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# Low-$T_c$ magnetically ordered phase of $SrRuO_3$

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Magnetic susceptibility and electrical resistivity studies on polycrystalline $SrRuO_3$ synthesized at 900 °C and annealed at various temperatures in the range 950–1300 °C show the existence of two different phases of the compound, a phase with $T_c = 141$ K formed below 1100 °C and a second and normal phase having $T_c = 160$ K obtained at higher processing temperatures ($>1100$ °C). Both the phases have orthorhombic crystal symmetry with a marginal difference in their lattice parameters as evidenced from powder x-ray-diffraction measurements. [S0163-1829(97)00530-4]

Strontium ruthenate, $SrRuO_3$, having a distorted perovskite structure, is known for its high electrical conductivity and as a ferromagnetic oxide containing a single kind of magnetic ion. $SrRuO_3$ is the only conducting ferromagnetic oxide containing a second-row transition-metal ion and research work on this compound gained momentum in the recent past because of its various possible technological applications.[1–9] It has been shown that the compound can be deposited as thin films on various substrates. The films so obtained possess high thermal and chemical stability with good surface smoothness and high crystalline quality. Since the crystal structure of $SrRuO_3$ is compatible to high-$T_c$ superconductors and ferroelectric compounds, $SrRuO_3$ thin films can be used as a conducting buffer layer for various applications such as ferroelectric and electro-optic devices, superconductor-normal metal-superconductor Josephson junctions, etc.

At low temperatures $SrRuO_3$ becomes ferromagnetic. Resistivity and magnetization measurements on both single-crystal and polycrystalline samples showed Curie temperature as 160 K.[10–14] Substitution of Ca in $SrRuO_3$ reduces the Curie temperature[15] and finally the system becomes antiferromagnetic for $CaRuO_3$. Even though both $SrRuO_3$ and $CaRuO_3$ are isostructural with the same number of unpaired $d$ electrons, their extreme magnetic behavior is explained in terms of the extent of distortion of $RuO_6$ octahedra in the structure. Magnetic measurements on single-crystals of $SrRuO_3$ showed that the magnetic susceptibility is highly anisotropic.[10] Ferromagnetic moments of single-crystal samples saturate at very low applied magnetic fields, if the field is applied along the $\langle 110\rangle$ axis of the crystal whereas for polycrystalline samples there is no saturation observed even at very high magnetic fields. The experimentally observed saturation magnetic moment is found to be less than that calculated for a low-spin $Ru^{4+}(t_{2g}^4)$ state. The ferromagnetic moment at 4.2 K measured at a field of 125 kG is only $1.55\mu_B$ compared to the calculated $2\mu_B$ expected for the low-spin $Ru^{4+}$ ion. The effective magnetic moment $\mu_{\mathrm{eff}}$, calculated in the paramagnetic region is close to that expected for an $S=1$ low-spin $Ru^{4+}$. The reduced ferromagnetic moment was attributed to band ferromagnetism[12] and recent band structure calculations agree very well with this view.[16]

Recent studies of the transport and magnetic properties on thin films of $SrRuO_3$ show that for some of the films $T_c$ is 140 K.[1,7,17] In fact, it has been reported that the $T_c$ depends on the film thickness.[17] For a film thickness of 90 Å the magnetic transition is observed at 140 K and $T_c$ increases to 160 K for films of thickness 750 Å. In this paper, we show that for the polycrystalline compound also there exists two different magnetic ordering temperatures depending on the heat treatment conditions. Thus, when polycrystalline $SrRuO_3$ is processed below 1100 °C, $T_c$ is obtained as 141 K. Polycrystalline or single-crystal samples of $SrRuO_3$ are usually prepared at or above 1200 °C which gives a $T_c$ of 160 K.

Polycrystalline $SrRuO_3$ was prepared by mixing $SrCO_3$ and nanocrystalline $RuO_2$ taken in the stoichiometric ratio and heating initially at 900 °C for 72 h with six intermediate grindings. Formation of single-phase compounds was established by powder x-ray-diffraction (XRD) measurements. The compound so obtained was then ground well and annealed in air at various temperatures from 950 to 1300 °C for 12 h each.

Figure 1 shows the temperature variation of the ac magnetic susceptibility of polycrystalline $SrRuO_3$ heated at various temperatures. The ac susceptibility was measured at a frequency of 27 Hz and an applied field of 10 G. For the compound annealed at 1000 °C, a sharp symmetric peak is observed at 141 K. The same susceptibility behavior is observed for the compound heated up to 1050 °C. However, for the sample annealed at or above 1150 °C, a sharp peak in the ac susceptibility curve is observed at 160 K. Since the ac susceptibility behavior of the sample heated at 1050 and 1150 °C is entirely different, the material was annealed at 1100 °C for different time intervals. It was found that for the sample annealed for 6 h the ac susceptibility behavior is identical to that for the low-temperature-treated samples,

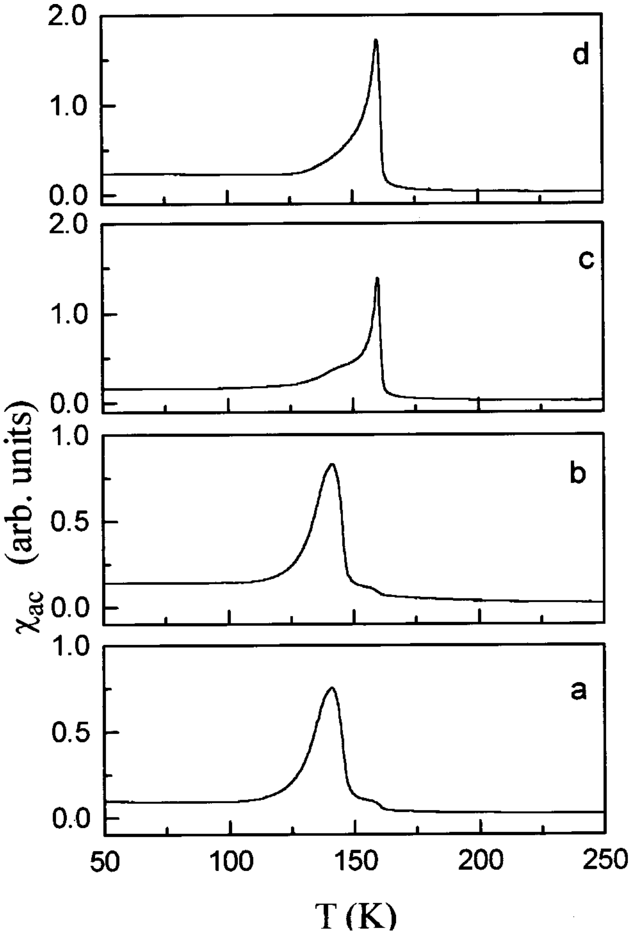

FIG. 1. Temperature variation of the ac magnetic susceptibility of $SrRuO_3$ annealed at (a) 1000 °C/12 h, (b) 1100 °C/6 h, (c) 1100 °C/24 h, and (d) 1200 °C/12 h.

whereas for the compound annealed for 24 h a sharp peak is observed at 160 K, but with a small shoulder at 141 K. At higher annealing temperatures above 1150 °C the only effect observed in the ac susceptibility curve is an increase in the peak value of the susceptibility. The temperature at which ac susceptibility is maximum, $T_{\chi\max}$, coincides with the reported $T_c$ values of 140 and 160 K for very thin films and polycrystalline or single crystal $SrRuO_3$, respectively. The maximum in the susceptibility ($\chi_{\max}$) observed in the ac susceptibility curves for the low-$T_c$ samples is lower than that for the high-$T_c$ samples.

Results of dc magnetization measurements on the samples annealed at 1000 and 1200 °C are shown in Fig. 2. Magnetization measurements were performed on a vibrating-sample magnetometer (VSM) at a field strength of 5000 G in the temperature range 80–300 K. It may be seen that there is a clear difference in the transition temperature of the compounds processed at low and high temperatures. $T_c$ values are obtained as 140 and 160 K, respectively, for the samples annealed at 1000 and 1200 °C. $M$-$H$ measurements at 80 K gave the saturation moments as $0.69\mu_B$ and $0.79\mu_B$, respectively, for the low- and high-$T_c$ samples, at a field strength of 15 kG. Both compounds obey Curie-Weiss behavior above 230 K, and effective magnetic moments calculated from the inverse susceptibility in the paramagnetic region are also almost identical ($2.7\mu_B$), indicating that there is no difference either in the oxidation state of Ru or the composition.

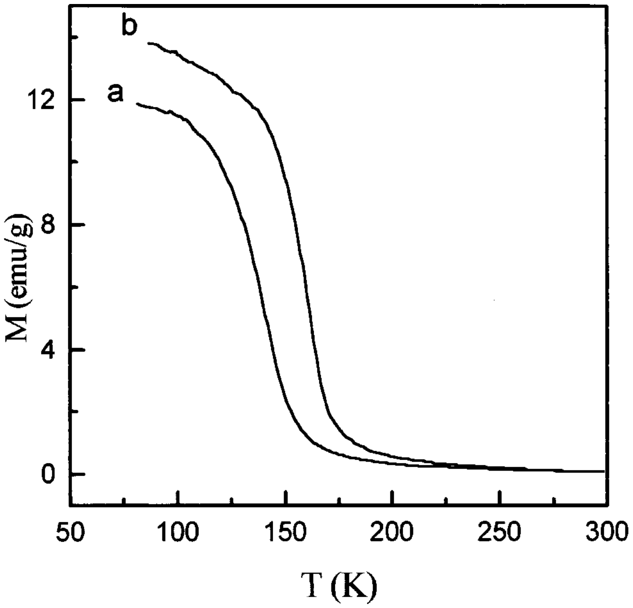

FIG. 2. Temperature dependence of the dc magnetization of $SrRuO_3$ annealed at (a) 1000 °C/12 h and (b) 1200 °C/12 h.

Resistivity measurements were performed on sintered pellets of the samples using the van der Pauw method. The temperature variation of resistance, $R(T)/R(300K)$, is shown in Fig. 3 for the samples heated at 1000 and 1200 °C. The shape of the curves is identical to that reported for the single-crystal or polycrystalline and thin-film samples.[13–16] A $T_c$ anomaly (due to spin-dependent scatter-

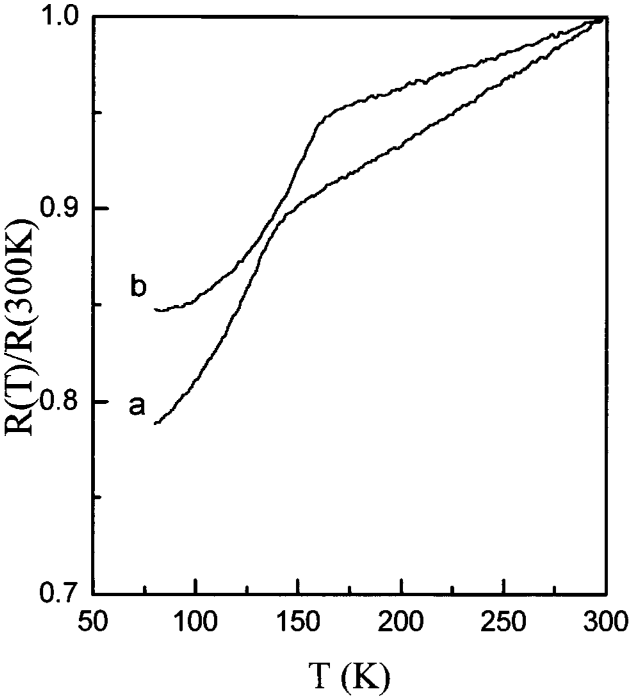

FIG. 3. Temperature dependence of the normalized electrical resistance of $SrRuO_3$ annealed at (a) 1000 °C/12 h and (b) 1200 °C/12 h.

ing of the conduction electrons) at 140 and 160 K, respectively, is observed on the resistivity curves of low- and high-temperature annealed samples.

The results from magnetic susceptibility and resistivity measurements on polycrystalline $SrRuO_3$ annealed at different temperatures indicate the existence of two different phases of the compound, a low-$T_c$ phase which is formed below 1100 °C and a high-$T_c$ phase formed above 1100 °C. The normal phase reported for $SrRuO_3$ is the one formed at high temperature. Both phases are stable at room temperature. The low-temperature phase transforms to the normal phase when heated above 1100 °C and the phase formation is not reversible. A small shoulder at 160 K in the ac susceptibility curve of the 1000 °C-heated sample (Fig. 1) indicates that the high-temperature phase, in minor amounts, is also formed at lower processing temperatures. The width of the ac susceptibility curves of the low-$T_c$ phase is larger than that of the high-$T_c$ phase. Identical behavior was reported for the transition widths of the temperature derivative of resistivity of thin films showing the two different $T_c$ values, the low $T_c$ film having a broader transition width.[16]

The reported crystal structure of $SrRuO_3$ is related to the $GdFeO_3$ structure, orthorhombic with lattice parameters $a=5.57$ Å, $b=5.53$ Å, and $c=7.85$ Å, and space group $Pbnm$.[18] The $RuO_6$ octahedra in the structure are slightly distorted and for the isostructural compound $CaRuO_3$ the $RuO_6$ octahedra is highly distorted. The two compounds show extreme magnetic behavior; $CaRuO_3$ orders antiferromagnetically below 110 K.[11,12] For the composition $Sr_{1-x}Ca_xRuO_3$, the ferromagnetic transition temperature decreases as the calcium concentration is increased.[15] Shikano *et al.*[19] have shown that the decrease in the Curie temperature of $SrRuO_3$ at high pressures is comparable to that observed in the calcium-substituted samples. Cho *et al.*[16] have commented that the reduced $T_c$ of very thin films is possibly due to distortion in the basal plane of $SrRuO_3$, the distortion occuring due to the lattice mismatch between the substrate and the compound. Thus it is possible that the two phases of $SrRuO_3$ will have slightly different lattice parameters. Expansion of the lattice parameter along the growth direction is also reported for thin films of $SrRuO_3$ showing the 140 K transition.[1]

Powder XRD patterns of both the low- and high-$T_c$ phases were found to be identical. However, the nature of the XRD peaks corresponding to the basal plane reflections (along ⟨110⟩) was found to be sensitive to the annealing conditions. The effect of annealing at various temperatures on the shape of one of these XRD peaks is shown in Fig. 4. The symmetric diffraction pattern shown for the high-temperature-heated sample corresponds to the (220) and (004) reflections of the high-$T_c$ phase. For the samples annealed below 1100 °C an additional weak reflection is observed as a shoulder at lower diffraction angles. As the processing temperature is increased, the reflection becomes more and more symmetric. The (220) and (004) reflections are observed at $d=1.96$ Å for the high-$T_c$ phase. The intense peak for the low-$T_c$ phase in this region is observed at the same $d$ value and the position of the shoulder corresponds to $d\simeq 1.98$ Å. If the reflection at $d=1.98$ Å is from the (220) plane, the lattice parameters $a$ and $b$ would be close to 5.6 Å, and are almost equal to that reported by Emo *et al.*[1] for thin films which show the 140 K transition (the pseudocubic lattice parameter $a_c$ along the growth direction $d_{110}=3.96$ Å compared to 3.93 Å for the high-$T_c$ phase, $a\simeq b=\sqrt{2}a_c$). This difference in the $d$ values of the two reflections ($d_{220}$ and $d_{004}$) indicate that the lattice parameters for the low-$T_c$ phase are different from that of the high-$T_c$ phase. The low-$T_c$ phase, thus, may correspond to another distorted orthorhombic structure.

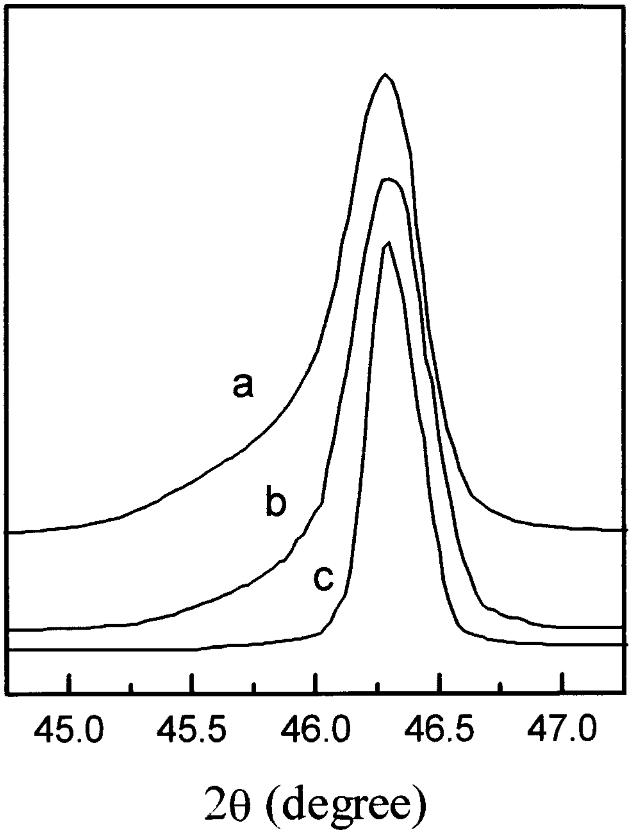

FIG. 4. Powder x-ray-diffraction patterns corresponding to the (220) and (004) reflections of $SrRuO_3$ annealed at (a) 1000 °C/12 h, (b) 1100 °C/12 h, and (c) 1200 °C/12 h.

It is concluded that $SrRuO_3$ exists in two different crystallographic forms, both having orthorhobmic crystal structure with a marginal difference in their lattice parameters as evidenced from powder XRD studies. Measurements of both the magnetic and electric properties showed two different magnetic ordering temperatures for these two forms. The observed difference in the shape of the ac magnetic susceptibility curves for the two phases may be an indication of a different type of magnetic ordering for the low-$T_c$ phase as against the ferromagnetic transition at 160 K for the high-$T_c$ phase.

## ACKNOWLEDGMENTS

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