positions, respectively, and their occupancies were not varied. The refinement converged successfully, giving $R = 0.017$ and $wR = 0.026$, where $wR = [w(|F_o| - |F_c|)^2/w|F_o|^2]^{1/2}$, with weights w proportional to $[\sigma^2(I) + (0.03I)^2]^{-1/2}$. The refined atomic coordinates and anisotropic thermal parameters are given in Table V, and bond distances and angles are shown in Table VI.

Discussion

The crystal structure of $(Cr_{0.2}Fe_{0.8})VO_4$ consists of an infinite network of clusters of four edge-sharing MO_6 octahedra linked to other clusters by VO_4 tetrahedra. A fuller description of this structure type is given in Ref. (*11*). The bond distances and angles given in Table VI are comparable to those in $CrVO_4$ and $FeVO_4$, and show that both the octahedra and tetrahedra are highly distorted. The mean M–O distances for the two octahedral sites are very similar, indicating that the trivalent cations are not ordered between the two M sites.

TABLE V

ATOMIC AND THERMAL PARAMETERS FOR $(Cr_{0.2}Fe_{0.8})VO_4$ (esd's IN PARENTHESES),

Fractional Coordinates (×10,000) in $C2/m$ (No. 12), and Isotropic Thermal Prameters

Atom	Symmetry position	x	y	z	B_{iso}
M(1)	4h	0	1855.0(6)	5000	0.4(0)′
M(2)	4i	7963.1(5)	0	1368.1(7)	0.4(0)′
V(1)	4g	0	2501.2(6)	0	0.4(0)′
V(2)	4i	2714.7(6)	0	4014.6(9)	0.4(0)′
O(1)	4i	3596(2)	5000	4573(4)	0.5(1)′
O(2)	4i	2019(3)	0	1426(4)	1.1(1)′
O(3)	8j	1419(2)	3536(2)	1093(3)	1.0(0)′
O(4)	8j	4544(2)	3460(2)	2019(3)	0.6(0)′
O(5)	8j	3636(2)	1563(2)	4743(3)	1.2(0)′

Anisotropic thermal parameters ($\beta \times 10{,}000$) $\exp[-(\beta_{11}h^2 \ldots + 2(\beta_{12}hk \ldots))]$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
M(1)	11.1(6)	13.3(7)	22.2(13)	0	4.8(6)	0
M(2)	9.0(6)	15.0(6)	22.2(12)	0	4.5(6)	0
V(1)	11.8(6)	14.5(7)	23.0(14)	0	7.2(6)	0
V(2)	10.7(6)	16.4(7)	23.5(14)	0	7.1(6)	0
O(1)	14(2)	21(3)	28(5)	0	8(3)	0
O(2)	26(3)	56(4)	42(6)	0	12(3)	0
O(3)	30(2)	33(2)	62(4)	−15(2)	16(2)	−7(2)
O(4)	17(2)	25(2)	29(4)	4(1)	6(2)	−1(2)
O(5)	33(2)	38(2)	87(5)	−16(2)	27(2)	−8(3)

TABLE VI

BOND DISTANCES AND ANGLES FOR $(Cr_{0.2}Fe_{0.8})VO_4$ (esd's IN PARENTHESES)

Bond distances (Å)			
M(1)–O(1)^a (×2)	2.131(2)	V(1)–O(3) (×2)	1.661(2)
M(1)–O(4)^b (×2)	1.973(2)	V(1)–O(4)1 (×2)	1.799(2)
M(1)–O(5)^b (×2)	1.930(2)	Mean V(1)–O distance =	1.730(2)
Mean M(1)–O distance =	2.011(2)		
		V(2)–O(1)^c	1.838(3)
M(2)–O(1)^h	2.093(3)	V(2)–O(2)	1.697(3)
M(2)–O(2)^i	1.919(3)	V(2)–O(5) (×2)	1.665(3)
M(2)–O(3)^h (×2)	1.981(2)	Mean V(2)–O distance =	1.716(3)
M(2)–O(4)^h (×2)	2.033(2)		
Mean M(2)–O distance =	2.007(2)	Mean V–O distance =	1.723(2)
Mean M–O distance =	2.009(2)		
Bond angles (degrees)			
O(1)^a–M(1)–O(1)^c	77.3(1)	O(3)–V(1)–O(3)^m	112.1(1)
O(1)^a–M(1)–O(4)^d	79.07(9)	O(3)–V(1)–O(4)^d	107.2(1)
O(1)^a–M(1)–O(4)^b	88.1(1)	O(3)–V(1)–O(4)^l	103.8(1)
O(1)^a–M(1)–O(5)^d	98.7(1)	O(4)^l–V(1)–O(4)^d	122.7(1)
O(1)^a–M(1)–O(5)^b	174.9(1)	O(1)^c–V(2)–O(2)	114.9(1)
O(4)^b–M(1)–O(4)^d	163.6(1)	O(1)^c–V(2)–O(5)	104.63(8)
O(4)^b–M(1)–O(5)^d	97.75(8)	O(2)–V(2)–O(5)	109.01(9)
O(4)^b–M(1)–O(5)^b	94.32(8)	O(5)–V(2)–O(5)^k	114.7(2)
O(5)^b–M(1)–O(5)^d	85.4(1)	M(1)^e–O(1)–M(1)^b	102.7(1)
O(1)^h–M(2)–O(2)^i	162.9(1)	M(1)^e–O(1)–M(2)^f	96.90(8)
O(1)^h–M(2)–O(3)^h	94.46(8)	M(1)^b–O(4)–M(2)^f	104.15(8)
O(1)^h–M(2)–O(4)^h	78.65(7)	M(1)^e–O(1)–V(2)^g	117.58(8)
O(2)^i–M(2)–O(3)^h	98.33(8)	M(2)^f–O(1)–V(2)^g	121.1(1)
O(2)^i–M(2)–O(4)^h	88.86(8)	M(2)^i–O(2)–V(2)	156.7(2)
O(3)^h–M(2)–O(3)^j	83.0(1)	M(2)^f–O(3)–V(1)	159.5(1)
O(3)^h–M(2)–O(4)^j	172.77(9)	M(1)^b–O(4)–V(1)^l	134.0(1)
O(3)^h–M(2)–O(4)^h	95.2(1)	M(2)^f–O(4)–V(1)^l	120.8(1)
O(4)^h–M(2)–O(4)^j	85.6(1)	M(1)^b–O(5)–V(2)	162.1(1)

Symmetry operation codes

^{a} $-\frac{1}{2} + x, -\frac{1}{2} + y, z$;
^{b} $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$;
^{c} $\frac{1}{2} - x, -\frac{1}{2} + y, 1 - z$;
^{d} $-\frac{1}{2} + x, \frac{1}{2} - y, z$;
^{e} $\frac{1}{2} + x, \frac{1}{2} + y, z$,
^{f} $-\frac{1}{2} + x, \frac{1}{2} + y, z$;
^{g} $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$;
^{h} $\frac{1}{2} + x, -\frac{1}{2} + y, z$;
^{i} $1 - x, y, -z$;
^{j} $\frac{1}{2} + x, \frac{1}{2} - y, z$;
^{k} $x, -y, z$;
^{l} $\frac{1}{2} - x, \frac{1}{2} - y, -z$;
^{m} $-x, y, -z$.

The above results show that at ambient pressures, $(Cr_xFe_{1-x})VO_4$ solid solutions adopt the α-$MnMoO_4$ structure over a wide range of compositions, in preference to the structures of either $CrVO_4$ or $FeVO_4$. The unit cell parameters of the solid solutions appear to vary smoothly with composition, suggesting that the iron and chromium ions are disordered over the two crystallographically distinct M sites across the range of compositions studied.

The formation of a solid solution with a structure that is different from those of the end members of the series is unusual and, in this case, may represent a compromise between the distorted cation environments in $FeVO_4$ and the regularity of the $CrVO_4$ structure. The iron coordination polyhedra in $FeVO_4$ (*4*) form doubly bent chains of deformed octahedra and trigonal bipyramids linked by distorted VO_4 tetrahedra. Although the polyhedra are as distorted as those in $(Cr_{0.2}Fe_{0.8})VO_4$, this structure type would be disfavored by the occupation of the 5-coordinate site by Cr^{3+} ions, which would result in a loss of LFSE, or by the loss of entropy required to prevent Cr^{3+} from occupying this site. $CrVO_4$ has a structure of much higher symmetry (*7*), with parallel, infinite chains of trans edge-sharing CrO_6 octahedra bound to each other by VO_4 tetrahedra. The disorder caused by the incorporation of Fe^{3+} ions into this lattice evidently destabilizes this structure type with respect to the less dense α-$MnMoO_4$ structure at ambient pressures, but at 3000 atm, the reduction in volume [1.7% for $(Cr_{0.5}Fe_{0.5})VO_4$] makes the formation of the $CrVO_4$ type polymorph favorable. A transition between these two structure types is also observed in $MgCrO_4$ and $CdCrO_4$ (*13, 14*), which are isostructural with $CrVO_4$ at low temperatures and form α-$MnMoO_4$ type polymorphs at high temperatures. This polymorphism has not been observed in any transition metal chromates.

Thus, a transition between low-temperature, high-pressure $CrVO_4$ type polymorphs and high-temperature, low-pressure α-$MnMoO_4$ type polymorphs is observable in chromates and vanadates when the cations have no strong preference for regular octahedral coordination, as in $MgCrO_4$ and $CdCrO_4$, or are disordered, as in the $(Cr_xFe_{1-x})VO_4$ solid solutions.

Anion disorder also seems to destabilize the $CrVO_4$ structure, as the substitution of small amounts of phosphate into $CrVO_4$ causes it to adopt the α-$MnMoO_4$ structure, although the stable form of $CrPO_4$ is isostructural with $CrVO_4$. At high pressure, the denser $CrVO_4$ type solid solution is again stable. At higher phosphate concentrations the system becomes more complicated, and we are investigating the mixtures of phases formed.

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