

for the expression for  $|F|^2 - |\bar{F}|^2$  and  $\sin \alpha$  (Raman, 1960, equation 11).  $\sigma = |F|^2/S$  is the factor including the absorption correction, scale factor *etc.*

Comparison of equations (7) and (8) with equations (5) and (6) shows the superiority of the ratio method except for values of  $|F_N^0|f_P^0/|F_P^0|$  which are very much greater than 1. Frequently  $|F_N^0|f_P^0/|F_P^0|$  is less than or of the order of 1, if there are many normal scatterers and only few anomalous scatterers in the molecule, as for example in organic molecules with 'heavy atoms'.

Moreover, comparison of equation (7) with equation (8) suggests that preference should be given to the re-

sults obtained by Raman's equation (12) (Raman, 1960) if  $\alpha \simeq (2n+1)\pi/2$ , and Raman's equation (11) if  $\alpha \simeq n\pi$ .

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## High-Temperature Phase Transitions in SrZrO<sub>3</sub>

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Differential thermal analysis of samples of strontium zirconate up to 1000°C shows peaks which indicate phase transitions during heating at 730 and 860°C. A high-temperature X-ray investigation revealed that the peaks correspond to crystallographic transformations. The orthorhombic form found at room temperature exists up to 700°C, at which temperature a tetragonal modification with  $c/a < 1$  is formed. At 830°C another tetragonal modification is formed but with  $c/a > 1$ . This exists up to 1170°C where it transforms to a cubic form. A few very faint 'extra' lines in the diffraction patterns are observed even at the highest temperatures where the structure is cubic. This indicates that the true unit cells of the zirconate in the high-temperature phases are multiples of the simple small-cell perovskite. It is found that the 'extra' lines could be satisfactorily indexed on the basis of a unit cell containing 8 formula units where the axes of the true unit cell are twice the cell-edges of the ideal small-cell.

### Introduction

Strontium zirconate is a ceramic substance which belongs to the group of perovskites and has a melting point of *ca.* 2800°C. Funk, Nemeth & Tinklepaugh (1964) found that polycrystalline specimens of SrZrO<sub>3</sub> exhibited a measurable amount of mechanical yield or deformation at room temperature. They therefore investigated its thermal behaviour by dilatometry and X-ray analysis; the results were interpreted as indicating a possible phase transition between 850 and 1000°C. Krainik (1958) examined the dielectric constant for the system PbZrO<sub>3</sub>-SrZrO<sub>3</sub> from room temperature up to 450°C. He did not investigate higher molecular concentrations of SrZrO<sub>3</sub> than 30% and found that there existed five different phases for concentrations above 10%, one of which disappeared at about 30% SrZrO<sub>3</sub> at room temperature. Krainik considered it possible to extrapolate the phase diagram to higher molecular concentrations of SrZrO<sub>3</sub> and suggested that two high-temperature transitions would be found for pure SrZrO<sub>3</sub>, one of them at *ca.* 700°C.

Our attempts to grow single crystals of SrZrO<sub>3</sub> both by a flux-method and the Verneuil method with plasma heating, proved it to be difficult to obtain crystals larger than of millimetre dimensions. These were also of poor quality and showed a high degree of twinning which may indicate phase transitions during cooling. An investigation with differential thermal analysis showed two peaks between room temperature and 1000°C which suggested the occurrence of phase transitions. It was therefore decided to carry out high-temperature investigations up to 1300°C, this being the highest temperature at which available equipment could be used.

### Structure

At room temperature the structure of SrZrO<sub>3</sub> is orthorhombic, as Roth (1957) was the first to point out. Earlier publications by *e.g.* Zachariasen (1928), Hoffman (1935) and Megaw (1946) considered the structure to be cubic with one formula unit per unit cell and with a unit-cell edge of *ca.* 4.09 Å. The orthorhombic structure was verified by Swanson, Cook, Isaacs &

Evans (1960) who found that:  $a_0=5.814$ ,  $b_0=8.196$ ,  $c_0=5.792$  Å, where  $a_0 \simeq \sqrt{2}a'$ ,  $b_0 \simeq 2a'$ ,  $c_0 \simeq \sqrt{2}a'$  where  $a'$  is equal to the cell edge of the cubic small-cell perovskite.

For investigations of phase transitions of perovskites it is often advisable to express the orthorhombic structure in pseudomonoclinic parameters. In this case the relation between orthorhombic and monoclinic parameters are:

$$\begin{aligned} a_0 &= 2a' \sin \beta/2 \\ b_0 &= 2b' \\ c_0 &= 2a' \cos \beta/2. \end{aligned}$$

The transformation matrix for the conversion of the index from the orthorhombic to the pseudomonoclinic system then becomes:

$$\begin{array}{|ccc|} \hline \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & \frac{1}{2} & 0 \\ \frac{1}{2} & 0 & \frac{1}{2} \\ \hline \end{array}$$

### Experimental procedure

Differential thermal analysis was carried out with conventional equipment, *e.g.* see Kingerey (1959). The temperature was measured with a Pt-Pt/10% Rh thermo-element and the accuracy was estimated to be  $\pm 5^\circ\text{C}$ . Owing to the slow cooling of the furnace, measurements could be made only during heating.

High-temperature X-ray investigations were made with a Philips high-angle goniometer; the detector system consisted of a scintillation detector combined with a pulse-height analyser. Cu  $K\alpha$  radiation was used. The goniometer was equipped with a high-temperature device similar to the one described by Chiotti (1954). The heating element was made of tantalum and the sample-holder of molybdenum. The temperature was measured with a Pt-Pt/10% Rh thermo-element which was placed underneath, but in contact with, the sample. The thermo-element was calibrated before commencing the measurements against readings from another element inside a test specimen which had been placed in the sample-holder and heated. The sample was in the form of a 2 mm thick disc sintered at  $1500^\circ\text{C}$  during 4 hours. The raw material had been supplied by Semi-Elements, Inc., Saxonburg, U.S.A. According to the manufacturer it was of the following purity: HfO<sub>2</sub> 0.008%, SiO<sub>2</sub> 0.10%, Fe<sub>2</sub>O<sub>3</sub> 0.05%, TiO<sub>2</sub> 0.01%, MnO<sub>2</sub> 0.005%, CaO 0.005% and BaO 0.005%. A very faint line in the diffraction pattern indicated the presence of unreacted ZrO<sub>2</sub> in the sample. After the test-disc had been mounted in the sample-holder a diffraction pattern was run at room temperature. The lines showed a slight shift towards lower values in  $2\theta$  compared with the diffraction pattern obtained with an ordinary sample-holder. This indicated that the sample was not correctly adjusted in height with respect to the goniometer axes. A correction curve was run with the correction as a function of  $2\theta$  and this was used for the calculations.

### Measurements

#### Differential thermal analysis

Ten different measurements were made by differential thermal analysis. It proved to be difficult to reproduce the results, especially with regard to the temperature at which the first transition commenced on heating.

The points where the curve began to deviate from its previous inclination were taken as transition temperatures. Fig. 1 illustrates a typical measurement.

#### X-ray measurements

In order to determine the structure of the unknown phases, diffractograms were run at four different temperatures in the  $2\theta$  range of  $20$  to  $150^\circ$  and with a goniometer speed of  $1^\circ 2\theta.\text{min}^{-1}$ . The temperature was adjusted and kept constant for half an hour before starting the measurements. The following temperatures were chosen: 600, 820, 1000 and  $1200^\circ\text{C}$ .

The appearance of the diffractogram at  $600^\circ\text{C}$  was fundamentally the same as that of the one at room temperature, but lines such as 640 and 046 indexed on the basis of the orthorhombic system now displayed a considerably decreased separation. The diffractogram run at  $820^\circ\text{C}$  showed that a crystallographic transformation had taken place and that the peak at  $730^\circ\text{C}$ , obtained by differential thermal analysis measurements, did in fact correspond to a crystallographic transformation. A distinct indication that a new phase had developed was that the single line 404 in the orthorhombic system now had split into two components. Most lines, especially at higher angles, displayed a distinct splitting into two components (other than  $\alpha_1\alpha_2$  splitting) with the approximate ratio of intensity of 2:1 and with the weaker component situated at a higher

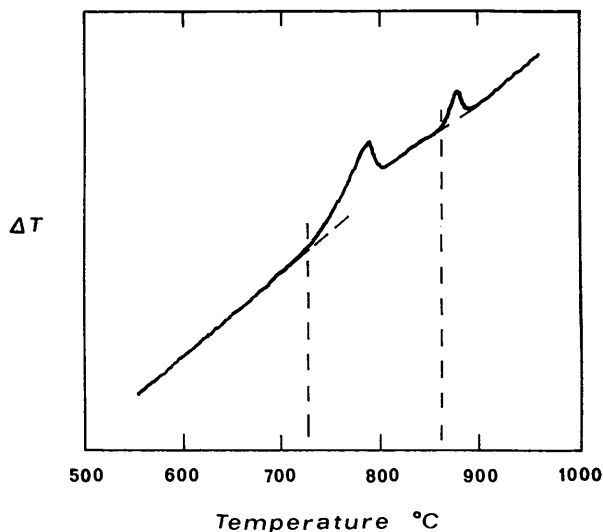


Fig. 1. Differential thermal analysis curve of SrZrO<sub>3</sub>. Endothermic peaks at about  $730$  and  $860^\circ\text{C}$  represent transitions from orthorhombic to pseudotetragonal and from one pseudotetragonal phase to another.

angle. With the line intensities used, no lines (beside the split ones) could be detected apart from those belonging to the simple small-cell perovskite structure.

It was obvious that the orthorhombic phase had undergone a transformation to a tetragonal phase with  $c/a < 1$ . The lines were indexed on the basis of this structure and from the observed  $\sin^2\theta$  values a computer calculation was made of the lattice parameters by the least-square method. The calculation was carried out with a program by Lindquist. The agreement between  $\sin^2\theta_{\text{obs}}$  and  $\sin^2\theta_{\text{calc}}$  was very good and the calculation verified the tetragonal structure. 21 values of  $\sin^2\theta$  were processed.

The diffractogram run at 1000°C again showed the splitting of certain lines into two components with the approximate ratio of intensity of 2:1 but with the difference that the weaker component now was situated at the lower angle. This suggested that the peak obtained by differential thermal analysis at 860°C corresponded to a crystallographic transformation from the tetragonal structure, existing at 820°C with  $c/a < 1$ , to another tetragonal modification with  $c/a > 1$ . The computer calculation verified the structure and also that the deviations between  $\sin^2\theta_{\text{obs}}$  and  $\sin^2\theta_{\text{calc}}$  were very small. 26 values of  $\sin^2\theta$  were processed.

The diffraction pattern taken at 1200°C showed that a further crystallographic transformation had occurred since no splitting of any lines could be detected and thus a transformation to the cubic small-cell perovskite had taken place. 18 lines were measured for which computer calculation showed good agreement between  $\sin^2\theta_{\text{obs}}$  and  $\sin^2\theta_{\text{calc}}$ .

40 measurements at different temperatures between room temperature and 1300°C of certain high-angle lines were then made in order to determine the variations of the cell parameters with temperature. The measurements were made with a goniometer speed of  $\frac{1}{3}^\circ 2\theta \cdot \text{min}^{-1}$ . The sample was kept at the measuring temperature for *ca.* 15 minutes before commencing each measurement. For the determination of the parameters in the cubic and tetragonal phases the lines 400 and 422 situated at approximately  $2\theta = 95^\circ$  and  $130^\circ$  were chosen. These lines displayed the greatest splitting in the tetragonal phases and seemed the best choice to find the transition temperatures. To calculate the parameters in the orthorhombic phase, existing below 700°C, there are no especially suitable lines since most are multiplets. The best choice appeared to be the study of the splitting between 640 and 046 (orthorhombic parameters) which lies at  $2\theta \sim 120^\circ$  and which, combined with the line 482, situated at  $2\theta \sim 145^\circ$ , gave three values for the determination of  $a_0$ ,  $b_0$  and  $c_0$ . Of these lines 046 is superimposed on 165 and 482 on 406, and this creates a certain uncertainty in the determination of the parameters. The calculated values obtained for the parameters at room temperature also show small deviations from the correct ones. The values obtained at room temperature are:  $a_0 = 5.8106$ ,  $b_0 = 8.1940$ ,  $c_0 = 5.7939$  Å. Fig. 2 illustrates the appearance of some of the lines in question at different temperatures.

A special search was made to investigate whether any lines besides those of the small cell-patterns were detectable in the high-temperature phases. It was found that a few very faint lines, situated between the ones

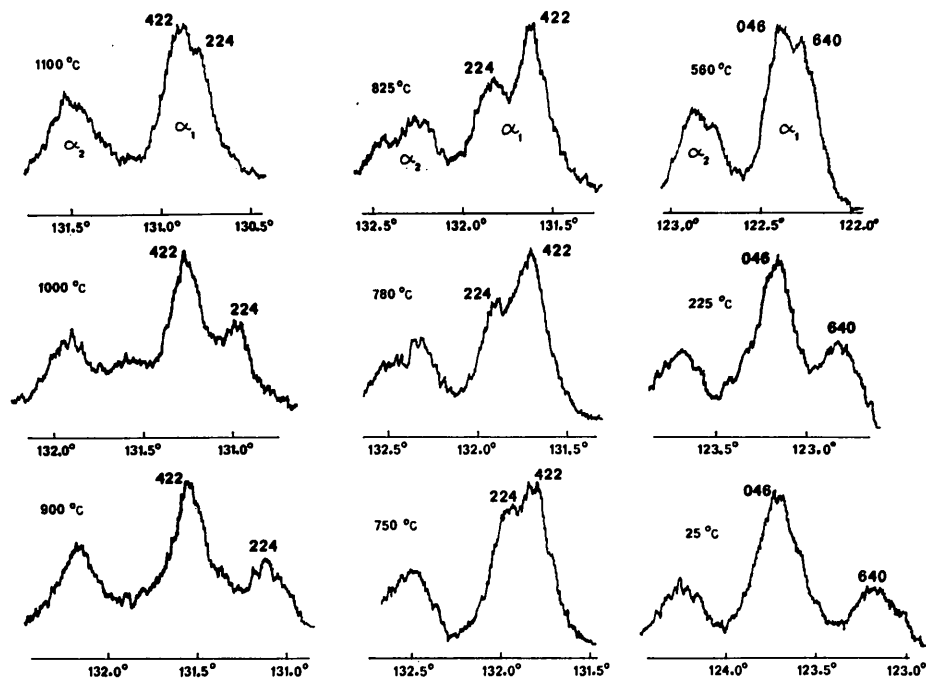


Fig. 2. X-ray intensity profiles at different temperatures. The lines are indexed on the basis of the small-cell perovskite above 700°C and of the orthorhombic structure below 700°C.

belonging to the ideal cubic pattern, could be seen in the diffraction pattern of our SrZrO<sub>3</sub>. The intensities of these 'extra' lines decreased approximately linearly with increasing temperature but even at 1200°C, where the structure was supposed to be cubic, faint indications of lines were still detectable. In order to index these lines, a unit cell containing 8 formula units was required and this true unit cell was obtained by doubling the cell edges of the small-cell structure. The correct classification of the two tetragonal phases is thus pseudotetragonal. The faint remainders which were also detectable in the cubic phase indicate a pseudo-cubic structure but it can be suspected that these faint remainders may originate from a cooler part of the sample where the pseudotetragonal phase still exists. These faint lines could only be seen at low values of  $2\theta$  when a large section of the sample was exposed to the X-rays; at a temperature as high as 1200°C the temperature gradient along the sample is likely to be considerable thereby making the above explanation plausible.

### Results

The results of the differential thermal analysis showed that the transition from the orthorhombic to the tetragonal phase occurs at  $730 \pm 25^\circ\text{C}$  and that from the tetragonal with  $c/a < 1$  to the tetragonal with  $c/a > 1$  at  $860 \pm 25^\circ\text{C}$ . The results of the X-ray measurements are illustrated in Fig. 3.

The result of the computer calculations is shown in Table 1, which also gives the stability ranges for the different high-temperature phases.

### Discussion

The agreement between transition temperatures obtained by differential thermal analysis and X-ray measurements is quite good. The difference may be explained by a thermal hysteresis which may have occurred since the differential thermal analysis is carried out under a rapidly rising temperature ( $20^\circ\text{min}^{-1}$ ) while the X-ray measurements are made at temperatures which have been kept constant during a longer period of time.

Regarding subcell parameters it can be seen from Fig. 3 that the values obtained when only one or two lines were studied show good agreement with the ones from the computer calculation where all  $2\theta$  values between  $20$  and  $150^\circ$  had been measured. The only deviation worth mentioning occurs in the  $c$  values at  $820^\circ\text{C}$ .

This deviation is partly dependent on the ratio  $c/a$  in this phase being close to 1, causing the splitting of most lines to be very small, and partly because the weaker component is situated at a higher angle than the stronger and thus falls between its  $\alpha_1$  and  $\alpha_2$ , making a correct reading more difficult.

From the uncorrected  $\theta$  values at  $1200^\circ\text{C}$  the lattice constants in the cubic system were calculated according to the method of Nelson & Riley (1945) in order to control the correction curve used and to check that no change in the position of the test specimen in relation to the goniometer axes had occurred. The curve for the lattice constant as a function of  $\frac{1}{2}(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$  proved to be a straight line, and on extrapolating to  $\theta=90^\circ$  the same value for the lattice constant was obtained as by computer calculation with the corrected values. This proved that the correction curve used was reliable.

Besides the measurements mentioned, preliminary measurements were made of the dielectric constant and the resistivity as a function of temperature up to  $1250^\circ\text{C}$ . These measurements are difficult to accomplish partly because the material becomes electrically

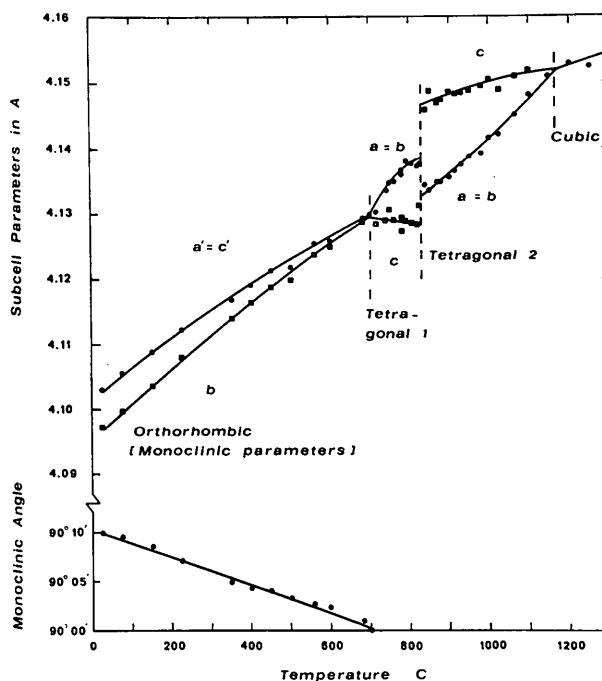


Fig. 3. Perovskite subcell parameters of SrZrO<sub>3</sub> as a function of temperature.

Table 1. Computed subcell parameters in the high-temperature phases and stability ranges for the different phases

The errors stated are three times the standard deviations.

Structure	Stability range	Subcell parameters at stated temperatures (Å)		
		T	a' = b'	c'
Pseudotetragonal	700–830°C	820°C	4.138 ± 0.002 Å	4.131 ± 0.003 Å
Pseudotetragonal	830–1170	1000	4.141 ± 0.002	4.150 ± 0.003
Cubic	1170–	1200	4.152 ± 0.002	

conductive at such high temperatures and partly because of the difficulties in obtaining stable conductive coatings on the relatively porous ceramic disc. The latter inconvenience can, however, be overcome by shaping the condenser into a pressed tablet; inside this, two thin foils of platinum were placed with a thin layer of powder in between. Before pressing, a piece of platinum wire was welded to each foil to serve as electrical connexions. The measurement was made at 1 MHz with a Wayne Kerr transformer bridge. The preliminary measurement showed that the dielectric constant increases with temperatures up to ca. 1200°C where it reaches its peak and after which it decreases with further rise in temperature. Small anomalies were also observed at 700 and 850°C. The appearance of the curve indicates that the transition at 1170°C is either a ferroelectric to paraelectric transition or an antiferroelectric to paraelectric one. The fact that the tetragonal modification is of multiple cell type indicates an antiferroelectric modification since according to Megaw (1957) this is physically more likely than a ferroelectric for multiple cell perovskites. Resistivity data indicate that at temperatures above 1000°C the zirconate behaves as a semiconductor in the intrinsic range with a band gap of  $\sim 2.1$  eV. No anomaly in the electrical conductivity was detectable at the transition at 1170°C.

It is of interest to note that the predictions made by Krainik regarding crystallographic transformations of pure SrZrO<sub>3</sub> are in good agreement with our findings. An extrapolation of Krainik's phase diagram to 100% SrZrO<sub>3</sub> shows that a transformation between a nonpolar and a paraelectric phase should take place at ca. 1100°C; this compares favourably with the one experimentally found between the cubic and the pseudotetragonal phase at 1170°C. Krainik's next transformation found between the nonpolar phases was to occur at ca. 700°C compared with our result between the two pseudotetragonal phases at 830°C. The lines in Krainik's phase diagram indicating the next transformation between a nonpolar and an antiferroelectric phase displays no straight part, making an extrapolation impossible. This transformation may correspond to the

one at 700°C between the pseudotetragonal and orthorhombic phases. The sequence of phase transitions of SrZrO<sub>3</sub> shows marked differences compared with known features of other perovskites. If more than one tetragonal or pseudotetragonal phase appears,  $c/a$  values in other perovskites are generally both  $< 1$  or both  $> 1$ . It is remarkable that the corresponding transformation in SrZrO<sub>3</sub> goes from one phase with  $c/a < 1$  to another with  $c/a > 1$ .

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## Linear Programming and the Refinement of Structures

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A new technique is developed for the perturbation of the coordinates of a structure away from a false least-squares minimum. The perturbation is a function of the accuracy of the individual components of the data. The technique could be used as an alternative method of refinement.

### Introduction

The primary requirement of a well devised X-ray diffraction experiment is the collection of data, the indi-

vidual components of which have a reasonably well defined error or standard deviation. Usually this information is only used to devise a least-squares weighting scheme and there are no explicit constraints to fit