3. Zsakó, I. *Studii cercetari chim. Filiala Cluj* **7** (1956) 53.
4. Yatsimirskii, K. B. and Vasil'eva, V. N. *Zhur. Neorg. Khim.* **1** (1956) 1983.
5. Blomstrand, C. W. *J. prakt. Chem.* [2] **40** (1889) 328.
6. Tong, J. Y. and King, E. L. *J. Am. Chem. Soc.* **76** (1954) 2132.
7. King, E. L. and Neptune, J. A. *J. Am. Chem. Soc.* **77** (1955) 3186.
8. Krauss, H.-L. and Gnatz, G. *Chem. Ber.* **92** (1959) 2110.
9. Penfield, S. L. *Am. J. Sci.* [3] **48** (1894) 30.
10. Raff, P. and Brotz, W. *Z. anal. Chem.* **133** (1951) 241.
11. Gran, G. *Acta Chem. Scand.* **4** (1950) 559.

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Crystallographic Data of Sr_2CrO_4

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Rather few compounds containing tetravalent chromium are reported in literature and the information about their crystallographic properties is incomplete. The syntheses of CrF_4 and $CrBr_4$ have been reported [1,2] but no crystallographic data are available for these substances. In 1950 the fluoro complexes M_2CrF_6 (M = K, Rb, and Cs) were prepared [3] and Bode and Voss [4] found that these complexes have the octahedral arrangement with discrete CrF_6^{2-} ions. The coordination number 6 is also found in CrO_2 which phase is of a rutile type [5,6].

Scholder and Sperka [7,8] have reported the syntheses of Ba_2CrO_4, Ba_3CrO_5 and Sr_2CrO_4, containing chromium with an average oxidation number of + 4. According to these authors, there exist structural relationships between the compounds M_2TiO_4 and M_2CrO_4 (M = Ba and Sr).

The crystal structure of Ba_2TiO_4 has been determined by Bland [9]. The space group is $P2_1/n$ and the cell dimensions are:

$a = 6.12$ Å, $b = 7.70$ Å, $c = 10.50$ Å, $\beta = 93°8'$

The structure is of the β-K_2SO_4 type and is closely related to β-Ca_2SiO_4. The environment of the titanium atom is unusual; it is approximately tetrahedral and the structure is considered as an arrangement of discrete TiO_4-groups and barium atoms.

Sr_2TiO_4 belongs according to Balz and Plieth [10] to an interesting group of oxide compounds with the same crystal structure as K_2NiF_4 and K_2MgF_4[11]. The space group is $I4/mmm$ and the cell dimensions are:

$$a = 3.88 \text{ Å} \qquad c = 12.58 \text{ Å}$$

The structure is formed by somewhat distorted TiO_6-octahedra arranged in layers with the composition TiO_2 by sharing corners. In the direction of the tetragonal c axis an alternation of two SrO-layers with one TiO_2 layer can be distinguished.

By a partial substitution of Sr^{2+} ions (about 5 mole %) in Ba_2TiO_4, specimens with the orthorhombic β-K_2SO_4 structure were obtained by Kwestroo and Paping [12]. The solid solution area ends at a composition with a Ba^{2+}/Sr^{2+} ratio of about 1:3. The structure of Sr_2CrO_4 has been investigated by the present authors and preliminary results are given in this paper.

Crystals of Sr_2CrO_4, suitable for single-crystal X-ray studies, were prepared from chromium(III)oxide, strontium chromate(VI) and carbonate-free strontium hydroxide in a platinum crucible at 900°C with argon as a protecting gas.

$$Cr_2O_3 + SrCrO_4 + 5\ Sr(OH)_2 = 3\ Sr_2CrO_4 + 5\ H_2O$$

The excess of strontium hydroxide was extracted with water-free methanol. The crystals obtained were small blue-black prisms stable in air and insoluble in hot acetic acid.

The hexavalent chromium was determined iodometrically, the total chromium after oxidation by hydrogen peroxide in alkaline solution. The strontium was determined gravimetrically as strontium sulphate in chromium-free solutions. The reproducibility of the analyses was found to be good and the results in fair agreement with the values calculated for Sr_2CrO_4.

	Chromium (VI), %	Chromium total, %	Strontium %
Found	5.88 ± 0.05	17.62 ± 0.05	60.2 ± 0.1
Calc.	5.95	17.85	60.17

Table 1. Crystallographic data of Sr_2CrO_4.

Laue symmetry: *mmm*
Unit-cell dimensions: $a = 14.193$ Å
$b = 10.033$ Å
$c = 5.790$ Å
Absent spectra: $hk0$ with h odd
$0kl$ with $k + l$ odd
Space group: No. 33 $Pn2_1a$
Density observed: 4.54 g cm^{-3}
Density calculated: 4.50 g cm^{-3} (for $Sr_{16}Cr_8O_{32}$)

Approximate values of the cell dimensions were obtained from Weissenberg photographs (CuK radiation). More accurate values were then obtained from a Guinier powder photograph (80 mm diameter, transmission position) with strictly monochromatized CuK_1 radiation. Potassium chloride (Analar, British Drug Houses, $a = 6.2919$ Å at 20°C, Hambling [13]) was added to the specimen as an internal standard. A few very weak extra lines showed the presence of a small content of non-identified impurities in the specimen.

Rotation photographs around [100], [010] and [001] and Weissenberg photographs (hkl: $h = 0-8$, $k = 0-6$ and $l = 0-3$) showed the crystal to be orthorhombic. There seems to be an almost exact relationship between the lengths of the cell edges $a:b:c = \sqrt{6}:\sqrt{3}:1$ (Table 1). The reflexions systematically absent are characteristic of the space groups No. 62 *Pnma* and No 33 $Pn2_1a$. All attempts to solve the structure on the basis of the space group No. 62 *Pnma* failed and it was concluded that the space group might be No. 33 $Pn2_1a$.

The present stage of the structure determination is in accordance with the latter symmetry. Thus studies of the Patterson and electron density projections have lead to a structure containing the 16 strontium and 8 chromium atoms in 6 sets of 4-fold positions (4a) of the space-group $Pn2_1a$. The distribution of the metal atoms indicates that Sr_2CrO_4 is isomorphous neither with K_2NiF_4 nor with K_2CrO_4 (low-K_2SO_4-type), but that the structure very likely contains discrete four-coordinated chromium-oxygen complexes similar to those found in K_2CrO_4. The refinement of the structure will be continued according to this assumption.

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1. Wartenberg, H. von *Z. anorg. Chem.* **247** (1941) 135.
2. Sime, R. J. and Gregory, N. W. *J. Am. Chem. Soc.* **82** (1960) 93.
3. Huss, E. and Klemm, W. *Z. anorg. Chem.* **262** (1950) 25.
4. Bode, H. and Voss, E. *Z. anorg. Chem.* **286** (1956) 136.
5. Michel, A. and Bénard, J. *Compt. rend.* **200** (1935) 1316.
6. Wilhelmi, K.-A. and Jonsson, O. *Acta Chem. Scand.* **12** (1958) 1532.
7. Scholder, R. and Sperka, G. *Z. anorg. Chem.* **285** (1956) 49.
8. Sperka, G. Dissertation 1952, Karlsruhe.
9. Bland, J. A. *Acta Cryst.* **14** (1961) 875.
10. Balz, D. and Plieth, K. *Z. Elektrochem.* **59** (1955) 545.
11. Brehler, B. and Winkler, H. G. F. *Heidelberger Beiträge zur Mineralogie und Petrographie* **4** (1954) 6.
12. Kwestroo, W. and Paping, H. A. M. *J. Am. Ceram. Soc.* **42** (1959) 292.
13. Hambling, P. G. *Acta Cryst.* **6** (1953) 98.

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