

Diskussion. $\text{SrTe}_5\text{O}_{11}$ kann als eine durch SrO stabilisierte TeO_2 -Modifikation mit Fluoritstruktur aufgefasst werden. Dabei bleibt aber unverständlich, wie sich vierwertiges Tellur in die hexaedrisch koordinierten Plätze dieser Struktur einfügt. Die Regeln, die für die Sauerstoffkoordination des vierwertigen Tellurs gelten (Brown, 1974; Trömel, 1980), lassen sich mit deformiert oktaedrischen Sauerstoffumgebungen gut vereinbaren (vgl. auch Alcock, 1972), während in hexaedrischer Umgebung die erforderliche Anordnung dreier Sauerstoffatome in einem nahezu gleichseitigen Dreieck mit Seitenlängen von *ca* 2,8 Å fehlt. Wird daher Tellur(IV) in eine Fluoritstruktur eingebaut, so hat man starke, von Gitterplatz zu Gitterplatz wechselnde Verschiebungen der Tellur- und Sauerstoffatome aus ihren Lagen zu erwarten, denen sich auch Strontium mit seiner wenig starren Koordinationsgeometrie anpassen kann. Diese Verschiebungen kommen in den extrem hohen scheinbaren Temperaturfaktoren zum Ausdruck, die hier mit Sicherheit nicht durch die thermische Bewegung der Atome bedingt sind.

Da diese regellosen Verschiebungen aus den idealen Lagen beide Atompositionen betreffen, liegt hier eine kristalline Substanz mit ungewöhnlich starker und vielfältiger Fehlordnung vor: statistische Verteilung zweier Schweratome auf den Metallplätzen in Verbindung mit ausgeprägter dreidimensionaler Lagefehlordnung; dazu noch stärkere dreidimensionale Lagefehlordnung des statistisch unvollständig besetzten Anionenteilgitters. Die hochgradige Fehlordnung kommt auch im Infrarotspektrum der Verbindung zum Ausdruck, für dessen Anfertigung wir Herrn Dr. E.-J. Zehnder danken: Es zeigt nur zwei sehr breite, unstrukturierte, wenig charakteristische Banden, die mit Maxima bei *ca* 330 cm^{-1} bzw. *ca* 620 cm^{-1} (Schulter bei *ca* 720 cm^{-1}) im Bereich der bei kristallinen

Telluraten(IV) auftretenden Schwingungsbanden liegen. Das Spektrum ähnelt damit stark dem von Telluritgläsern. Während Gläser keine Fernordnung zeigen, aber in den einfachsten Fällen, z.B. im SiO_2 -Glas, eine ausgeprägte Nahordnung aufweisen, liegen die Verhältnisse hier gerade umgekehrt. Die Nahordnung ist so stark gestört, dass sie kaum noch als definiert angesehen werden kann. Dagegen findet sich eine ausgeprägte Fernordnung hoher Symmetrie. Es liegt nahe, hier von einem 'Anti-Glas' zu sprechen. Ermöglicht wird diese eigenartige Fehlordnung wohl hauptsächlich durch die Variabilität der Sauerstoffkoordination des vierwertigen Tellurs, das auch in kristallinen Verbindungen Koordinationszahlen zwischen 3 und 5 und vielfältige Übergänge zwischen ihnen aufweist (Brown, 1974; Trömel, 1980).

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Literatur

- ALCOCK, N. W. (1972). *Adv. Inorg. Chem. Radiochem.* **15**, 1–58.
 BROWN, I. D. (1974). *J. Solid State Chem.* **11**, 214–233.
International Tables for X-ray Crystallography (1968). Bd. III. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1974). Bd. IV. Birmingham: Kynoch Press.
 STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. W. & HALL, S. R. (1972). XRAY-System. Tech. Rep. TR192. Computer Science Center, Univ. Maryland, College Park, Maryland.
 TRÖMEL, M. (1980). *J. Solid State Chem.* **35**, 90–98.

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Powder Neutron Diffraction Study of the Perovskites CaTiO_3 and CaZrO_3

BY H. J. A. KOOPMANS, G. M. H. VAN DE VELDE AND P. J. GELLINGS

Twente University of Technology, Laboratory of Inorganic Chemistry and Materials Science, PO Box 217, 7500 AE Enschede, The Netherlands

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Abstract. CaTiO_3 : $M_r = 136.0$, orthorhombic, *Pcmm*, $a = 5.3829$ (3), $b = 7.6453$ (4), $c = 5.4458$ (3) Å, $V = 224.12$ (4) Å³, $Z = 4$, $D_x = 4.031$ g cm⁻³, $R_{\text{profile}} = 4.52\%$ for 54 reflections. CaZrO_3 : $M_r = 179.3$, orthorhombic, *Pcmm*, $a = 5.5912$ (1), $b = 8.0171$ (2),

$c = 5.7616$ (1) Å, $V = 258.26$ (2) Å³, $Z = 4$, $D_x = 4.611$ g cm⁻³, $R_{\text{profile}} = 4.01\%$ for 55 reflections. Both compounds: $\lambda(\text{neutrons}) = 2.5907$ (3) Å, $T = 300$ K. The structures consist of slightly deformed BO_6 octahedra ($B = \text{Ti}, \text{Zr}$), which are rotated with respect

to their positions in the ideal perovskite structure. These rotations reduce the coordination number of the Ca²⁺ ions from 12 (ideally) to 8.

Introduction. Although the mineral CaTiO₃ has given its name to the whole family of perovskites, no precise crystal parameters have been published for this compound. Kay & Bailey (1957) have described the X-ray diffraction results of a number of natural and synthetic crystals, but their findings are not in agreement with the more recent data in JCPDS diffraction file 22-153 (1971) [*Natl. Bur. Stand. (US) Monogr.* 25, Sect. 9]. Therefore, a neutron powder diffraction study was undertaken for CaTiO₃ and for CaZrO₃, which were believed to be isostructural (Tilloca & Perez y Jorba, 1964). In this research the exact positions of the O²⁻ ions, coordinated to the Ca²⁺ and Ti⁴⁺ (respectively Zr⁴⁺) ions, are investigated. In a further study these findings will be used to calculate the zero-field-splitting parameters, observed in the ESR powder spectra of Gd³⁺-doped samples of these perovskites (Koopmans, Brevoord, Nieuwenhuijse & Gellings, 1984).

Experimental. CaTiO₃ and CaZrO₃ prepared by mixing stoichiometric amounts of CaO and TiO₂ or ZrO₂ and heating at 1723 K for four days with ball-milling for one hour each day. X-ray diffraction showed no traces of other compounds and the line-widths indicated that the products were homogeneous. X-ray fluorescence analysis showed the compositions (wt %) to be close to the desired ones: (theoretical values in parentheses) CaTiO₃: Ca 29.3 (29.5), Ti 35.2 (35.2); CaZrO₃: Ca 22.5 (22.4), Zr 51.5 (50.9).

Neutron scattering experiments performed at $T = 300$ K on the powder diffractometer at the Petten High Flux reactor. Experimental details have been described elsewhere (van Dijk, Helmholdt & Burggraaf, 1980); however, the BeF₃ counters have been replaced by ³He counters. Data collected in the range $5 < 2\theta < 160^\circ$ in steps of 0.1° . Diffraction patterns analysed by means of Rietveld's (1969) method, using the neutron scattering lengths published by Bacon (1972).

As a trial model the structure of Kay & Bailey (1957) was used with space group *Pcmn* and the atom positions: Ti or Zr in 4(*b*) ($\frac{1}{2}, 0, 0$), Ca in 4(*c*) ($x, \frac{1}{4}, z$), O(1) in 4(*c*) and O(2) in 8(*d*) (x, y, z). The parameters in the refinement were: a scale factor *c*, three half-width parameters defining the Gaussian lineshape, the counter zero error, the unit-cell parameters, the atomic positional parameters and the isotropic temperature factors. By minimizing the function $\chi^2 = \sum w[y(\text{obs.}) - (1/c)y(\text{calc.})]^2$, this model resulted in the following *R* factor for CaTiO₃: $R_{\text{profile}} = \sum |y(\text{obs.}) - (1/c)y(\text{calc.})| / \sum y(\text{obs.}) = 4.52\%$, where $y(\text{obs.})$ and $y(\text{calc.})$ are the observed and calculated profile data points, and *w* is the statistical weight allotted to each data point. The noncentrosymmetric space group *Pna2*₁ has been tested

also. Even though all atom positions (x, y, z) have been used as refinement parameters in this case, only a small but insignificant improvement has been obtained ($R_{\text{profile}} = 4.37\%$). Therefore, the choice of *Pcmn* is preferred. The space group *Amm2* as suggested by Balachandran & Eror (1982) did not fit the diffraction data at all ($R_{\text{profile}} = 24.0\%$), which was also apparent from the fact that some experimental reflections had much higher intensity than calculated, even with double cell units.

The space group *Pcmn* could also be used successfully for the perovskite CaZrO₃ ($R_{\text{profile}} = 4.01\%$).

Discussion. The powder-profile-fitting curves for both perovskites are shown in Fig. 1, whereas the lattice parameters and fractional atomic coordinates are given in Table 1.*

* Tables giving the numbered intensity of each measured point on the profiles of the two compounds, as a function of 2θ , have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38696 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

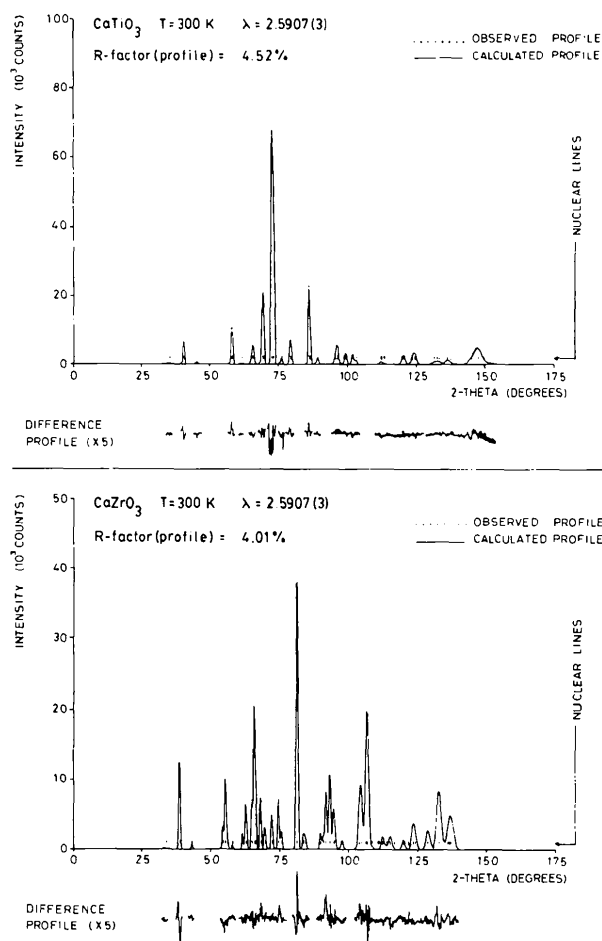


Fig. 1. Powder-profile-fitting curves for CaTiO₃ and CaZrO₃ at $T = 300$ K.

Table 1. Lattice parameters (Å), fractional atomic coordinates and isotropic thermal parameters (Å²)

			CaTiO ₃		CaZrO ₃	
<i>a</i>			5.3829 (3)*	5.3670†	5.5912 (1)	
<i>b</i>			7.6453 (4)	7.6438	8.0171 (1)	
<i>c</i>			5.4458 (3)	5.4439	5.7616 (2)	
Ca	4(c)	<i>x</i>	0.0083 (7)	0.000	0.0121 (5)	
		<i>z</i>	0.0360 (5)	0.030	0.0496 (3)	
		<i>B</i>	1.01 (7)	—	0.66 (5)	
O(1)	4(c)	<i>x</i>	0.5726 (5)	0.537	0.6032 (3)	
		<i>z</i>	-0.0173 (4)	-0.018	-0.0381 (3)	
		<i>B</i>	0.94 (6)	—	0.51 (3)	
O(2)	8(d)	<i>x</i>	0.2901 (3)	0.268	0.3026 (2)	
		<i>y</i>	0.0369 (2)	0.026	0.0548 (2)	
		<i>z</i>	0.2877 (3)	0.268	0.3007 (2)	
Ti/Zr	4(b)	<i>B</i>	0.94 (6)	—	0.51 (3)	
		<i>B</i>	0.59 (12)	—	0.23 (4)	

* This work.

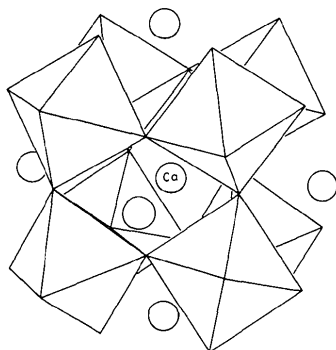
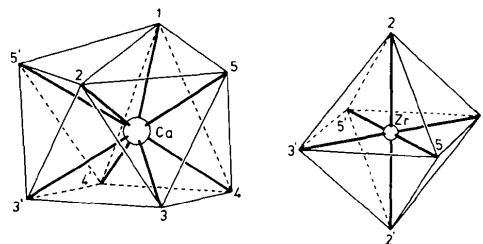
† Kay & Bailey (1957).

Table 2. Interatomic distances (Å) and angles (°)

The numbering of the O²⁻ ions is the same as in Fig. 3.

	CaTiO ₃	CaZrO ₃
B—O(2)*	1.953 (2)	2.097 (1)
B—O(3)	1.963 (2)	2.091 (1)
B—O(5)	1.952 (2)	2.101 (1)
Ca—O(1)	2.363 (4)	2.341 (3)
Ca—O(2)	2.471 (3)	2.461 (3)
Ca—O(3)	2.614 (3)	2.680 (3)
Ca—O(4)	2.379 (3)	2.362 (2)
Ca—O(5)	2.667 (2)	2.844 (1)
O(2)—B—O(3)	89.4 (1)	88.0 (1)
O(2)—B—O(5)	89.2 (1)	88.2 (1)
O(3)—B—O(5)	90.5 (1)	90.9 (1)
O(1)—Ca—O(2)	86.9 (2)	87.3 (1)
O(1)—Ca—O(4)	112.4 (3)	107.3 (2)
O(1)—Ca—O(5)	66.9 (2)	70.3 (2)
O(2)—Ca—O(3)	65.6 (2)	68.8 (1)
O(2)—Ca—O(5)	64.4 (1)	66.4 (1)
O(3)—Ca—O(4)	66.8 (2)	71.0 (1)
O(3)—Ca—O(5)	63.5 (1)	65.4 (1)
O(3)—Ca—O(3')	77.1 (2)	71.5 (2)
O(4)—Ca—O(5)	80.9 (1)	78.2 (1)
O(4)—Ca—O(4')	86.4 (2)	83.0 (1)

* B = Ti or Zr.

Fig. 2. Impression of the structure of CaZrO₃. The ZrO₆ octahedra are rotated with respect to their positions in the ideal perovskite structure. Almost the same figure applies for CaTiO₃.Fig. 3. Coordination spheres for Ca and Zr in CaZrO₃. For distances and angles see Table 2. Almost the same drawings apply for CaTiO₃.

In the present refinement no large discrepancies have been found with the X-ray diffraction results of Kay & Bailey (1957), although the atomic coordinates and cell parameters show some significant differences. The cell parameters are in agreement with the data in JCPDS diffraction file 22-153 (1971). Therefore, the above-mentioned differences are probably due to the large twinning in the crystals as reported by Kay & Bailey.

The structure of both perovskites can be described as almost regular BO₆ octahedra (with B = Ti, Zr), which are rotated with respect to their positions in the ideal perovskite structure (see Fig. 2), with larger rotations for CaZrO₃. Although the coordination of the A ion in ideal ABX₃ perovskites consists of twelve X ions, the coordination of the Ca²⁺ ions is reduced to eight O²⁻ ions due to the rotations of the octahedra. In this O cage the mean Ca—O distances are 2.52 and 2.57 Å for CaTiO₃ and CaZrO₃ respectively. This is in agreement with the expected value of 2.54 Å for eightfold coordination (Shannon & Prewitt, 1969). The other Ca—O distances are in the range 3.0–3.6 Å. A list of the more important interatomic distances and angles is given in Table 2, and Fig. 3 shows the coordination of the Ca²⁺ and Zr⁴⁺ ions in CaZrO₃.

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References

- BACON, G. E. (1972). *Acta Cryst.* **A28**, 357–359.
 BALACHANDRAN, U. & EROR, N. G. (1982). *Solid State Commun.* **44**, 815–818.
 DIJK, T. VAN, HELMHOLDT, R. B. & BURGGRAAF, A. J. (1980). *Phys. Status Solidi B*, **101**, 765–774.
 KAY, H. F. & BAILEY, P. C. (1957). *Acta Cryst.* **10**, 219–226.
 KOOPMANS, H. J. A., BREVOORD, E., NIEUWENHUISE, B. & GELLINGS, P. J. (1984). In preparation.
 RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
 SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925–946.
 TILLOCA, G. & PEREZ Y JORBA, M. (1964). *Rev. Hautes Temp. Réfract.* **1**, 331–342.