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THE CRYSTAL STRUCTURE OF $Ca_3(CrO_4)_2$

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$Ca_3(CrO_0)_2$ *crystallizes in the trigonal space group* $R3c$. *The lattice parameters in the rhombohedral* (*R*) *and in the corresponding hexagonal* (*H*) *description are as follows:* $a_R = 1.4148(3)$ *nm,* $\alpha = 44.77(1)°$, $Z_R = 7$ *and* $a_H = 1.0776(2)$ *nm,* $c_H = 3.8119(5)$ *nm,* $Z_H = 21$. $Ca_3(CrO_4)_2$ *is isostructural with* $Ca_3(VO_4)_2$, $Ca_3(AsO_4)_2$ *and* $\beta\,Ca_3(PO_4)_2$. *The structure was refined* (*isotropic temperature factors, 1749 independent difractions*) *up to* $R = 0.087$. *The* Ca *atoms are coordinated by 6, 7 or 8 oxygen atoms. The coordination of* Cr *is tetrahedral.*

INTRODUCTION

The compound $Ca_3(CrO_4)_2$ is a significant phase in the system CaO—CrO_x. Its formation reduces refractoriness of calcium-rich compositions of these systems in an oxidizing atmosphere [1].

EXPERIMENTAL

Single crystals of $Ca_3(CrO_4)_2$ in a form suitable for structural analysis were synthetized by Figusch and Pánek [1]. They are opaque, black, dark-green translucent in thin layers, with a more or less irregular habit exhibiting two and rarely three developed faces. The crystals show conchoidal fracture and are optically anisotropic.

The selected monocrystal of $Ca_3(CrO_4)_2$ was ground to a spherical shape with 0.038 cm in diameter. The lattice parameters and the intensities of individual diffractions were measured on the SYNTEX $P2_1$ automatic diffractometer with a graphite monochromator, using $Mo_{K\alpha}$ radiation. The lattice parameters were refined by the least-squares method from the data on 15 diffractions at 293 K:

$a_R = 1.4148(3)$ nm, $\alpha = 44.77(1)°$, $Z_R = 7$ and $a_H = 1.0776(2)$ nm, $c_H = 3.8119(5)$ nm, $Z_H = 21$. The space group is R3c, $\varrho_{cal} = 3.20$ Mg/m³, $\varrho_{exp} = 3.15(1)$ Mg/m³.

The intensity data were obtained in the interval $0° < 2\Theta < 70°$ using the $\Theta - 2\Theta$ scanning technique with a variable scanning speed from 4—27° min^{-1}. The stability of measurements was checked by means of two standard diffractions.

The intensities and their standard deviations were computed by the program INTER (XTL system) [2]. Among 2666 diffractions measured (reduced to 1901 symmetrically independent ones) 1749 complied with the condition $I > 1.96\ \sigma(I)$. The intensities were corrected for Lorentz and polarization factor, as well as for absorption ($\mu = 50.9\ cm^{-1}$) by the NRC2A program modified by Hašek (1978) [3].

On the basis of similarity of the diffraction pattern of $Ca_3(CrO_4)_2$ with that of $Ca_3(VO_4)_2$ [4], $Ca_3(AsO_4)_2$ [5] and $\beta Ca_3(PO_4)_2$ [6] and of similar values of the lattice parameters of these compounds, close similarity of their crystal structures was assumed. The initial model of the structure of $Ca_3(CrO_4)_2$ was based on the analogy with the structure of $Ca_3(VO_4)_2$. This model was refined by the least-squares method using block diagonal approximation [7]. After six cycles (with individual isotropic temperature factors) the R-factor dropped from 0.368 to 0.087. Atomic scattering curves have been taken from [8]. At this stage, electron-density difference synthesis and interatomic distances and angles were calculated with programs [7], [9]. All the calculations were carried out on the SIEMENS 4004/150 computer. The results are listed in Table I (hexagonal axes).

RESULTS AND DISCUSSION

An interpretation of the electron-density difference synthesis proved the correctness of the principal features of the $Ca_3(CrO_4)_2$ crystal structure.

The results of electron paramagnetic resonance measurements have confirmed the presence of Cr^{5+} in the investigated structure [10]. This follows also from the structural analogy of $Ca_3(CrO_4)_2$ with $Ca_3(VO_4)_2$, $Ca_3(AsO_4)_2$ and $\beta Ca_3(PO_4)_2$.

Table I

Structural parameters of $Ca_3(CrO_4)_2$

Atom	x	y	z	B	occupancy
Cr(2)	0.3107(2)	0.1395(2)	0.1332(1)	0.45(2)	1
Cr(3)	0.3511(2)	0.1548(2)	0.2346(1)	0.56(2)	1
Ca(1)	0.2840(3)	0.1572(3)	0.9400(1)	1.48(4)	1
Ca(2)	0.2729(2)	0.1366(2)	0.8345(1)	0.75(2)	1
Ca(3)	0.3881(2)	0.1808(2)	0.0349(1)	0.80(3)	1
O(1)	0.2817(13)	0.0864(13)	0.0916(3)	1.77(15)	1
O(2)	0.2358(12)	0.2358(11)	0.1471(3)	1.44(13)	1
O(3)	0.2759(9)	—0.0171(9)	0.1543(2)	0.62(9)	1
O(4)	0.4916(11)	0.2465(11)	0.1420(3)	1.20(12)	1
O(5)	0.3879(13)	0.1812(13)	0.2772(3)	1.76(15)	1
O(6)	0.4013(10)	0.0340(10)	0.2230(2)	0.93(11)	1
O(7)	0.4300(13)	0.3187(13)	0.2164(3)	1.72(15)	1
O(8)	0.1738(10)	0.0774(9)	0.2238(2)	0.86(10)	1
O(10)	—0.0038(11)	0.1444(9)	0.0132(2)	1.02(11)	1
Cr(1)	0	0	0	1.50(5)	1
Ca(4)	0	0	0.2675(2)	0.99(4)	1
Ca(5)	0	0	0.0744(7)	1.00	0.07(2)
O(9)	0	0	0.9533(6)	1.71	0.58(7)

The structure of $Ca_3(CrO_4)_2$ contains discrete CrO_4 groups similarly to all the so far known compounds of Cr^{5+} [11]. The mean Cr—O distances for three independent tetrahedra are 0.165, 0.168 and 0.170 nm, respectively. The Ca atoms are coordinated by 6, 7 and 8 O atoms, respectively and the corresponding Ca—O distances vary from 0.234 to 0.281 nm.

In connection with the location of Ca(5) and O(9) atoms on the threefold axis (cf. Table I) the present authors encountered similar problems as the investigators of the analogous structures mentioned above. The higher values of the thermal parameters for these atoms are explained by their positional disorder. The refinement of the structure of $Ca_3(CrO_4)_2$ was accompanied by a distinct decrease of the occupancies of Ca(5) and O(9) atoms. This CaO deficit is in agreement with $\varrho_{exp} = 3.15(1)$ Mg/m³ as well as with the result of the electron-density difference synthesis. The ideal content of the hexagonal unit cell with respect to the formula $Ca_3(CrO_4)_2$ and the number of formula units in it is $Ca_{63}Cr_{42}O_{168} = 21\ Ca_3Cr_2O_8$. This content of the cell corresponds to $\varrho_{cal} = 3.20$ Mg/m³. In view of the occupancy factors of the Ca(5) and O(9) atoms, the observed unit cell content is $Ca_{60\cdot 42}Cr_{42}O_{165\cdot 48} = 21\ Ca_{2\cdot 88}Cr_2O_{7\cdot 88}$, which means that the structure contains vacancies in the positions of atoms Ca(5) and O(9).

A detailed treatment of this problem and its crystallochemical implications will be the subject of a separate study.

References

[1] *Thermodynamics and Properties of Condensed Silicate and Oxide Systems* (in Russian). Smolenice 1976, Veda, Publishing House of the Slovak Academy of Sciences, Bratislava 1976.

[2] Langer V.: *INTER — Program for the Reduction of Diffractometric Data.* Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague 1977.

[3] Hašek J.: *Program NR2CA — Preparation of the Input Set for the MULTAN and NRC System.* (In Czech.) Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague 1978.

[4] Gopal R., Calvo C.: Z. Kristallogr. *137*, 67 (1973).

[5] Gopal R., Calvo C.: Can. J. Chem. *49*, 1036 (1971).

[6] Schroeder L. W., Dickens B., Brown W. E.: J. Solid State Chem. *22*, 253 (1977).

[7] Ahmed F. R., Hall S., Pippy M., Huber C. P.: *NRC — Cryst. Programs for the IBM — 360 System.* World List of Cryst. Computer Programs, Utrecht, Oosthoek 1966.

[8] *International Tables for X-ray Crystallography*, Vol. IV, p. 72, Kynoch Press, Birmingham 1974.

[9] Zalkin A.: *DRF — A Program for the Calculation of Fourier Summation.* Lawrence Radiation Laboratory, University of California, Berkeley, California 1970.

[10] Plesch G.: Private Communication (1979).

[11] Wilhelmi K. — A., Jonsson O.: Acta Chem. Scand. *19*, 177 (1965).

KRYŠTÁLOVÁ ŠTRUKTÚRA $Ca_3(CrO_4)_2$

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$Ca_3(CrO_4)_2$ kryštalizuje v trigonálnej sústave, priestorová grupa symetrie R3c. Mriežkové parametre v romboédrickom (R) a zodpovedajúcom hexagonálnom (H) popise sú: $a_R = 1{,}4148(3)$ nm, $\alpha = 44{,}77(1)°$, $Z_R = 7$ a $a_H = 1{,}0776(2)$ nm, $c_H = 3{,}8119(5)$ nm, $Z_H = 21$. $Ca_3(CrO_4)_2$ je izoštruktúrny s $Ca_3(VO_4)_2$, $Ca_3(AsO_4)_2$ a $\beta Ca_3(PO_4)_2$. Štruktúra sa spresňovala s izotrópnymi teplotnými faktormi do hodnoty $R = 0{,}087$ pre 1749 pozorovaných nezávislých difrakcií. Atómy Ca sú koordinované 6, 7 alebo 8 atómami kyslíka. Koordinácia atómov Cr je tetraédrická. Pri riešení kryštálovej štruktúry $Ca_3(CrO_4)_2$ sa vyskytli analogické problémy ako v prípade izoštruktúrnych zlúčenín.

КРИСТАЛЛИЧЕСКАЯ СТРУКТУРА $Ca_3(CrO_4)_2$

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$Ca_3(CrO_4)_2$ кристаллизует в тригональной системе, пространственная группа симметрии R3c. Параметры решетки в ромбоэдрическом (R) и соответствующем гексагональном (H) описании являются: $a_R = 1,\ 4148(3)$ нм, $\alpha = 44{,}77(1)$, $Z_R = 7$ и $a_H = 1{,}0776(2)$ нм, $c_H = 3{,}8119(5)$ нм, $Z_H = 21$. $Ca_3(CrO_4)_2$ изоструктурен с $Ca_3(VO_4)_2$, $Ca_3(AsO_4)_2$ и $\beta Ca_3(PO_4)_2$. Структура уточнялась с изотропными температурными факторами до величины $R = 0{,}087$ для 1749 исследуемых независимых дифракций. Атомы Ca координированы 6, 7 или 8 атомами кислорода. Координация атомов Cr является тетраэдрической. При решении кристаллической структуры $Ca_3(CrO_4)_2$ встречались аналогичные проблемы, как и в случае изоструктурных соединений.