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LETTER TO THE EDITOR

The structural phase transitions in strontium zirconate revisited

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Abstract. The structures of SrZrO₃ have been studied in fine temperature steps, from room temperature to 1230 °C, by very high resolution neutron powder diffraction. It has been concluded that SrZrO₃, orthorhombic in space group *Pnma* at room temperature, changes by a continuous transition to a pseudo-tetragonal structure in *Imma* at about 750 °C, then by a discontinuous transformation to tetragonal *I4/mcm* at about 840 °C, and finally, continuously, to cubic at 1070 °C. The sequence of structures is rationalised by reference to a recent group theoretical analysis (Howard C J and Stokes H T 1998 *Acta Crystallogr. B* **54** 782).

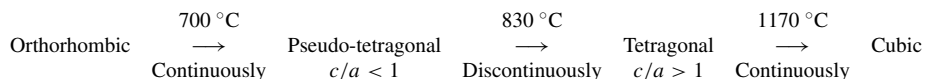
There is continuing interest in the structural variants and phase transitions in perovskites, ABX₃, associated with both their technological applications [1], and their pervasiveness in the earth sciences [2, 3]. The transitions between the different variants are often central to the technological applications. In the earth sciences, the influence of these transitions on the elastic constants may be of particular significance [4]. In spite of the countless studies of these materials driven by the above interests, the structural variants are often poorly determined, and the structural sequences not well understood.

In this letter we report new results, from room temperature to 1230 °C, obtained from the apparently simple perovskite SrZrO₃ by high-resolution neutron powder diffraction.

That the room temperature structure of SrZrO₃ is orthorhombic was established by x-ray diffraction many years ago [5]. It is well known [6–8] that the orthorhombic distortion in ABX₃ perovskites arises from the coupled tilting (relative to their orientation in the cubic aristotype) of corner-linked BX₆ octahedra—such tilting leads not only to distortion, seen as splitting of the main perovskite peaks, but also to the appearance of weak superlattice peaks due to the concomitant enlargement of the unit cell. The superlattice peaks depend on scattering from the anions which, for x-rays, is weak relative to that from the heavier cations, so it was only in a subsequent neutron diffraction study [9] that the superlattice peaks were identified and the space group *Pnma*, assigned. This space group is the one most commonly adopted by perovskites under ambient conditions [10].

It is generally considered that an orthorhombic perovskite, in *Pnma*, will transform through higher symmetries upon heating, eventually (if it does not decompose or melt first) to cubic. There are relatively few instances, however, in which the sequence has been followed in any

detail [11–14]. In the case of SrZrO_3 , a good start was made by Carlsson [15] using laboratory x-ray diffraction in conjunction with differential thermal analysis. Carlsson examined the crystal systems, and presented apparently good data on lattice parameters as a function of temperature. His observations as to the sequence of phases can be summarized as follows:



As indicated above, Carlsson did not suggest space groups for these different structures, presumably because the superlattice reflections were not well determined in his work. He was however intrigued by the first-order transition at $830\text{ }^\circ\text{C}$ involving the reversal of tetragonality. The occurrence of two transitions in the temperature range below $1000\text{ }^\circ\text{C}$ seems to have been confirmed quite recently by de Ligny and Richet [16] who, measuring heat capacity by drop calorimetry, reported specific heat anomalies at $720\text{ }^\circ\text{C}$ and $830\text{ }^\circ\text{C}$. Ahtee *et al* [17] recorded two neutron diffraction patterns at elevated temperatures, in an attempt to investigate Carlsson's pseudo-tetragonal ($c/a < 1$) and tetragonal ($c/a > 1$) phases, and concluded that the space groups were $Cmcm$ (orthorhombic) and $I4/mcm$ respectively. Kennedy *et al* [18] recently reported on a high temperature neutron powder diffraction study carried out at the Oak Ridge Laboratory, but the focus of that study was the detail of the transition from tetragonal $I4/mcm$ to the cubic $Pm\bar{3}m$. The superlattice reflections were well defined, but the peak resolution was poorer and the lattice parameters less well determined than in Carlsson's x-ray work, and except in the vicinity of the high-temperature transition to cubic, the temperature steps were coarse. The occurrence of the $Cmcm$ phase at lower temperatures was uncritically accepted.

The results presented here were obtained using the high-resolution neutron powder diffractometer, HRPD, at the ISIS facility, Rutherford Appleton Laboratories [19]. This provides lattice parameter data of better precision than laboratory x-rays, and at the same time offers the advantages of neutrons as regards enhancing the intensities of the superlattice peaks. The powdered sample of SrZrO_3 was from Aldrich, and was pre-annealed for 24 hours at $1200\text{ }^\circ\text{C}$ prior to measurement. The sample was loaded into an 11 mm diameter vanadium can, which was mounted in turn into the RAL vacuum furnace. This furnace has vanadium elements, the thermometry is based on tungsten-rhenium type W5 thermocouples, and the sample temperature was controlled to $\pm 0.2\text{ K}$. The diffraction patterns were recorded from the sample at the 1 m position, in the back-scattering detector bank, over the time-of-flight range 30–130 ms, corresponding to d -spacings from 0.6 to 2.6 \AA . The patterns were normalized to the incident beam spectrum as recorded in the upstream monitor, and corrected for detector efficiency according to prior calibration with a vanadium scan. The patterns were recorded first at room temperature, then in steps of 20° from 100 to $660\text{ }^\circ\text{C}$, in steps of 10° to $970\text{ }^\circ\text{C}$, in steps of 5° to $1190\text{ }^\circ\text{C}$, and finally in steps of 10° to a maximum temperature $1230\text{ }^\circ\text{C}$. Most patterns were recorded to a total incident proton beam of $10\text{ }\mu\text{A h}$, for approximately 15 min, which was sufficient to give a good determination of lattice parameters. About one pattern in five was recorded for a longer period, to $40\text{ }\mu\text{A h}$, the pattern recorded at $660\text{ }^\circ\text{C}$ was measured to $150\text{ }\mu\text{A h}$, and the pattern recorded at $780\text{ }^\circ\text{C}$, within the temperature range of the pseudo-tetragonal phase, was counted for a total of $400\text{ }\mu\text{A h}$ incident proton beam, for about 10 hours.

The diffraction patterns recorded at several temperatures are shown in part in figure 1. The main peaks have been indexed as for the cubic perovskite. Peak splitting due to the various distortions can be seen—the 111 peak shows definite splitting in the orthorhombic phase at room temperature, whereas the 002 peak shows splitting in both the pseudo-tetragonal and tetragonal phases. The superlattice peaks have been marked according to their origin, from R-point distortions (octahedra in successive layers tilting in opposite sense, the reflections

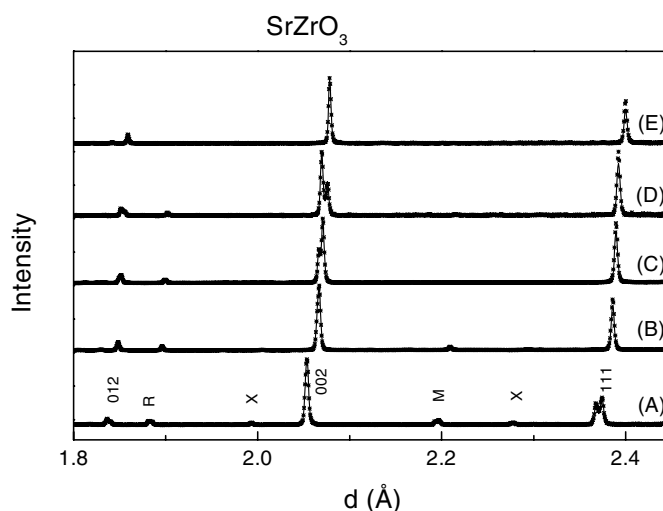


Figure 1. A segment from the observed diffraction patterns (crosses) from SrZrO_3 , showing the fundamental perovskite reflections, and the superlattice reflections arising from octahedral tilting. The patterns were recorded at room temperature (A), 660 °C (B), 780 °C (C), 880 °C (D) and 1130 °C (E). The continuous lines are fits obtained by the Rietveld method assuming structures in $Pnma$ (A,B), $Imma$ (C), $I4/mcm$ (D) and $Pm\bar{3}m$. The significance of the splitting of fundamental peaks and the presence or absence of superlattice reflections is explained in the text.

having half-integral indices on the cubic perovskite cell), from M-point distortions (octahedra in successive layers tilting in the same sense, reflections having one integral, two half-integral indices), or X-point distortions (occurring when R-point and M-point distortions operate in concert). The reader is referred to the literature [6–8, 20–22] for a more detailed analysis of these different distortions, and especially to Glazer [8] for the assignment of the superlattice reflections to the different distortions. The arguments to follow will be assisted by reference to the scheme obtained by Howard and Stokes [22] from their group theoretical analysis, reproduced here as figure 2. That figure shows the space groups for the perovskite structures obtained by ‘simple’ octahedral tilting, together with the Glazer [7] description of each tilt system. For the purposes of this letter, it suffices to say of the Glazer notation that the superscripts + and – are associated with M- and R-point distortions respectively.

We find no reason to doubt that the room temperature structure is orthorhombic, in space group $Pnma$. The peak positions are consistent with an orthorhombic metric, and the R-point, M-point and X-point superlattice reflections are all in evidence. The splitting of the 111 peak is consistent with space group $Pnma$ but not with $Cmcm$. As can be seen in figure 1, the fit obtained by the Rietveld method using the GSAS computer program [23] is quite satisfactory—there are no unaccounted reflections and, but for one or two very weak X-point reflections, every calculated reflection is observed. The refined values for the co-ordinates are in good agreement with those reported in earlier work [9, 18]. Diffraction patterns have been recorded, and the structure refined in space group $Pnma$, for temperatures up to 750 °C, and the refined values for the lattice parameters are included in figure 3. It can be seen that the a - and b -parameters become almost equal at the higher temperatures, so the structure becomes metrically tetragonal. The reason for this is not known. As the splitting of the 111 diminishes it becomes increasingly difficult to distinguish $Pnma$ from $Cmcm$, since the diffraction patterns now differ only by certain very weak M-point reflections that are space group forbidden in $Pnma$ but not in $Cmcm$; such reflections are not in fact observed. But it can be seen from figure 2

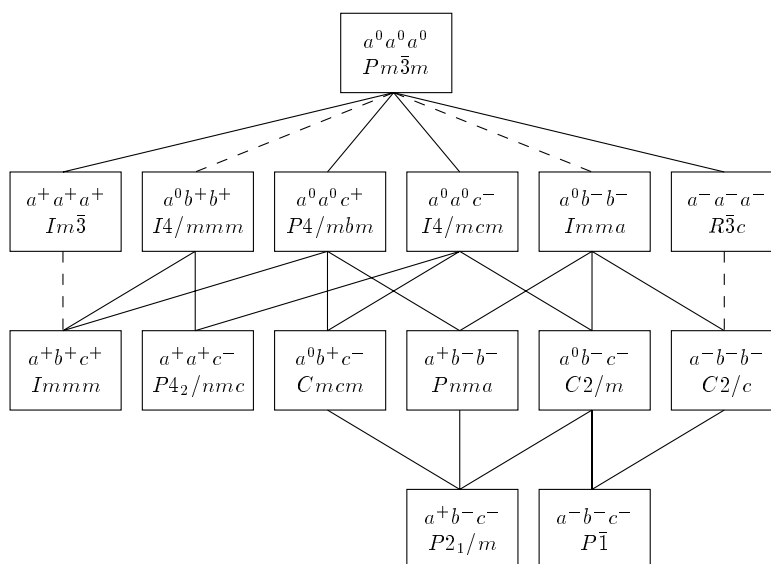


Figure 2. A schematic diagram indicating the group-subgroup relationships among the 15 space groups associated with octahedral tilting in perovskites. A dashed line joining the group with its subgroup indicates that the corresponding phase transition is required by Landau theory to be first order. This figure is reproduced from Howard C J and Stokes H T 1998 *Acta Crystallogr. B* **54** 782.

that there is no reason to expect a transition from *Pnma* to *Cmcm*, and such a transition, if it did occur, would necessarily be discontinuous. The evolution of the lattice parameters in the temperature range of interest is notable for its continuity, so we conclude that the structure remains in *Pnma* as long as both M-point and R-point superlattice reflections can be seen.

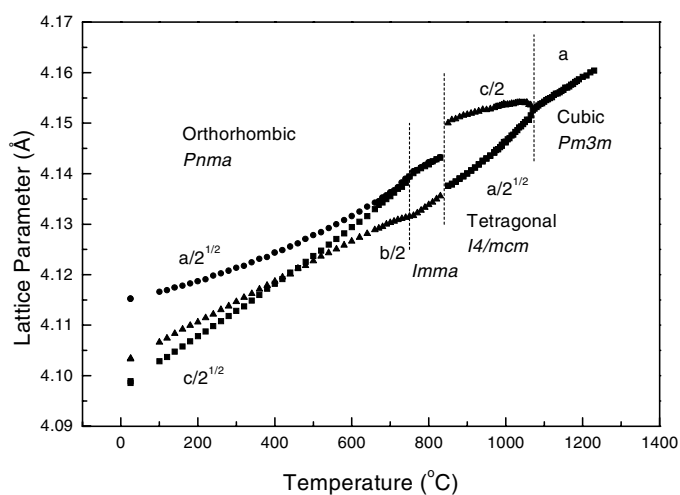


Figure 3. Temperature dependence of the reduced lattice parameters for SrZrO_3 . The first-order transition at 840 °C, and the second-order transitions at about 750 °C and 1070 °C are indicated on this plot. The structures in *Pnma* and *Imma* are described on the same unit cell.

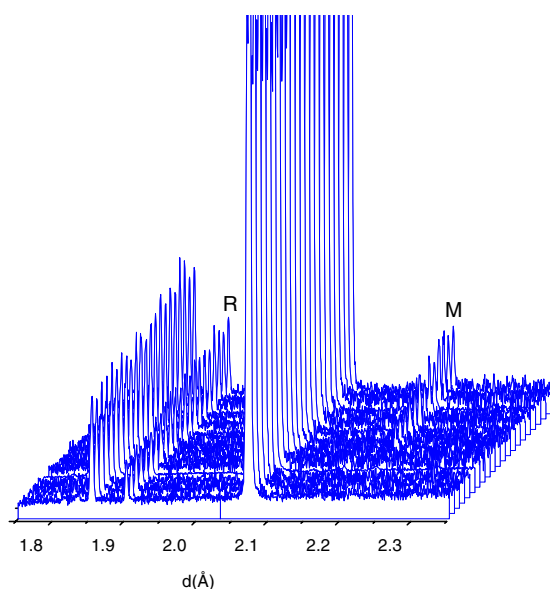


Figure 4. The R- and M-point reflections, near 1.9 and 2.2 Å respectively, recorded at temperatures from 580 °C (at back of figure) to 830 °C. The M-point reflections disappear at around 750 °C.

The M-point reflections become progressively weaker and disappear entirely at around 750 °C (see figure 4), but the R-point reflections remain. The 002 peak develops a splitting (refer figure 1) not resolved in our earlier neutron study [18]. Thus, from about 750 °C to 840 °C, we have a structure with only R-point distortions that is, as it was in the orthorhombic *Pnma* at temperatures just below 750 °C, metrically tetragonal with $c/a < 1$. This new structure corresponds to the pseudo-tetragonal structure reported by Carlsson [15]. The transition from *Pnma* to the new phase is evidently continuous, whereas at 840 °C there is a clearly first-order but volume-conserving transition to the accepted tetragonal structure in *I4/mcm*. Referring to figure 2, the only space group showing only R-point distortions (superscript – in Glazer’s notation) that can be reached by continuous transition from *Pnma* is the orthorhombic *Imma*, and the transition from this space group to *I4/mcm* would have to be discontinuous, as observed. From this we infer that the correct space group for Carlsson’s pseudo-tetragonal structure is *Imma*. However, the question as to whether this pseudo-tetragonal structure might be truly tetragonal (i.e. in a tetragonal space group) warrants further consideration. According to figure 2, or indeed the earlier analyses of perovskite structures [7, 8, 20], the (only) possible tetragonal space groups are *I4/mmm*, *P4/mbm*, *P4₂/nmc*, and *I4/mcm*. None of these are accessible by continuous transformation from *Pnma*, and all but the last are characterized by M-point distortions and presumably the corresponding reflections. Such reflections are not observed in the pseudo-tetragonal phase. The possibility of a curious first-order transition between two variants of *I4/mcm*, one with $c/a < 1$ and the other with $c/a > 1$, can be ruled out directly from the diffraction. By fitting and inspection of, for example, the R-point reflection near 1.9 Å, it can be seen (figure 5) that this reflection has a structure that can be accounted for in *Imma* but not in tetragonal *I4/mcm*. By these arguments, the possibility that the structure is truly tetragonal seems to be ruled out, reinforcing our conclusion that *Imma* is the correct space group.

Around 840 °C there is a reversal of the intensities in the 002 reflection pair, occurring over

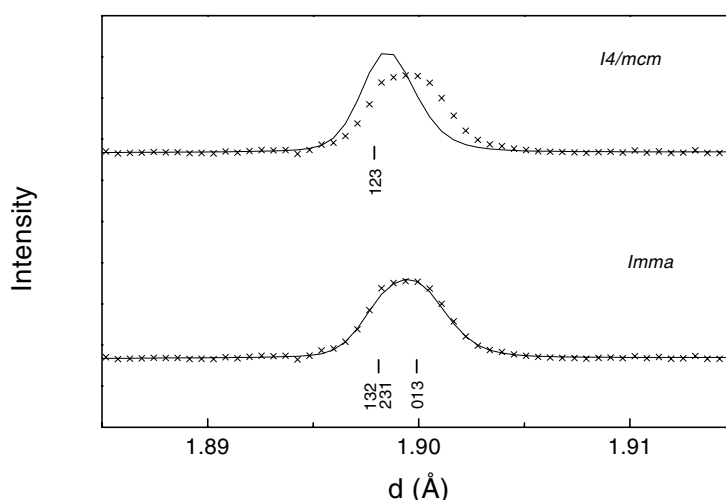


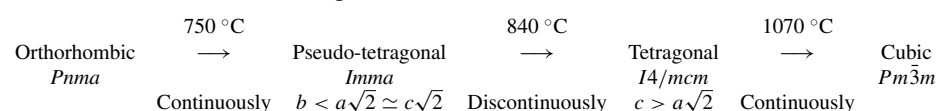
Figure 5. The R-point reflection near 1.9 Å in the pattern recorded at 780 °C. The continuous lines show the best Le Bail fits obtained assuming space groups *Imma* and *I4/mcm*. The positions of allowed reflections are indicated. The 031 in *I4/mcm*, which would correspond to the 013 in *Imma*, is disallowed by the space group reflection conditions.

a narrow temperature range, and implying a transition from *Imma* to a tetragonal structure with $c/a > 1$. The R-point reflections persist through this transition. The structure above 840 °C is, as previously observed [17, 18], tetragonal in space group *I4/mcm*. Though the transition *Imma* to *I4/mcm* is quite clearly first order, there is no measurable discontinuity in cell volume. The nature of this first-order volume-conserving transition is not yet fully understood.

The tetragonal splitting in *I4/mcm* decreases with increasing temperature, and the R-point reflections diminish in intensity, until the tetragonal transforms to cubic *Pm $\bar{3}$ m* at about 1070 °C. The transition here shows tricritical character [18].

The discussion so far has been based on the examination and analysis of diffraction patterns recorded at successively higher temperatures. Additional patterns were recorded on cooling, with emphasis on the temperature range from 860 °C down to 570 °C. At the temperature interval used in this scan (10°) there was no evidence for any hysteresis.

The conclusions from the present work can be summarized in the schematic



Thus, we confirm the sequence described by Carlsson [15], and identify the corresponding space groups. The space groups differ from those proposed by Ahtee *et al* [17] only in respect of the identification of the pseudo-tetragonal phase, but the sequence and the transitions (whether continuous or otherwise) can now be understood by reference to figure 2, taken from the work of Howard and Stokes [22]. In their work Ahtee *et al* examined SrZrO₃ at 760 °C, taken to be in the pseudo-tetragonal phase, but commented upon the appearance of both R- and M-point reflections in their diffraction pattern. Comparison with the present results suggest that their pattern was recorded at a temperature below the transition to the pseudo-tetragonal phase, in fact in orthorhombic *Pnma*. But as mentioned earlier, it can be difficult to distinguish *Pnma* from *Cmcm*, and the authors chose the latter presumably because they believed they had passed through the transition to the pseudo-tetragonal phase. In our own previous study of

SrZrO₃ [18], we refined the structure in *I4/mcm* from 750 °C to 1080 °C. The lattice parameter variation in figure 1 of our paper shows however some unusual features, now seen to resemble the changes seen through the *Imma* to *I4/mcm* transition in the present work. We now believe the structure to have been *Imma* at 750 °C and 800 °C, but not recognised as such since we did not resolve the (reversed) 002 tetragonal splitting. We note with interest that a similarly high-resolution study of BaCeO₃ [12] revealed a sequence of phases, *Pnma* → *Imma* → *R3c* → *Pm3m*, that, referring to figure 2, is closely analogous to the sequence reported here.

Perovskite pseudo-symmetry has made the SrZrO₃ crystallographic problem a challenging one. It will be interesting to revisit the phase sequences in other perovskites (e.g. SrHfO₃ and CaTiO₃), and specifically to examine more recent reports of certain *Cmcm* perovskites in the light of the present work.

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