Crystal structure of a mixed dicalcium ferrite, $\text{Ca}_2\text{Fe}_{1.66}\text{V}_{0.34}\text{O}_5$

N. A. Harringer^I, H. Presslinger^{II} and K. O. Klepp^{*I}

^I University of Linz, Institute of General and Inorganic Chemistry, Altenbergerstrasse 69, A-4040 Linz, Austria

^{II} Voest Alpine AG, Division steel, Voest Alpine Strasse 3, A-4031 Linz, Austria

Received January 13, 2004; accepted and available on-line February 6, 2004; CSD no. 409757

Abstract

$\text{Ca}_2\text{Fe}_{1.66}\text{O}_5\text{V}_{0.34}$, orthorhombic, *Pnma* (no. 62), $a = 5.4171(6)$ Å, $b = 14.774(4)$ Å, $c = 5.584(2)$ Å, $V = 446.9$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.032$, $wR_{\text{ref}}(F) = 0.037$, $T = 294$ K.

Source of material

The title compound was obtained as coarse platelets by reacting a powdered mixture of 837.3 mg CaO (ex CaCO_3 , p.a.; Merck), 7715.2 mg $\alpha\text{-Fe}_2\text{O}_3$ (99.9 %, Fluka) and 447.6 mg V_2O_3 (99.9 %, Fluka) in a Tammann furnace at 1400°C, followed by slow cooling.

Experimental details

The high ratio of U_{22}/U_{11} (Fe1, V1) originates from the fact that the U_{11} value is rather small which must be attributed to persisting extinction problems, though the crystal was quenched in liquid nitrogen.

Discussion

The dicalcium ferrite ($\text{Ca}_2\text{Fe}_2\text{O}_5$) phase – a major slag component in the steel production – offers the possibility to incorporate non-ferrous metals by substitution of Fe(III) through their corresponding trivalent cations. In this context the pseudobinary system $\text{Ca}_2\text{Fe}_{2-x}\text{V}_x\text{O}_5$ was investigated by X-ray diffraction. Despite the similarity of the ionic radii of Fe(III) and V(III) (0.785 and 0.78 Å [1]) samples prepared at high temperatures show a very limited tendency to incorporate vanadium, due to the formation of the concurrent phase $\text{Ca}_{10}\text{V}_{5.2}\text{Fe}_{0.8}\text{O}_{24}$ [2]. In order to determine the vanadium limit content in dicalcium ferrite, a single crystal selected from a sample with nominal composition $\text{Ca}_2\text{Fe}_{1.2}\text{V}_{0.8}\text{O}_5$ was studied by single crystal diffractometry.

The refinement of the crystal structure shows that only the octahedral site (Fe(1)) in 4a is affected by partial substitution through V(III). Further refinements of the population parameters assuming full occupation of this site by the metal cations reveal, in fair agreement with an EDX analysis (yielding a V:Fe ratio of 0.36:1.64), that about 1/3 of the Fe(III) cations in this position are replaced. $M(1)\text{—O}$ bond lengths in the octahedron are 1.959(2) Å (2×); 1.965(2) Å (2×) and 1.959(2) Å (2×) and are thus virtually identical to those of $\text{Ca}_2\text{Fe}_2\text{O}_5$ [3]. This applies also for the bond distances within the FeO_4 -tetrahedron ($d(\text{Fe}(2)\text{—O})$: 1.841(2) Å (2×), 1.910(5) Å and 1.921(3) Å, respectively).

Table 1. Data collection and handling.

Crystal:	black-metallic platelet, size $0.03 \times 0.18 \times 0.25$ mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ :	82.93 cm ⁻¹
Diffractometer, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$
$2\theta_{\text{max}}$:	63.92°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	934, 933
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 639
$N(\text{param})_{\text{refined}}$:	48
Programs:	SIR92 [4], CRYSTALS [5], ATOMS [6]

* Correspondence author (e-mail: kurt.klepp@jku.at)

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ca(1)	8d		0.4802(1)	-0.10854(4)	-0.0228(1)	0.0089(3)	0.0093(3)	0.0084(2)	0.0010(2)	-0.0015(2)	-0.0002(2)
Fe(1)	4a	0.66	½	0	½	0.0012(3)	0.0115(3)	0.0047(3)	0.0001(2)	0.0000(2)	-0.0004(2)
Fe(2)	4c		0.4475(1)	-1/4	0.4351(1)	0.0046(3)	0.0076(3)	0.0079(3)	0	-0.0000(2)	0
V(1)	4a	0.34	½	0	½	0.0012	0.0115	0.0047	0.0000	0.0000	-0.0005
O(1)	8d		0.5232(4)	-0.3599(2)	0.5720(4)	0.0129(9)	0.012(1)	0.0084(8)	0.0011(7)	0.0009(7)	0.0013(7)
O(2)	4c		0.5984(5)	-1/4	0.1259(5)	0.004(1)	0.013(1)	0.011(1)	0	0.001(1)	0
O(3)	8d		0.7358(3)	-0.0157(1)	0.2358(4)	0.0037(8)	0.0115(9)	0.0096(8)	0.0003(6)	0.0036(7)	0.0005(7)

References

1. Shannon, R. D.; Prewitt, C. T.: Effective ionic radii in oxides and fluorides. *Acta Crystallogr. B* **25** (1969) 925-946.
2. Klepp, K. O.; Harringer, N. A.; Preßlinger, H.: Ca₁₀V_{5.2}Fe_{0.8}O₂₄, a Novel Oxometalate with Discrete Complex Anions. *Z. Naturforsch.* **58b** (2003) 1112-1116.
3. Colville, A. A.: The crystal structure of Ca₂Fe₂O₅ and its relation to the nuclear electric field gradient at the iron sites. *Acta Crystallogr. B* **26** (1970) 1469-1473.
4. Altomare, G.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.: SIR92 - a program for automatic solution of crystal structures by direct methods. *J. Appl. Crystallogr.* **27** (1994) 435-436.
5. Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W.; Cooper, R. I.: CRYSTALS. Issue 11. Chemical Crystallography Laboratory, Oxford, England 2001.
6. Dowty, E.: ATOMS for Windows and Macintosh, Version 5.2b. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA 1999.