

$\text{Ca}_{10}\text{V}_{5.2}\text{Fe}_{0.8}\text{O}_{24}$, a Novel Oxometalate with Discrete Complex Anions

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Lustrous needle shaped prismatic single crystals of the new compound $\text{Ca}_{10}\text{V}_{5.2}\text{Fe}_{0.8}\text{O}_{24}$ were obtained out of a sample with nominal composition $\text{Ca}_2\text{Fe}_{1.6}\text{V}_{0.4}\text{O}_5$ prepared at 1400 °C. The crystals are opaque and stable to humid air. $\text{Ca}_{10}\text{V}_{5.2}\text{Fe}_{0.8}\text{O}_{24}$ crystallizes with a new structure type, space group *Pnma* with $a = 6.803(3)$, $b = 16.015(8)$, $c = 10.418(7)$ Å, $Z = 2$, $R = 0.041$. The crystal structure is characterized by two mononuclear tetrahedral species, MO_4 , which differ significantly from each other with respect to their M–O bond lengths. One with an average bond distance of 1.709(8) Å represents an orthovanadate ion. The other with a significantly larger value $d(\text{M–O}) = 1.744(6)$ Å corresponds to a mixed occupation of its centre according to $[\text{V}_{0.8}\text{Fe}_{0.2}\text{O}_4]^{3.5-}$. In the crystal structure the complex anions are arranged in separate sheets parallel to the (010) plane. They are separated from each other by three crystallographically independent Ca^{2+} ions which are each coordinated by 7 oxygen atoms in distorted pentagonal bipyramidal and trigonal prismatic configurations, respectively.

Key words: Complex Oxides, Vanadium, Iron

Introduction

As a consequence of the increasing use of scrap for the production of steel a number of nonferrous metals are introduced into the slag during the process of slag formation. In view of the broad application of slag as building materials it is of great importance with respect to our environment in which chemical form elements like Cr or V are incorporated in the slag.

In this context one of the major slag components, the dicalciumferrite, $\text{Ca}_2\text{Fe}_2\text{O}_5$, phase is of particular interest since it offers two geometrically different sites, one tetrahedral and one octahedral per formula unit (both occupied by Fe^{3+} in pure $\text{Ca}_2\text{Fe}_2\text{O}_5$) for substitution by transition metal ions. The latter should be particularly suitable for transition metal ions of appropriate size, which due to their d-electron configuration should possess high octahedral site preference energy (OSPE) like Cr^{3+} or V^{3+} . It has been verified by neutron powder diffraction, that Cr(III) can replace Fe(III) on this site up to 50% [1]. Due to the similarity of the ionic radii of V^{3+} and (high spin) Fe^{3+} for octahedral coordination the substitution of Fe(III) on the octahedral sites of the $\text{Ca}_2\text{Fe}_2\text{O}_5$ by V(III) is expected to be even more favoured. Surprisingly this is not the case in samples prepared from the melt where the vanadium rich samples reveal the appearance of a

new phase, $\text{Ca}_{10}\text{V}_{5.2}\text{Fe}_{0.8}\text{O}_{24}$, which shows no relations to the dicalciumferrite phase. Its structural peculiarities are presented below.

Experimental Section

Samples in the (pseudo)binary section $\text{Ca}_2\text{Fe}_{2-x}\text{V}_x\text{O}_5$ ($0 < x < 1$) were synthesized by reacting intimate mixtures of the binary oxides $\alpha\text{-Fe}_2\text{O}_3$ (99.99%), V_2O_3 (99.99%) and CaO (freshly prepared from CaCO_3 , p.a.) in the proposed stoichiometries. These mixtures were placed in small platinum crucibles and heated under argon in a Tammann furnace at 1400 °C. The samples were kept at this temperature for 2d, brought to 800 °C at a controlled rate of 5°/h followed by free cooling to ambient temperature.

The ingots obtained by this treatment were opaque and showed metallic lustre. Needle shaped prismatic single crystals up to 2 mm in length could be observed with samples of higher vanadium contents ($x \geq 0.4$). They were stable against air and humidity. Powder diagrams showed that in these samples apparently a new solid, not related to the dicalciumferrite phase had been formed. An EDX analysis performed on a scanning electron microscope (JSM-6400, Tracor; JPN) indicated that the new compound was in essence a calcium vanadate with only minor amounts of iron.

For determination of its crystal structure a single crystal with the dimensions $0.2 \times 0.05 \times 0.05$ mm³ was isolated from the sample with nominal composition $\text{Ca}_2\text{Fe}_{1.6}\text{V}_{0.4}\text{O}_5$,

Table 1. Crystallographic data and structure refinement details for Ca₁₀V_{5.2}Fe_{0.8}O₂₄.

Pearson Symbol	<i>oP80</i>
<i>a</i> [Å]	6.803(3)
<i>b</i> [Å]	16.015(8)
<i>c</i> [Å]	10.418(7)
Space group	<i>Pnma</i>
<i>Z</i>	2
<i>V</i> [Å ³]	1135
<i>dx</i> [gcm ⁻³]	3.20
<i>M_r</i>	1094.23
<i>μ</i> (Mo-K α) [cm ⁻¹]	51.11
<i>Structure refinement:</i>	
Unique reflections	1410
Observed reflections	719 $\geq 3\sigma(I)$
Variables	100
<i>R</i> ; <i>R_w</i> ^a	0.041; 0.039
$R = \sum F_o - F_c / \sum F_o $	0.041
$R_w = [\sum w F_o - F_c ^2 / \sum w F_o ^2]^{1/2}$	0.039
$w = [\sigma(F_o^2)^2 + (0.0055F_o^2)^2]^{-1/2}$	
Extinction coefficient	6.34×10^{-8}
Goodness of fit	1.32
Residual electron density [eÅ ⁻³]	1.67/−1.12

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w||F_o| - |F_c||^2 / \sum w|F_o|^2]^{1/2}$, $w = [\sigma(F_o^2)^2 + (0.0055F_o^2)^2]^{-1/2}$.

mounted on the top of a glass fibre and transferred to a four circle diffractometer (Nonius Turbo CAD4) operated with graphite monochromated Mo-K α -radiation ($\lambda = 0.71073$ Å). Preliminary X-ray investigations revealed a primitive orthorhombic unit cell, the serial extinctions $0kl : k + l \neq 2n$ and $hk0 : h \neq 2n$ indicated *Pnma* or *Pn2₁a* as possible space groups. Intensity data were collected over one quadrant of the sphere of reflections up to $2\theta = 56^\circ$ applying the $\omega - 2\theta$ scan mode (scan width $1.05^\circ + 0.35^\circ \tan \theta$, maximum scan time 100 s). Crystal and orientational stability were monitored by three periodically determined control reflections which, however, showed only the usual statistical fluctuations of their counting rates. A total of 3574 reflections were determined. They were corrected for Lorentz and polarisation effects.

Merging symmetry equivalent reflections yielded a set of 1410 unique reflections out of which 719 with $I \geq 3\sigma(I)$ were considered as significant ($R_{\text{int}} = 0.076$).

The atomic arrangement of the metal atoms Ca and V was determined by direct methods in the centrosymmetric space group *Pnma* deploying the SIR92 [2] programme. Oxygen positions were obtained from difference Fourier maps indicating the presence of two discrete tetrahedral oxoanions one centred by V in *4c*, the other in *8d*. Since the EDX analysis performed on the same crystal showed the presence of Fe, both metal centres were alternatively considered for a mixed occupation by V and Fe. Least squares' refinements with Fe/V in the *4c* position led unambiguously to significantly larger *R*-values and were hence discarded. Refinements allowing a mixed occupation for the *8d* position however soon converged at $R = 0.041$ ($R_w = 0.039$) for a Fe/V population ratio of 0.200 : 0.800 (estimated standard deviation = 0.015) resulting in the formula Ca₁₀V_{5.2}Fe_{0.8}O₂₄. A final difference Fourier map was featureless.

All calculations were performed with programs of the MolEN [3] crystallographic software package. A correction for secondary extinction was applied in the final cycles of refinement. Precise lattice constants were obtained from the least squares' refinement of the angular positions of 25 well centred reflections in the range $32^\circ < 2\theta < 38^\circ$. They are listed in Table 1 together with other crystallographic and structure refinement data. The atomic positions and anisotropic displacement parameters are summarized in Table 2. Interatomic distances and selected bond angles are given in Table 3.

Further details on the structure refinement have been deposited with the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen under CSD No. 391248.

Discussion

Ca₁₀V_{5.2}Fe_{0.8}O₂₄ crystallizes with a new structure type characterized by the formation of mononuclear

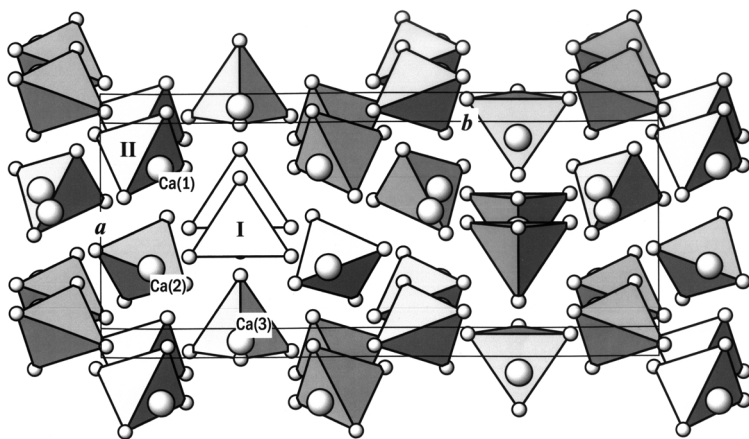
Table 2. Atomic positions and anisotropic displacement parameters for Ca₁₀V_{5.2}Fe_{0.8}O₂₄.

Atom	Wyckoff pos.	<i>x</i>	<i>y</i>	<i>z</i>	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃	B _{eq} ^a
Ca(1)	8 <i>d</i>	0.3277(3)	0.1073(1)	0.3328(2)	0.0347(9)	0.0197(7)	0.022(1)	0.0075(8)	0.0088(9)	0.0067(8)	2.00(4)
Ca(2)	8 <i>d</i>	0.3737(2)	0.09116(9)	0.9365(2)	0.0204(7)	0.0134(7)	0.0229(9)	0.0007(8)	−0.003(1)	0.0044(8)	1.49(3)
Ca(3)	4 <i>c</i>	0.0463(4)	1/4	0.8159(3)	0.025(1)	0.0113(9)	0.042(2)	0	−0.007(2)	0	2.05(5)
M(1)	8 <i>d</i>	0.3603(2)	0.07181(7)	0.6298(1)	0.0142(5)	0.0112(5)	0.0144(6)	0.0014(6)	−0.0017(7)	−0.0019(6)	1.05(2)
V(2)	4 <i>c</i>	0.0243(4)	1/4	0.4215(2)	0.040(1)	0.0097(7)	0.016(1)	0	0.003(1)	0	1.73(4)
O(1)	8 <i>d</i>	0.0427(8)	0.1195(3)	0.9617(5)	0.023(3)	0.029(3)	0.015(3)	−0.002(3)	0.002(3)	0.005(3)	1.8(1)
O(2)	8 <i>d</i>	0.4242(8)	0.9908(3)	0.7317(6)	0.029(3)	0.016(2)	0.024(3)	0.006(2)	−0.007(3)	0.002(3)	1.8(1)
O(3)	8 <i>d</i>	0.281(1)	0.1514(3)	0.7298(6)	0.044(3)	0.009(2)	0.014(3)	0.002(3)	0.000(4)	−0.004(3)	1.8(1)
O(4)	8 <i>d</i>	0.1828(8)	0.0426(3)	0.5137(5)	0.027(3)	0.010(2)	0.016(3)	−0.003(3)	0.001(3)	−0.003(3)	1.4(1)
O(5)	8 <i>d</i>	0.448(1)	0.1584(3)	0.1437(6)	0.049(3)	0.012(2)	0.019(3)	−0.002(3)	0.004(4)	0.002(3)	2.1(1)
O(6)	4 <i>c</i>	0.276(2)	1/4	0.408(1)	0.122(9)	0.007(3)	0.055(6)	0	0.027(9)	0	4.8(3)
O(7)	4 <i>c</i>	0.442(1)	1/4	0.9240(8)	0.037(5)	0.013(3)	0.016(5)	0	−0.010(5)	0	1.7(2)

^a $B_{\text{eq}} = \frac{8\pi^2}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

Table 3. Interatomic distances (up to 3.4 Å) and selected bond angles for $\text{Ca}_{10}\text{V}_{5.2}\text{Fe}_{0.8}\text{O}_{24}$.

a) Coordination of the Ca ²⁺ ions											
Ca(1)	O(5)	2.286(7)		Ca(2)	O(4)	2.302(6)		Ca(3)	O(3)	2.418(7)	2×
Ca(1)	O(4)	2.367(6)		Ca(2)	O(1)	2.312(6)		Ca(3)	O(3)	2.446(7)	2×
Ca(1)	O(2)	2.401(6)		Ca(2)	O(4)	2.320(5)		Ca(3)	O(1)	2.584(6)	2×
Ca(1)	O(6)	2.443(5)		Ca(2)	O(3)	2.442(7)		Ca(3)	O(7)	2.60(1)	
Ca(1)	O(2)	2.552(6)		Ca(2)	O(5)	2.465(7)		Ca(3)	O(7)	2.92(1)	
Ca(1)	O(1)	2.600(7)		Ca(2)	O(7)	2.589(2)					
Ca(1)	O(5)	2.718(8)		Ca(2)	O(2)	2.693(7)					
Ca(1)	M(1)	3.153(2)		Ca(2)	V(2)	3.116(2)		Ca(3)	M(1)	3.172(1)	2×
Ca(1)	V(2)	3.216(3)		Ca(2)	M(1)	3.211(2)					
				Ca(2)	M(1)	3.396(2)					
b) Geometry of the complex anions								c) Shortest interanionic contacts			
M(1)	O(2)	1.732(6)		O(1)	M(1)	O(3)	103.2(3)	O(3)	O(7)	2.79(1)	
M(1)	O(3)	1.732(6)		O(1)	M(1)	O(4)	103.2(3)	O(4)	O(4)	2.85(1)	
M(1)	O(1)	1.741(7)		O(2)	M(1)	O(3)	105.1(3)	O(2)	O(5)	2.854(8)	
M(1)	O(4)	1.772(6)		O(2)	M(1)	O(4)	113.0(3)	O(4)	O(5)	2.945(9)	
				O(3)	M(1)	O(4)	113.1(3)	O(1)	O(3)	2.95(1)	
				O(1)	M(1)	O(2)	119.0(3)				
V(2)	O(5)	1.697(6)	2×	O(5)	V(2)	O(6)	105.7(3)	2×			
V(2)	O(7)	1.704(1)		O(5)	V(2)	O(7)	106.1(3)	2×			
V(2)	O(6)	1.72(1)		O(6)	V(2)	O(7)	113.8(6)				
				O(5)	V(2)	O(5)	119.7(5)				

Fig. 1. The crystal structure of $\text{Ca}_{10}\text{V}_{5.2}\text{Fe}_{0.8}\text{O}_{25}$ in polyhedral representation Type I tetrahedra are by V, those of Type II by $\text{M} = \text{V}_{0.8}\text{Fe}_{0.2}$.

nuclear tetrahedral groups MO_4 which – as shown in Fig. 1 – are arranged in slabs parallel to (010). There are two crystallographically independent tetrahedral MO_4 groups, type I and type II, respectively, with significantly different bond distances which will be discussed in greater detail below. Type I tetrahedra are centred by the metal atoms in $4c$. They lie on the mirror planes and have C_s -symmetry pointing alternately in the $[100]$ and $[\bar{1}00]$ directions. Type II tetrahedra are centred by the metal atoms in $8d$ and show different orientations with two opposite edges roughly parallel to the ab -plane. Both tetrahedral species are distorted with bond angles ranging from $103.2(3)^\circ$ to $119.7(5)^\circ$.

Each of the three crystallographically independent calcium atoms in the structure is coordinated to seven oxygen atoms. Ca(1) and Ca(2) are in distorted trigonal bipyramidal coordinations through oxygen while the coordination of Ca(3) is a monocapped trigonal prism. Their average Ca–O bond distances are within the narrow range of 2.462(6) for Ca(2) to 2.499(7) Å for Ca(3). Details of their coordinations are given in Fig. 2. Together with the M(1) atoms Ca(1) and Ca(2) are arranged on slightly corrugated 3^6 -nets forming pairs of adjacent layers which run parallel to (010). Their stacking is interrupted by an open planar layer of Ca(3) and V(2) which both lie on the mirror plane. The crystal

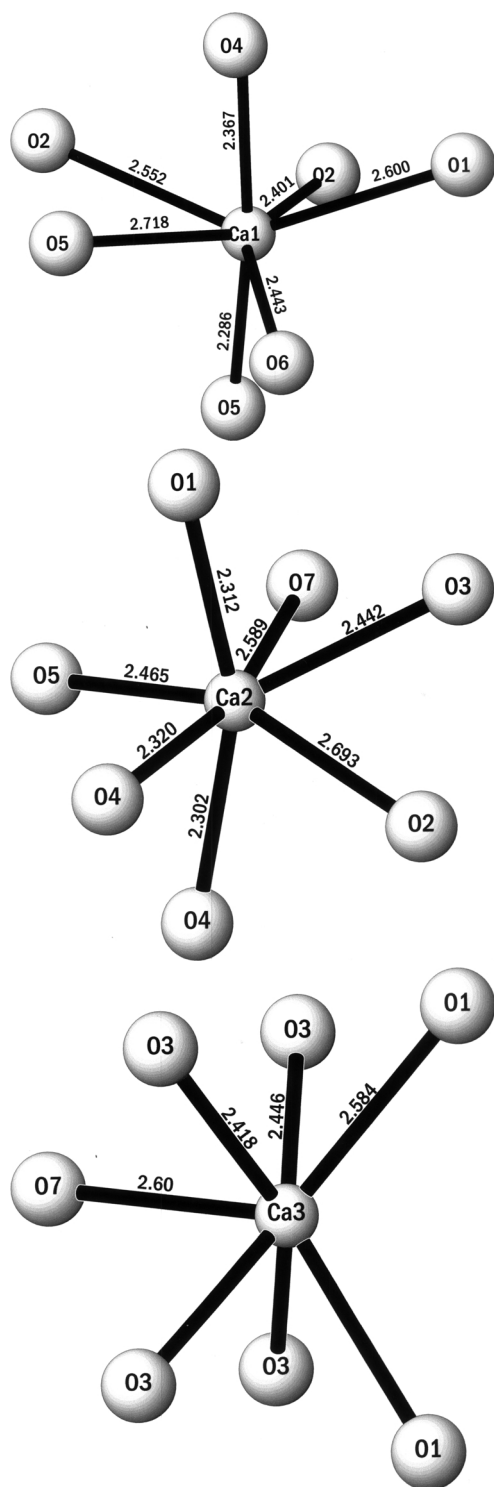


Fig. 2. The oxygen coordination of the calcium atoms.

structure is thus apparently not based on a close packed arrangement. Since the formula type $\text{A}_5\text{B}_3\text{O}_{12}$ has so far not been found with other *ortho*-tetraoxometalates apparent similarities with their crystal structures do not exist.

There are six anionic groups per formula unit to compensate the 20 cationic charges which requires an average anionic charge of -3.33 and therefore species with different oxidation states as central atoms of the oxoanions. This should be reflected in the bond lengths, unless the different central species were evenly distributed over all tetrahedral anions. A critical inspection of the bond lengths is hence particularly valuable in cases where, as in $\text{Ca}_{10}\text{V}_{5.2}\text{Fe}_{0.8}\text{O}_{24}$, the X-ray scattering power of the central atoms is very similar.

For $\text{Ca}_{10}\text{V}_{5.2}\text{Fe}_{0.8}\text{O}_{24}$ the bond distances in the complex anions of type I lie in the narrow range of $1.697(6)$ to $1.72(1)$ Å. The mean value $\bar{d} = 1.709(8)$ Å compares well with the sum of the Shannon radii [4] of tetrahedrally coordinated V^{5+} ($r = 0.95$ Å) and O^{2-} ($r = 1.21$ Å). For crystal chemical reasons and in accord with the results of the crystallographic refinements this anionic group can therefore be identified as an orthovanadate ion, $[\text{VO}_4]^{3-}$. Its central atom in Tables 2 and 3 is hence labelled as V. Comparable V–O bond lengths are for instance found in $\text{Ca}_3(\text{VO}_4)_2$ [5].

The situation with the type II anions is less obvious. Here the individual M–O distances as well as their spread are distinctly larger ($d_{\text{M}(1)-\text{O}} = 1.732(6) - 1.772(6)$ Å). The average value is calculated as $1.744(6)$ Å, larger than expected for an *ortho*-vanadate, yet much smaller than 1.84 Å, the sum of the Shannon radii for Fe^{3+} tetrahedrally coordinated by oxygen ($r_{\text{Fe}^{3+}(\text{h.s.})} = 0.63$ Å, $r_{\text{O}^{2-}} = 1.21$ Å). Given a linear relationship between the M–O bond length and the degree of substitution of V by Fe ions, this indicates that about 19% of the V^{5+} is substituted by Fe^{3+} . This comes close to the value obtained by the structure refinement. The validity of this assumption can be checked by calculating an average M–O bond length for the ferrite garnet mixed crystal $\text{Ca}_3\text{Fe}_{3.5}\text{V}_{1.5}\text{O}_{12}$ [6]. Here an interpolation of the M–O bond distance yields 1.801 Å, in fair agreement with the experimental value of 1.803 Å. This seems to justify the assignment of the central atom in *8d* as $\text{M}(1) = \text{V}_{0.8}\text{Fe}_{0.2}$. However, the anionic charge of the $[\text{V}_{0.75}^{\text{V}}\text{Fe}_{0.25}^{\text{III}}\text{O}_4]$ unit calculates as $3.4-$, less than $3.5-$, the value required from the electroneutrality bal-

ance. This charge could be matched by assuming a slightly different composition: $[\text{V}_{0.75}^{\text{V}}\text{Fe}_{0.25}^{\text{III}}\text{O}_4]^{3.5-}$. Interestingly, this is not supported by the structure analysis where a model with these population parameters leads to a slightly, yet significantly higher R -value in the least squares refinements. This discrepancy might be explained by slight cation defects in the Ca^{2+} substructure which currently cannot be proven by the structure refinement, or alternatively by the presence of a small amount of V^{IV} in the complex anion which should in principle be verifiable by careful susceptibility measurements. Unfortunately, the EDX analyses, though performed on the same crystal, do not help to clear up this situation since the stoichiometric differences between these alternative models

are well within the standard deviations of the analysis. Hopefully future investigations will clear up this open question.

The most surprising feature of $\text{Ca}_{10}\text{V}_{5.2}\text{Fe}_{0.8}\text{O}_{24}$ is its formation from the educts CaO , V_2O_3 , and Fe_2O_3 . Since the high temperature reaction was carried out under an inert atmosphere the formation of V^{5+} must be attributed to a redox reaction between V^{3+} and Fe^{3+} . This is corroborated by the fact that the bulk samples are ferromagnetic even at temperatures $> 650^\circ\text{C}$ which indicates the presence of elemental iron in the reaction products. A detailed thermoanalytical study – currently in progress – should give more insight into the phase relationships of this section of the quaternary system Ca/V/Fe/O .

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