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# Synchrotron x-ray diffraction reexamination of the sequence of high-temperature phases in $SrRuO_3$

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The crystal structure of $SrRuO_3$ at high temperatures has been studied at fine temperature intervals using high-resolution synchrotron diffraction. It has been shown that $SrRuO_3$, orthorhombic in space group *Pnma*, at room temperature, changes by a continuous transition to a structure in *Imma* at about 685 K, then by a discontinuous transformation to tetragonal $I4/mcm$ at about 825 K, and finally, continuously, to cubic at near 950 K.

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## INTRODUCTION

$CaRuO_3$ and $SrRuO_3$ are isostructural and belong to the family of perovskites with the general formula $ABO_3$. $SrRuO_3$ is an unusual example of a ferromagnetic metallic oxide with a partially filled $4d$ shell. Replacement of the Sr with Ca in $CaRuO_3$ removes the magnetic ordering although the oxide remains metallic.[1–6] Studies of the ruthenium perovskites have indicated that small variation in the Ru-O distances and Ru-O-Ru angles can significantly influence the electrical and magnetic properties of these oxides. Yet calculations in both the observed orthorhombic and idealized cubic structure suggest $SrRuO_3$ should be metallic.[7,8] The perovskite structure is based on a network of corner linked $RuO_6$ octahedra with the 12-coordinate Sr cations occupying the resulting central cavities. At room temperature $SrRuO_3$ has an orthorhombic ($\sqrt{2}a\times\sqrt{2}a\times 2a$) structure, in which the $RuO_6$ octahedra are tilted.[9,10] Following Glazer this tilting can be described as $a^-a^-c^+$ corresponding to space group *Pnma*.[11] Heating $SrRuO_3$ above *ca* 950 K results in a transition to the archetypal cubic perovskite structure in which there are no tilts of the $RuO_6$ octahedra, that is $a^0a^0a^0$, and the space group is $Pm\overline{3}m$.[10,12,13] Powder neutron-diffraction (PND) measurements have shown the presence of an intermediate tetragonal phase that contains only out-of-phase tilts, and the structure was described in $I4/mcm$ with $a^0a^0c^-$.[10,12] Using powder x-ray diffraction measurements Cuffini, Guevara, and Mascarenhas suggested the presence of an orthorhombic intermediate in space group *Imma*, $a^-a^-c^0$.[13]

Recent PND studies on $SrZrO_3$ have revealed that when orthorhombic *Pnma* structure is heated above room temperature both *Imma* and $I4/mcm$ phases are intermediate in the transition to the cubic $Pm\overline{3}m$ structure.[14] The identification of the two intermediate phases required the use of very high-resolution diffraction and fine temperature steps. Given the coarse temperature steps previously employed in the study of high-temperature structures of $SrRuO_3$[10,12] and the intense interest in the magnetic and electronic structures of $SrRuO_3$ (Ref. 1–9) we elected to reinvestigate the high-temperature structure of $SrRuO_3$ using high-resolution synchrotron diffraction and fine temperature intervals. This study has revealed the presence of both $I4/mcm$ and *Imma* phases.

## EXPERIMENT

A polycrystalline sample of $SrRuO_3$ was prepared by the solid-state reaction of stoichiometric quantities of $RuO_2$ (Aldrich, 99.9%) and $SrOO_3$ (Aldrich, 99.995%). The homogeneous mixture was compressed into 13-mm pellets and fired in air at 800 °C for 12 h and then at 1200 °C, with periodic regrinding and pressing until the reaction was complete. High-resolution synchrotron x-ray diffraction patterns were recorded using the 530-mm Debye-Scherrer diffractometer on beamline 20*B* (The ANBF) at the Photon Factory, Tsukuba.[15] This instrument uses image plates (IP) as detectors, each Fuji 20×40-cm IP covering a $2\theta$ angular range of 40°. The data are collected in 0.01° angular steps using two IP's covering an angular range of 5°–85°. Up to 31 diffraction patterns are recorded on each IP before removing it from the diffractometer. Variable-temperature measurements employed a custom built furnace and were conducted at $\lambda = 0.70$ Å, this being between the Sr and Ru *K* edges, with the samples housed in rotating 0.3-mm-diameter quartz capillaries. Powder neutron-diffraction patterns were recorded as described previously.[10]

Structures were refined using the Rietveld method implemented in the program RIETICA.[16] In these analyses the data from the individual IP's were treated as separate histograms in the refinements, with the instrumental and profile parameters constrained to be equal for each histogram.

## RESULTS AND DISCUSSION

The room-temperature synchrotron x-ray pattern of $SrRuO_3$ showed splitting of the main Bragg reflections indicative of orthorhombic symmetry, together with weaker superlattice reflections indicative of tilting of the $RuO_6$ octahedra. It was possible to identify both *M*-and *R*-point

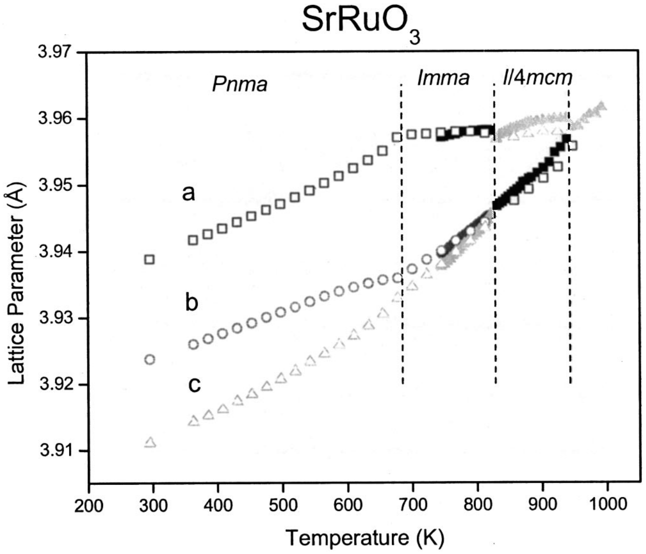

FIG. 1. Temperature dependence of the lattice parameters for $SrRuO_3$. The open and closed symbols give the results of duplicate measurements. The vertical dashed lines show the transitions between the three phases.

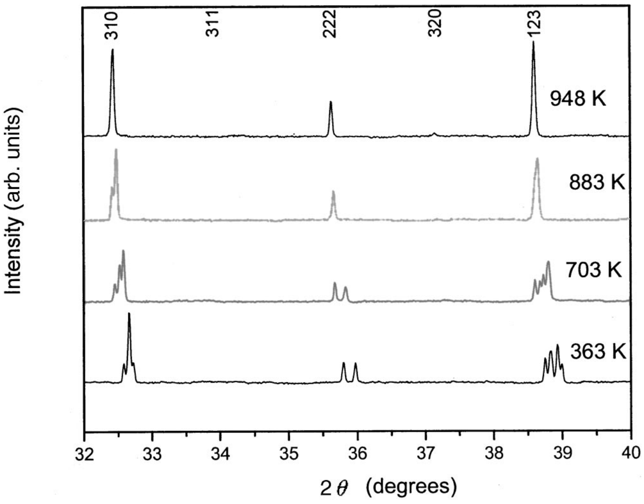

FIG. 2. Portions of the synchrotron diffraction patterns recorded at 363, 678, 883, and 948 K, showing the splitting indicative *Pnma*, *Imma*, $I4/mcm$ and $Pm\overline{3}m$ phases, respectively. The indices of the reflections in the cubic structure are indicated.

reflections indicating the presence of in-phase (+) and out-of-phase (−) tilts, respectively.[17] The data were well fitted to a model in *Pnma* as found in previous PND studies.[9,10,12] The suggestion that $SrRuO_3$ is cubic at room temperature is clearly incorrect.[18] Likewise the suggestion that $SrRuO_3$ transforms to a tetragonal phase upon cooling is very surprising,[19] and possibly in error. Heating the sample results in a marked decrease in the orthorhombicity, until near 825 K the sample becomes tetragonal (Fig. 1). A most remarkable feature of the study is the variation in lattice parameters near 685 K. Here the lattice appears to undergo a continuous transformation from one orthorhombic structure to another. The lattice parameters between 685 and 825 K are nearly tetragonal; however, the structure is clearly orthorhombic as seen from the splitting of the Bragg reflections (Fig. 2). The variation in the lattice parameters is consistent with the previous PND studies,[10,12] the use of much finer temperature intervals here considerably enhancing the transition near 685 K.

The second notable feature in the temperature variation of the lattice parameters is the discontinuity in the lattice parameters near 825 K. This, again, is consistent with the previous PND studies and is indicative of a first-order phase transition.[10,12] Small hysteresis effects were observed on cycling the sample above and below this transition. Near 950 K the sample undergoes a further transition to cubic, and this appears to be continuous. Unfortunately a small displacement of the sample at these highest temperatures caused a broadening and asymmetry in the diffraction peaks and this limited our ability to study this transition in more detail. The temperature of formation of the cubic phase found here is around 50° higher than that suggested from the neutron-diffraction studies.[10,12] In the latter case we assign cubic symmetry as the point at which the superlattice reflections are no longer observed. For the synchrotron study these are lost while the peaks clearly show a tetragonal splitting and the assignment of cubic symmetry is the point at which no asymmetry of the diagnostic reflections remains.

The diffraction data clearly reveal the presence of two intermediate phases between the room-temperature orthorhombic and high-temperature cubic forms. Examination of the individual profiles shows that the first of these intermediate phases is orthorhombic and the second tetragonal (Fig. 2). Within the sensitivity of the synchrotron measurements both these phases only involve *R*-point distortions, that is they only have out-of-phase tilts of the $RuO_6$ octahedra. As is illustrated in Fig. 3 the *M*-point reflections are no longer observed in the synchrotron diffraction patterns at 643 K, that is just below the point at which the lattice parameters

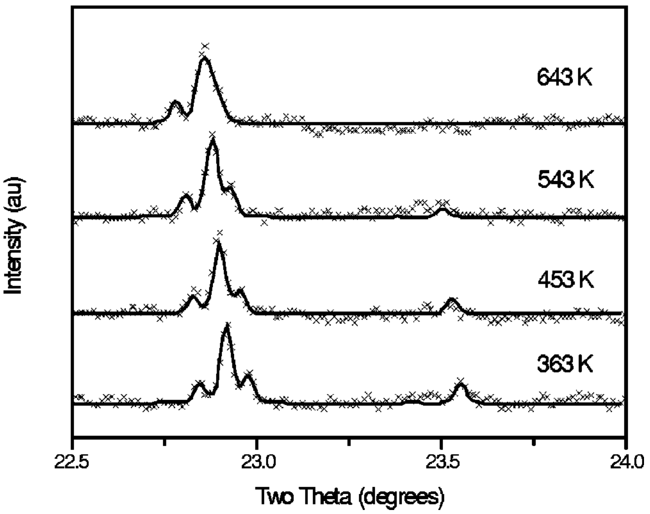

FIG. 3. Portions of the synchrotron diffraction patterns recorded at 363, 453, 543, and 643 K, showing the gradual loss of intensity of the (*Pnma*) 131 reflection as the transition to the *Imma* phase is approached.

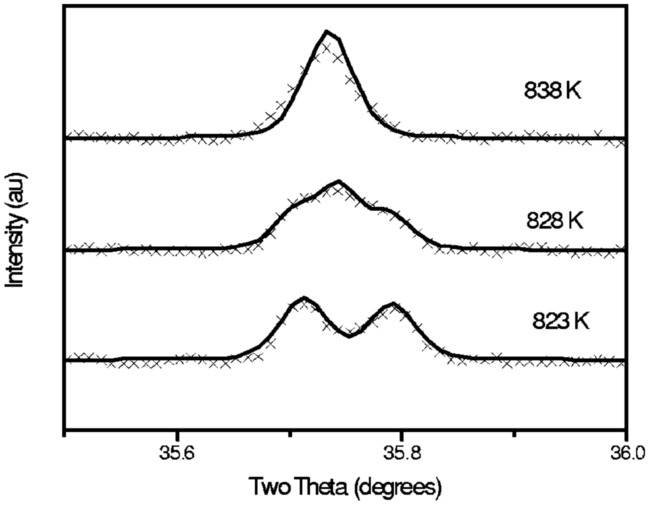

FIG. 4. Portion of the diffraction patterns for $SrRuO_3$ at 823, 828, and 838 K showing the first-order transformation of the *Imma* 440 and 044 reflections from 823 K to the single $I4/mcm$ 044 reflection at 838 K. Note the presence of all three reflections in the patterns at 828 K demonstrating the presence of a two-phase mixture. The pattern at 833 K also shows three peaks in this region.

show the first phase transition to occur. Reexamination of the PND data[10] also shows that between 773 and 923 K only *R*-point, and not *M*-point, reflections can be observed. Thus we have a continuous transition from one orthorhombic structure ($a^-a^-c^+$) to another orthorhombic structure that contains only out-of-phase tilts. The second orthorhombic structure then transforms discontinuously, without changing the sense of the tilts, to a tetragonal structure, which ultimately transforms continuously to the cubic structure. By examination of the work of Howard and Stokes[20] we propose the following sequence of transitions,

$$Pnma \xrightarrow{685\text{ K}} Imma \xrightarrow{825\text{ K}} I4/mcm \xrightarrow{945\text{ K}} Pm\bar{3}m.$$

This sequence of structures was confirmed by Rietveld analysis of the individual diffraction profiles and is the same sequence of transitions recently described for $SrZrO_3$.[14] We have fitted the profiles as follows: *Pnma* $T<685$ K; *Imma* $685<T<823$; $I4/mcm$ $835<T<950$ K and $Pm\bar{3}m$ $T>950$ K. It was not possible to satisfactorily fit the profiles collected at 828 and 833 K with models in either *Imma* or $I4/mcm$. This is clearly evident near $2\theta=36°$ where the (440) (044) pair of reflections in *Imma* transforms to a single (044) reflection in $I4/mcm$. As illustrated in Fig. 4 the *Imma* fit of the data at 823 K adequately fits both these reflections (and the rest of the pattern) while the $I4/mcm$ model fits the single reflection at 838 K. At both 828 and 833 K the reflection near $2\theta=36°$ apparently consists of three peaks and could only be adequately fitted to a two-phase $Imma$-$I4/mcm$ model (Fig. 5). The coexistence of these two phases is not surprising for such a first-order phase transition. The abundance of the two phases estimated from the Rietveld analysis are 16.4 (4) and 83.6 (1.7) mol % at 828 and 9.5 (3) and 90.5 (1.6) mol % at 888 K.

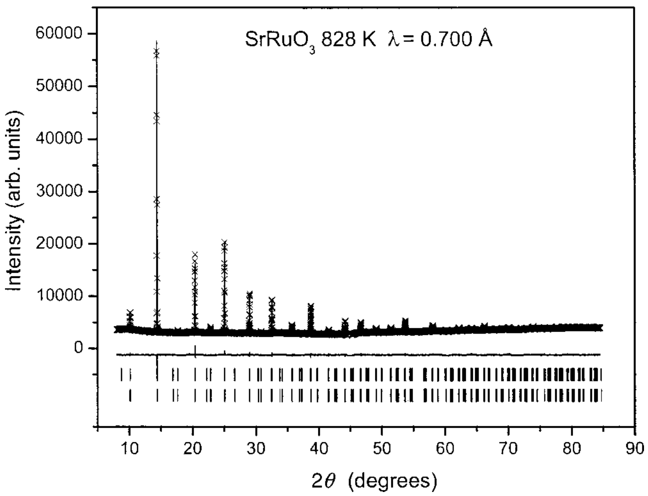

FIG. 5. Observed, calculated, and difference synchrotron diffraction profiles for $SrRuO_3$ at 828 K. The short vertical lines show the presence of the allowed Bragg reflections in *Imma* (top) and $I4/mcm$ (bottom).

In light of the evidence for the *Imma* phase we have reexamined the powder neutron-diffraction data described previously.[10] We find that the patterns recorded 773 and 823 can be adequately fitted to models in *Imma* with *R* factors comparable to those obtained for fits in *Pnma* (at 773 K $R_p$ 4.69 $R_{wp}$ 5.67 $\chi^2=2.94$ vs 4.74, 5.75, and 2.91%, respectively) or I4/$mcm$ (at 823 $R_p$ 7.89 $R_{wp}$ 9.31 $\chi^2=1.97$ vs 7.33, 8.82 and 1.94%, respectively). In both cases the $\chi^2$ value for the fit in *Imma* is given first. The slightly higher than usual values are associated with the use of a stainless steel container in the measurements that gives rise to additional peaks. The larger peak widths of the neutron-diffraction data (compared to the present synchrotron diffraction patterns) prevent the observation of the small splitting indicative of orthorhombic splitting at 773 and 823 K. The fit to the neutron pattern at 773 K is slightly worse than the others, suggesting a small a two-phase mixture may be present.

Calculation of the band structures in the four polymorphs shows a small reduction in the Ru $4d$ bandwidth as the symmetry decreases. These general features of our calculations are consistent with previous band-structure calculations.[7,8] Despite the narrowing of the Ru $4d$ band in the *Pnma* structure there is sufficient density of states near the Fermi level, coming from the Ru $4d$ and O $2p$ levels. This is consistent with the observed near linear increase in resistivity as $SrRuO_3$ is heated to 1000 K.[7] It appears that the structural transitions have little effect on the bulk physical properties of $SrRuO_3$, although they may influence the fine details. Accordingly it is unlikely that an electronic transition, such as the low-temperature transition to a ferromagnetic state, will drive a structural phase transition.

It is clear that while the *Pnma* structure is energetically favored there is little to distinguish the four structures, *Pnma*, *Imma*, $I4/mcm$, and $Pm\bar{3}m$, in $SrRuO_3$. Although this sequence of transitions is the same as that found in $SrZrO_3$[14] this need not always be the case. Indeed in $BaPbO_3$ the sequence is $C2/m$-*Imma*-$I4/mcm$-*Pm*3*m*.[21] The availability of precise and accurate structures at closely spaced temperatures for these three oxides in each of the four structural types provides the opportunity to examine the factors responsible for stabilizing each of these. Since the transitions from an orthorhombic structure (either *Pnma* or *Imma*) to the tetragonal $I4/mcm$ structure must be first order, it is feasible that systems will exist where the direct $Pnma$-$I4/mcm$ transition is observed. Proof of this will require the use of very fine temperature intervals near such a transition.

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