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# Neutron powder diffraction studies of $\text{Sr}_2\text{RuO}_4$ and $\text{SrRuO}_3$

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## Abstract

Neutron powder diffraction experiments have been carried out on two interesting perovskite compounds,  $\text{Sr}_2\text{RuO}_4$  ( $\text{K}_2\text{NiF}_4$  structure) and  $\text{SrRuO}_3$  (distorted perovskite), both of which are used as substrates for the growth of high-temperature superconducting thin films. The powder diffraction data have been refined at high and low temperatures to obtain lattice parameters and the lattice mismatch between these compounds and  $\text{YBa}_2\text{Cu}_3\text{O}_7$  over a wide temperature range is found to be good. No evidence has been found for any lattice distortions between 5 and 973 K in  $\text{Sr}_2\text{RuO}_4$  and between 100 and 300 K in  $\text{SrRuO}_3$ .

## 1. Introduction

The current interest in thin films of high-temperature superconductors has made the compatibility of film and substrate an important concern. To obtain an oriented film, a single crystal substrate is required with excellent lattice match, similar thermal-expansion coefficients and no disruptive phase transitions. There has been a lot of effort put into preparing thin films of the high-temperature superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (Y123) on available substrates such as  $\text{SrTiO}_3$  and  $\text{MgO}$  [1]. Conductivity in the high-temperature superconductors occurs mainly in the  $ab$  plane, and the highest critical currents in the films are also obtained when the material is fully oriented with the  $c$ -axis perpendicular to the substrate and having a minimum amount of grain boundaries. For these reasons the substrates used for epitaxial growth must have a good lattice match with the  $a$  or  $b$

lattice parameters of Y123. It is in this context that there has recently been renewed interest in the study of ternary ruthenium oxides like  $\text{BaRuO}_3$ ,  $\text{CaRuO}_3$ ,  $\text{SrRuO}_3$  and  $\text{Sr}_2\text{RuO}_4$  for use as metallic substrates for Y123 thin films. The ternary ruthenates, apart from being useful candidates for substrates are interesting in their own right.

$\text{Sr}_2\text{RuO}_4$  crystallises in the  $\text{K}_2\text{NiF}_4$  structure, similar to the  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  superconductor. It shows high metallic conductivity along the  $ab$  plane ( $\sim 10^{-6} \Omega \text{ cm}$ ) and a slightly lower conductivity along the  $c$ -axis [2]. It is therefore not surprising that superconductivity was recently discovered in  $\text{Sr}_2\text{RuO}_4$  at 0.9 K [3]. Thin films of Y123 superconductor have been successfully grown on  $\text{Sr}_2\text{RuO}_4$  and the lattice matching has been found to be satisfactory [2]. Our study of the structure of this compound was motivated because of the suitability of this compound as substrate over a wide range of temperature. Our investigation was carried out prior to the discovery of superconductivity in it and hence did not extend in temperature down to its supercon-

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Table 1

The results from Rietveld analysis of  $\text{SrRuO}_3$ 

Atom	$T = 100 \text{ K}$ (Pbnm), $R_{\text{wp}} = 8.1\%$ , $R_{\text{e}} = 4.5\%$ , $\chi^2 = 1.8$ ,				$T = 300 \text{ K}$ (Pbnm), $R_{\text{wp}} = 12.1\%$ , $R_{\text{e}} = 11.0\%$ , $\chi^2 = 1.1$ ,			
	$a = 5.5636(6) \text{ \AA}$	$b = 5.5206(6) \text{ \AA}$	$c = 7.8429(8) \text{ \AA}$		$a = 5.5639(6) \text{ \AA}$	$b = 5.5302(3) \text{ \AA}$	$c = 7.8441(3) \text{ \AA}$	
	$x$	$y$	$z$	$B_{\text{iso}} (\text{\AA}^2)$	$x$	$y$	$z$	$B_{\text{iso}} (\text{\AA}^2)$
Sr	-0.0025(4)	0.0196(3)	$\frac{1}{4}$	0.0881(2)	-0.0016(6)	0.0201(2)	$\frac{1}{4}$	0.3578(4)
Ru	$\frac{1}{2}$	0	0	0.1768(3)	$\frac{1}{2}$	0	0	0.1149(5)
O1	0.7226(6)	0.2774(4)	0.0283(7)	0.0406(2)	0.7225(9)	0.2777(9)	0.0288(4)	0.2540(1)
O2	0.0550(4)	$\frac{1}{2}$	$\frac{1}{4}$	0.0058(3)	0.0541(3)	$\frac{1}{2}$	$\frac{1}{4}$	0.4766(8)

ducting transition temperature. It, however, covers a temperature range wide enough to provide the necessary information for those interested in its use as a substrate as well as for those interested in its structure as a superconductor.

$\text{SrRuO}_3$  crystallises in the perovskite structure and is also metallic, having an in-plane resistivity of the same order of magnitude as  $\text{Sr}_2\text{RuO}_4$ . It has been used successfully as a substrate for deposition of

Y123 films [4].  $\text{SrRuO}_3$  is probably the only compound containing Ru to show ferromagnetic behaviour. It exhibits a change of slope in the resistivity at 160 K, and there is further evidence from magnetic-susceptibility measurements indicative of ferromagnetic ordering at this temperature [5]. The interesting magnetic properties of  $\text{SrRuO}_3$  make it a useful substrate in fabricating S–N–S junctions.

In this paper we report our investigations of the

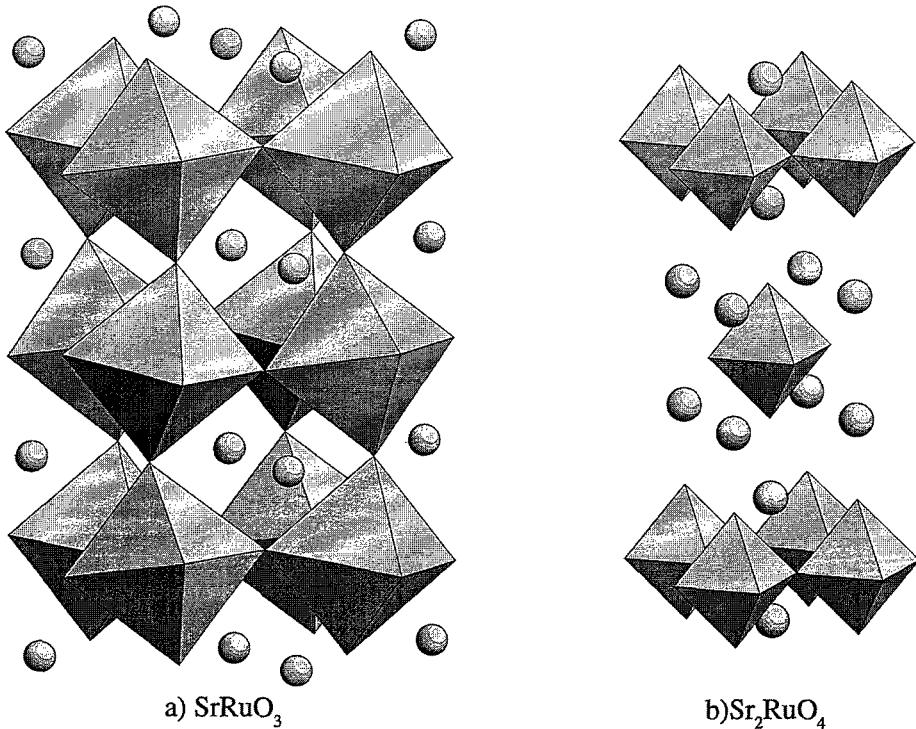


Fig. 1. The room-temperature structures of (a)  $\text{SrRuO}_3$ , distorted perovskite (Pbnm), and (b)  $\text{Sr}_2\text{RuO}_4$ ,  $\text{K}_2\text{NiF}_4$  (I4/mmm). The octahedral coordination of Ru and the Sr sites are shown.

temperature dependence of the lattice parameters for tetragonal  $\text{Sr}_2\text{RuO}_4$  over the temperature range of its use as a substrate. Thin films are normally deposited at elevated temperatures,  $\sim 973$  K, so we have carried out neutron powder diffraction experiments between 5 K and 973 K to obtain an accurate set of lattice parameters and also to look for any structural disorders in this temperature regime. In  $\text{SrRuO}_3$ , we have performed neutron powder diffraction experiments at room temperature and at 100 K (below the ferromagnetic transition temperature) to see if the ferromagnetic ordering is associated with a structural transition.

## 2. Experimental details

The polycrystalline samples were prepared by reacting, in air, appropriate proportions of  $\text{SrCO}_3$  (99.99%) and Ru metal (99.99%) for 24 h at  $1200^\circ\text{C}$  for  $\text{SrRuO}_3$  and 40 hours at  $1200^\circ\text{C}$  for  $\text{Sr}_2\text{RuO}_4$  with several intermittent grindings to ensure a complete reaction, before sintering at  $1300^\circ\text{C}$ . The samples prepared were single phase and were characterised by X-ray powder diffraction, resistivity and susceptibility measurements prior to the neutron experiment. The neutron powder diffraction experiments were carried out on the high-resolution pow-

der diffractometer (HRPD) at the pulsed neutron source, ISIS. The samples were enclosed in a vanadium container and then placed in a cryostat or furnace to carry out experiments between 5 K and 973 K. The refinement of the  $\text{Sr}_2\text{RuO}_4$  and  $\text{SrRuO}_3$  data was carried out assuming the tetragonal  $\text{K}_2\text{NiF}_4$ -type structure of space group I4/mmm and the orthorhombic space group Pbnm, respectively, and using the Rietveld refinement method. This method compares the complete calculated powder diffraction pattern with the one observed, and optimises the degree of fit by adjusting the various structural parameters by non-linear least square fitting.

## 3. Results and discussion

### 3.1. $\text{SrRuO}_3$ , low and room-temperature measurements

In Table 1 we present the results of Rietveld refinement for powder diffraction patterns obtained at 100 K and 300 K of  $\text{SrRuO}_3$ . At room temperature and 100 K the ternary ruthenium oxide,  $\text{SrRuO}_3$ , was found to possess the orthorhombic space group Pbnm and its unit cell is shown in Fig. 1. The refined parameters at room temperature agree well with those obtained by Jones et al. [6]. The interatomic distances at room temperature agree well with those published by Shikano et al. [5]. The structure is the perovskite structure with chains of ruthenium oxide forming the basal planes of elongated octahedrons. Fig. 2 shows the temperature dependence of the cell edge for  $\text{SrRuO}_3$  ( $(a^2 + b^2)^{1/2}/2$ ) which is effectively the length of the pseudo cell axis. These results give a lattice mismatch of no more than 0.2% [7] with the  $a$ -axis of Y123 over the entire temperature range of the experiment. This compares well with the lattice mismatch of other substrates in use such as  $\text{SrTiO}_3$  (1.16%) and  $\text{NdGaO}_3$  (0.27%) [1] with the high-temperature superconductor.

The similarity in the refined parameters of the 100 K and the room-temperature data suggests that no structural phase transitions take place between these two temperatures although it is known that a ferromagnetic transition takes place at 160 K [5].

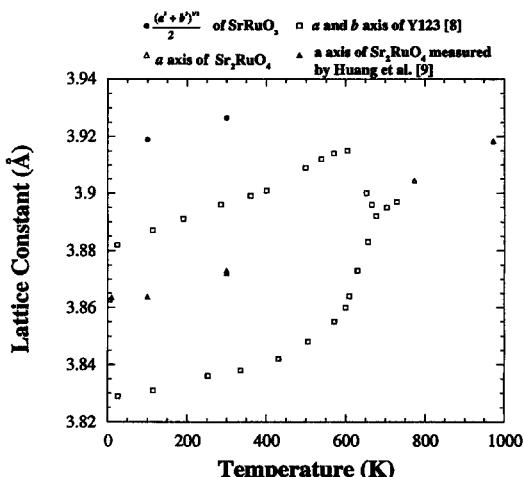


Fig. 2. The temperature dependence of the pseudo cell axis of  $\text{SrRuO}_3$  and the  $a$ -axis of  $\text{Sr}_2\text{RuO}_4$ . The lattice parameters of the tetragonal and orthorhombic phases of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  are also shown.

Table 2

The results from Rietveld analysis of  $\text{Sr}_2\text{RuO}_4$ 

Atom	$T = 5 \text{ K} (\text{I}4/\text{mmm})$ , $R_{\text{wp}} = 45\%$ , $R_e = 13.2\%$ , $\chi^2 = 3.4$ , $a = 3.8627(4) \text{ \AA}$ , $c = 12.7176(8) \text{ \AA}$				$T = 300 \text{ K} (\text{I}4/\text{mmm})$ , $R_{\text{wp}} = 30\%$ , $R_e = 17.7\%$ , $\chi^2 = 1.7$ , $a = 3.8720(3) \text{ \AA}$ , $c = 12.7345(7) \text{ \AA}$				$T = 973 \text{ K} (\text{I}4/\text{mmm})$ , $R_{\text{wp}} = 6.4\%$ , $R_e = 3.2\%$ , $\chi^2 = 2.0$ , $a = 3.9183(8) \text{ \AA}$ , $c = 12.7905(3) \text{ \AA}$			
	$x$	$y$	$z$	$B_{\text{iso}} (\text{\AA}^2)$	$x$	$y$	$z$	$B_{\text{iso}} (\text{\AA}^2)$	$x$	$y$	$z$	$B_{\text{iso}} (\text{\AA}^2)$
Sr	0	0	0.3530(8)	0.0083(3)	0	0	0.3519(6)	0.3594(7)	0	0	0.3528(1)	1.3418(3)
Ru	0	0	0	0.0025(5)	0	0	0	0.1689(7)	0	0	0	0.5642(5)
O1	0	0	0.1618(8)	0.0028(1)	0	0	0.1622(5)	0.6407(1)	0	0	0.1615(2)	1.7796(6)
O2	0	$\frac{1}{2}$	0	0.0026(1)	0	$\frac{1}{2}$	0	0.3739(7)	0	$\frac{1}{2}$	0	1.5842(8)

### 3.2. $\text{Sr}_2\text{RuO}_4$ , low- and high-temperature measurements

The tetragonal unit cell of  $\text{Sr}_2\text{RuO}_4$  with space group I4/mmm, is shown in Fig. 1. The strontium atom lies approximately in the basal plane of a quadratic pyramid of five oxygen atoms and the ruthenium atoms have a distorted octahedral coordination. The atomic arrangement is similar to that of  $\text{La}_2\text{CuO}_4$  and its Sr and Ba based derivatives except that the deformity in the octahedron is considerably less.

Rietveld analysis of  $\text{Sr}_2\text{RuO}_4$  neutron diffraction data at 5, 100, 300, 773 and 973 K was carried out between  $30\,000 \mu\text{s} < \text{t.o.f.} < 100\,000 \mu\text{s}$ , which includes approximately 250 observed reflections. The diffraction patterns at all the temperatures were fitted to the tetragonal I4/mmm structure and the refinement is summarised in Table 2. The lattice constants of  $\text{Sr}_2\text{RuO}_4$  change by 1.4% between 5 K and 973 K. The  $a$  and  $b$  lattice constants increase by only 0.5% between 5 K and room temperature and then increase more rapidly with temperature up to 973 K. As shown in Fig. 2, the lattice constants agree well with the lattice parameters of both the orthorhombic and tetragonal phases of Y123 over the entire temperature range of the experiment. The lattice mismatch between the  $a$ -axis of Y123 and the  $a(b)$ -axis of  $\text{Sr}_2\text{RuO}_4$  at 973 K was calculated to be 0.15% and this decreases to 0.12% [7] at 5 K. Huang et al. [9] have earlier reported the refinement of their neutron powder data on this compound at 300 K and 10 K and our parameters agree well with their data at these temperatures (see Fig. 2 for comparison). The interatomic distances obtained from our refinement

of  $\text{Sr}_2\text{RuO}_4$  agrees well with those of Huang et al. [9] at room temperature and low temperatures. Our interatomic distances at 973 K are as follows: Sr–O(1) = 2.694(9) Å, Sr–O(2) = 2.435(4) Å, Sr–O(2) = 2.744(7) Å, Ru–O(1) = 1.936(5) Å, Ru–O(2) = 2.056(6) Å.

Once again we found no evidence of any phase transitions over the whole temperature range of the experiment, indicating that  $\text{Sr}_2\text{RuO}_4$  substrates are excellent candidates for epitaxial growths of high-temperature superconducting Y123 thin films.

### 4. Conclusions

The lattice parameters of the metallic strontium ruthenates have been determined by neutron powder diffraction measurements over a wide temperature range to check their suitability for use as substrates for the high-temperature superconductors. The lattice parameters are found to agree well with the  $a(b)$  lattice constants of the high-temperature superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . The mismatch being as good as or better than that of the substrates commonly used such as  $\text{SrTiO}_3$  and  $\text{MgO}$ . It has been shown that  $\text{Sr}_2\text{RuO}_4$  does not undergo any structural transition between 973 K and 5 K and similarly  $\text{SrRuO}_3$  undergoes no structural transition between room temperature and 100 K although it becomes a ferromagnet below 160 K. Further experiments are planned on the superconducting  $\text{Sr}_2\text{RuO}_4$  to investigate possible structural instabilities close to the superconducting transition temperature and to also establish the structure in the superconducting state.

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## References

- [1] M. Sasaura, S. Miyazawa and M. Mukaida, *J. Appl. Phys.* 68 (1990) 3643.
- [2] F. Lichtenberg, A. Catana, J. Mannhart and D.G. Scholm, *Appl. Phys. Lett.* 60 (1992) 1138.
- [3] Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J.G. Bednorz and F. Lichtenberg, *Nature (London)* 372 (1994) 532.
- [4] X.D. Wu, S.R. Folty, R.C. Dye, Y. Coulter and R.E. Muenchausen, *Appl. Phys. Lett.* 62 (1993) 2434.
- [5] M. Shikano, T.K. Huang, Y. Inagumay, M. Itoh and T. Nakamura, *Solid State Commun.* 90 (1994) 115.
- [6] C.W. Jones, P.D. Battle, P. Lightfoot and W.T.A. Harrison, *Acta Crystallogr. C* 45 (1989) 365.
- [7] From the usual equation of  $|a_f - a_s|/[0.5 \times (a_f + a_s)]$ , where f and s denote film and substrate, respectively.
- [8] B. Rauschenbach, T. Reetz, W. Erfurth and H. Nafe, *Physica C* 153 (1988) 988.
- [9] Q. Huang, J. L. Soubeyroux, O. Chmaissem, I. Natali Sora, A. Santoro, R.J. Cava, J.J. Krajewski and W.F. Peck Jr., *J. Solid State Chem.* 112 (1994) 355.