Substitution at the Ru site in the itinerant ferromagnet SrRuO$_3$

Substitution at the Ru site in the itinerant ferromagnet SrRuO$_3$

Li Pi, A Maignan, R Retoux and B Raveau

Laboratoire CRISMAT, UMR 6508 Associée au CNRS, ISMRA et Université de Caen,
6 Boulevard du Maréchal Juin, 14050 Caen Cedex, France

Abstract
The doping of SrRuO$_3$ at the Ru sites with various cations was investigated,
controlling the oxygen composition in sealed tubes (STs). For these ST samples
SrRu$_{1-x}$M$_x$O$_3$, it is shown that doping with cations containing e$_g$ electrons,
M = Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{3+}, decreases T_C significantly from 166 K for
SrRuO$_3$ down to 105 K, whereas in contrast, doping with Cr^{3+} which contains
only t$_{2g}$ electrons increases T_C up to 188 K. All these samples exhibit negative
magnetoresistance, showing a maximum effect close to T_C. By synthesizing
the samples in air, it is shown that the resistivity of these oxides is significantly
modified, showing an upturn at low temperature and a disappearance of
the metal to metal transition, whereas the magnetic behaviour is practically
unchanged. This modification of the transport properties is believed to be due
to a variation of the oxygen stoichiometry at the grain boundary.

1. Introduction

The perovskite SrRuO$_3$ whose ferromagnetic properties and metallic character were evidenced
a long time ago [1] has recently been the object of a recrudescence of interest due to its
similarity with colossal-magnetoresistance manganites from which metallic ferromagnets were
also obtained [2]. This itinerant ferromagnet belongs to the class of bad metals generally called
strongly correlated systems and is remarkable for the anomalies of its transport and magnetic
properties [3–6] which are so far not completely explained.

The comparison of SrRuO$_3$ with the isostructural ruthenate CaRuO$_3$, which, in contrast,
exhibits antiferromagnetic exchange interaction to below 110 K [1], suggests that the lattice
distortions play a prominent role in the magnetic behaviour of this phase, as supported by
the thermal transport study of Sr$_{1-x}$Ca$_x$RuO$_3$ [7]. Thus, bearing in mind that the itinerant
ferromagnetism of SrRuO$_3$ originates from a narrow t$_{2g}$ Ru band [8], the bandwidth can be
dramatically modified by a small variation of the size of the A site cation (Sr or Ca), due
to the bending of the Ru–O–Ru bond. These considerations indicate that the substitution of
foreign elements at the Ru site should be of interest for understanding the properties of SrRuO$_3$,

since it may introduce local distortions, and also these elements may participate in the band formation, as recently shown for manganites [9, 10]. In this study, we report on the effect of the introduction of foreign species at the ruthenium sites, i.e. vacancies and M = Zn, Ni, Co, Cr, Mn. We show that the creation of Ru site vacancies, and the doping with cations containing e_g electrons (Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{3+}) significantly decreases T_C down to 100 K (to be compared to 160 K for $SrRuO_3$), whereas the doping with Cr^{3+} which contains only t_{2g} electrons increases T_C up to 185 K. The magnetoresistance properties of these oxides are also evidenced, showing a maximum effect close to T_C. Finally we demonstrate that the transport properties of these oxides are very sensitive to the atmosphere used for the synthesis (air or vacuum), due to variation of the oxygen stoichiometry at the grain boundary.

2. Experimental section

2.1. Chemical synthesis and elemental analysis

A first series of samples were prepared in sealed tubes (labelled STs) in order to control the oxygen stoichiometry fixed at 'O_3' in the perovskites $SrRu_{1-x}O_3$ and $SrRu_{1-x}M_xO_3$ with M = Zn, Ni, Co, Cr, Mn. The oxides SrO_2, SrO, RuO_2, and ZnO, NiO, Co_3O_4, Cr_2O_3, Mn_2O_3 were intimately mixed in appropriate proportions. The mixtures were pressed in the form of bars and heated up to 1250 °C at 200 °C h^{-1}, maintained at this temperature for 12 h, and finally cooled down at 200 °C h^{-1}.

To investigate the effect of oxygen stoichiometry upon the properties of the perovskites, a second series of syntheses were carried out in the same conditions but working in air instead of STs and using SrO_2 instead of SrO.

Energy dispersive spectroscopy (EDS) analysis was carried out for each sample (about 20 microcrystals were systematically analysed for each sample), using a Kevex analyser mounted on a JEOL 200 CX electron microscope.

Note that similar attempts were made for M = Ga, Fe, Cu, and Al. In these cases the EDS analysis indicated a very inhomogeneous cationic distribution, varying considerably from one grain to another, so these samples were not investigated further.

X-ray powder diffraction data were recorded at room temperature with a Philips Xpert Pro diffractometer using Cu Kα radiation. Patterns were recorded by step scanning with 0.02° 2θ increments between $10 < 2\theta < 100°$.

2.2. Magnetic and transport measurements

The resistivities of the samples was collected using a standard four-probe method in a PPMS Quantum Design system (5–400 K, 0–7 T). The temperature dependence of the magnetization $M(T)$ was measured with a vibrating sample magnetometer within 1.45 T from 4.2 to 300 K after a zero-field-cooling process. The magnetic field-dependent M-data were recorded with a dc SQUID magnetometer (0–5 T, 5–300 K).

3. Results and discussion

3.1. ST-synthesized samples

For the above experimental conditions, the EDS analyses performed on numerous crystals show a great homogeneity of the cationic distribution for each of the samples with the nominal composition $SrRu_{0.9}M_{0.1}O_3$ with M = Zn, Ni, Co, Cr, Mn. These analytical results, listed in

Table 1. Cationic composition and cell parameters of the sealed tube (ST) synthesized SrRu$_{0.9}$M$_{0.1}$O$_3$ oxides.

M	Cationic composition (EDS determined)	a (Å)	b (Å)	c (Å)	V (Å^3)
Cr	Sr$_{1.01}$Ru$_{0.90}$Cr$_{0.09}$	5.6114(3)	7.8320(5)	5.5241(3)	240.61(2)
Mn	Sr$_{0.99}$Ru$_{0.90}$Mn$_{0.11}$	5.5682(3)	7.8380(5)	5.5300(3)	241.35(2)
Co	Sr$_{1.03}$Ru$_{0.87}$Co$_{0.10}$	5.5716(3)	7.8469(5)	5.5351(3)	241.99(2)
Ni	Sr$_{0.98}$Ru$_{0.93}$Ni$_{0.09}$	5.5702(4)	7.8468(7)	5.5348(4)	241.91(4)
Zn	Sr$_{0.99}$Ru$_{0.89}$Zn$_{0.12}$	5.5763(5)	7.8543(8)	5.5300(5)	242.64(5)

table 1 show that the actual cationic composition is close to the nominal one within the limits of the experimental errors.

The x-ray diffraction patterns recorded for all these perovskites show their purity in agreement with the EDS measurements: in a first step, the Rietveldt profile refinements of these patterns using structure parameters (from [11, 12]) confirm their purity. For the sake of comparison, only the cell parameters were refined using the Fullprof program [14], leading to reliability factors R_p and R_{wp} always smaller than 13 and 20% respectively.

The first issue that has not been addressed to date concerns the influence of non-stoichiometry upon the magnetic and transport properties of 'SrRuO$_3$'. The $M(T)$ curve of a sample of stoichiometric composition SrRuO$_3$ (figure 1(a)) evidences a Curie temperature of 166 K in good agreement with the results previously observed ($T_C = 160$ K) for single crystal [7] and ceramics [1]. Here we define the Curie temperature as the peak temperature on the curves of the derivatives of $M(T)$ (table 2). Attempts to modify the strontium stoichiometry were unsuccessful: for instance, for a nominal composition Sr$_{0.9}$RuO$_3$ the sample was not pure. In contrast, the introduction of ruthenium vacancies in the perovskite structure modifies the magnetization behaviour significantly (figure 1(a)), leading for SrRu$_{0.95}$O$_3$ to a smaller $T_C = 151$ K.

Thus, the creation of vacancies in the perovskite matrix, according to the formula SrRu$_{1-x}$O$_3$, induces a significant decrease of T_C. Such a low T_C has never been observed to date in bulk samples of SrRuO$_3$, whereas a T_C of 150 K was evidenced in thin films [4], which may be due to either a Ru deficiency or a strain effect of the substrate.

The evolution of the zero-field resistivity versus temperature (figure 1(b)) shows a metallic behaviour involving two domains, corresponding to magnetic and non-magnetic resistivity below and above T_C, respectively, as previously described by Kats et al [6]. Note that the temperature T'_C corresponding to the rupture of the slope of the curve is larger than T_C which is obtained from magnetic measurement. This suggests that T'_C indicates the beginning of a magnetic transition. On the derivative-of-$\rho(T)$ curves the peak temperatures coincide with T_C at the limit of the errors.

The magnetic curves of the ruthenates SrRu$_{0.9}$M$_{0.1}$O$_3$ (figure 2) show that for M = Zn, Ni, Co, Mn the Curie temperature is significantly decreased, T_C ranging from 135 to 105 K depending on the nature of the doping cation, whereas remarkably for M = Cr, T_C is increased to 188 K. Bearing in mind that the narrow band of SrRuO$_3$ is based on the $(t_{2g})^4$ configuration of Ru^{4+}, the remarkable behaviour of chromium may be due to its $(t_{2g})^3e_g^0$ electronic configuration which favours hybridization with the t_{2g} band of Ru^{4+} and contributes to the broadening of the bandwidth. In contrast, all the other cations exhibit e_g electrons (Zn^{2+}(e_g^4), Ni^{2+}(e_g^2), Co^{2+} (e_g^1 or e_g^2), Mn^{3+} (e_g^1 HS)) and may lead to a decrease of the bandwidth. The participation in the band formation is certainly not the only factor responsible for this evolution. The size of the doping cation may also play a role: Zn^{2+}, Ni^{2+}, Co^{2+}, and Mn^{3+} have indeed a larger size

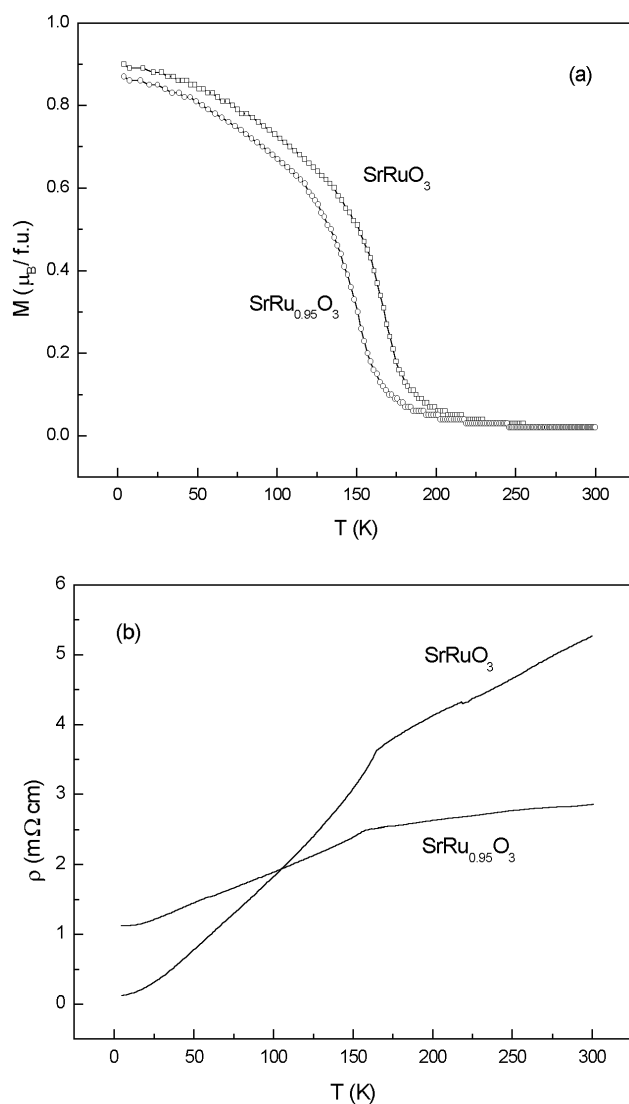**Figure 1.** (a) The temperature dependence of the magnetization of $SrRuO_3$ and $SrRu_{0.95}O_3$. (b) The temperature dependence of the resistivity of $SrRuO_3$ and $SrRu_{0.95}O_3$.

than Ru^{4+} and may induce local distortions which would contribute to the narrowing of the t_{2g} band, in contrast to Cr^{3+} whose size is very close to that of Ru^{4+} (0.615 against 0.62 Å). In any case, whatever the nature of the dopant, a valency effect is introduced due to the substitution of a lower-valency cation for Ru^{4+}, which generates Ru^{5+} species. This effect may contribute to the decrease of T_C, as shown for $SrRu_{0.95}^{+4.21}O_3$, whose T_C (151 K) is 15 K lower than for the stoichiometric $SrRu^{4+}O_3$.

The zero-field resistivity registered versus temperature for all the $SrRu_{0.9}M_{0.1}O_3$ oxides (figure 3) shows a great similarity with that of $SrRuO_3$, attesting to the metallic character of the materials over the whole temperature range. The two-slope system is characteristic of the magnetic and non-magnetic resistivity below and above T_C, respectively. It is worth pointing out that, except for nickel, the resistivity of the oxides $SrRu_{0.95}O_3$ and $SrRu_{0.9}M_{0.1}O_3$ at 5 K is
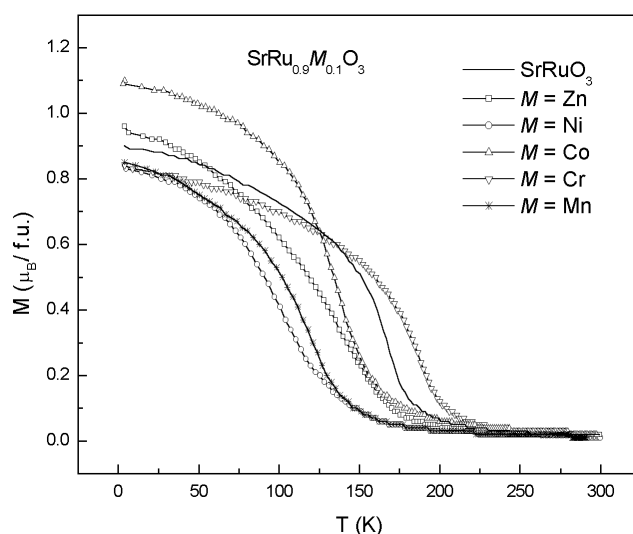
Figure 2. The temperature dependence of the magnetization of doped samples SrRu$_{0.9}$M$_{0.1}$O$_3$.

Table 2. Resistivity values and Curie temperatures of ST-SrRu$_{1-x}$M$_x$O$_3$ ruthenates deduced from the resistivity and magnetization curves.

Composition	ρ(5 K) (mΩ cm)	ρ(300 K) (mΩ cm)	$\rho(T_C)$ (mΩ cm)	T_C (K)
SrRuO$_3$	0.1	5.0	3.65	166
SrRu$_{0.95}$O$_3$	1.2	2.8	2.4	151
SrRu$_{0.9}$Zn$_{0.1}$O$_3$	0.98	2.1	1.6	138
SrRu$_{0.9}$Ni$_{0.1}$O$_3$	7.6	1.3	9.6	105
SrRu$_{0.9}$Co$_{0.1}$O$_3$	1.2	3.7	2.65	142
SrRu$_{0.9}$Cr$_{0.1}$O$_3$	2.0	4.5	3.8	188
SrRu$_{0.9}$Mn$_{0.1}$O$_3$	1.5	4.0	2.6	121

generally about one order larger than for SrRuO$_3$ and the resistivity at 300 K is slightly smaller than that of SrRuO$_3$ as shown in table 2. The larger magnitude of ρ at 5 K can be understood as the result of the large number of scattering centres in the Ru array in the case of substituted ruthenates which increase the residual resistivity. The resistivity at the transition temperature is generally smaller than that of SrRuO$_3$, except for chromium which exhibits a slightly higher resistivity (3.8×10^{-3} against 3.65×10^{-3} Ω cm) but at a higher T_C (188 instead of 166 K). In contrast, the nickel phase exhibits significantly higher values of the resistivity. These rather close values of the resistivity compared to those of SrRuO$_3$ demonstrate that the substitutions at the Ru sites do not significantly affect the room temperature resistivity, although significant T_C changes can be induced.

The $\rho(T)$ curves registered under 0 and 7 T (figure 3) show that all the samples are magnetoresistive. The observed negative magnetoresistance is weak, but more importantly it appears clearly that the maximum value of the magnetoresistance is obtained close to T_C. Such an effect is more clearly evidenced from the $\rho(H)$ curves, as shown for instance for the Co-doped sample (figure 4) which shows that the magnetoresistance under 7 T increases from 3.7% at 5 K to 9% at $T_C = 140$ K and decreases again to $\sim$0 at 250–300 K. These values of magnetoresistance are typical of the data reported for SrRuO$_3$ [4].
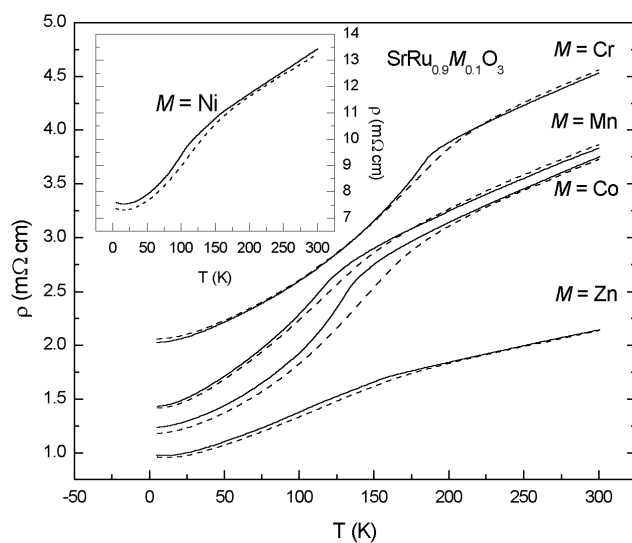
Figure 3. ρ–T curves of ST-synthesized $SrRu_{0.9}M_{0.1}O_3$. The dashed curves represent the data registered under a 7 T magnetic field.
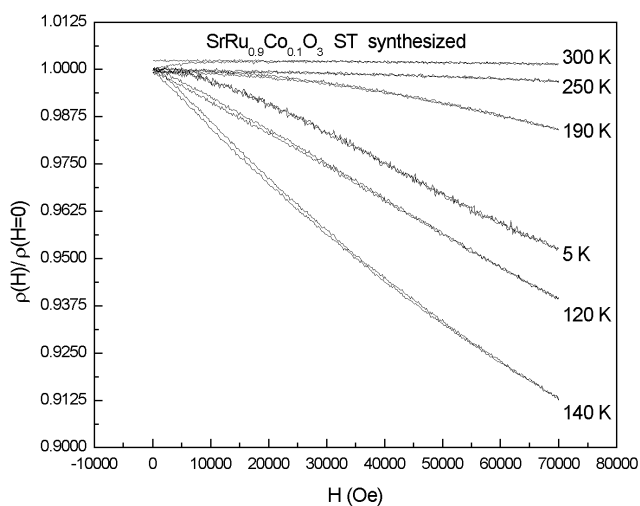

Figure 4. The field dependence of the resistivity of ST-synthesized $SrRu_{0.9}Co_{0.1}O_3$.

A last point concerns the upturn in the resistivity observed on the $\rho(T)$ curves below T_C, which tends to generate a minimum at very low temperature close to 5–10 K. This phenomenon is more clearly visible for the Ni-substituted phase which exhibits a minimum around 20 K (figure 3). Such an effect is reminiscent of the low-temperature upturn commonly observed in $SrRuO_3$ thin films [4] and helium-irradiated films [13], and which was interpreted by the authors as a weak-localization contribution, associated with an electron–electron interaction, intrinsic to $SrRuO_3$. Bearing in mind these results, samples of $SrRu_{0.9}M_{0.1}O_3$ perovskites were prepared in air, instead of evacuated ampoules, but in the same experimental conditions.
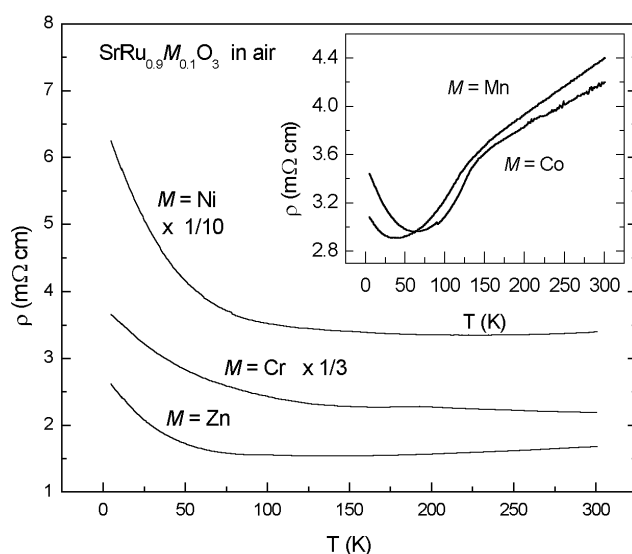
Figure 5. ρ–T curves of air-synthesized SrRu$_{0.9}$M$_{0.1}$O$_3$.

3.2. Air-synthesized samples

For all of these samples (figure 5), a clear upturn of the resistivity is observed at low temperature, as illustrated for M = Mn and Co. But more importantly the $\rho(T)$ curve is dramatically modified in other cases, leading to a disappearance of the 'two-slope' aspect of the resistivity, as shown for M = Zn, Ni and Cr, for which a resistivity minimum below T_C becomes hardly visible. In contrast, the magnetic behaviour of these samples is not dramatically modified with respect to the ST-synthesized samples: T_C is only moderately decreased in the case of Ni (96 instead of 105 K), Co (123 instead of 142 K), Cr (177 instead of 188 K), and Mn (110 instead of 121 K), the largest decrease being obtained for Zn (89 instead of 138 K). And inspection of the $M(H)$ loops collected at 5 K shows that the behaviours of ST- and air-synthesized samples are almost the same. The only difference is that the coercive field of the air-synthesized samples is larger than that of ST-synthesized samples (as an example, the curves for M = Co are shown in figure 6).

These results suggest that the bulk physical properties of these materials are not significantly modified by the thermal treatment, but that the surface of the grains is sensitive to oxidization, so the transport properties are changed at the grain boundaries. In order to check this point, the ST-synthesized perovskites have been annealed at 600 °C in air, and the air-synthesized perovskites have been annealed in ST at the same temperature. The $\rho(T)$ curves of these annealed samples show that for the air-synthesized samples annealed in vacuum, the upturn disappears, the curve becoming similar to that for the ST-synthesized sample, and for the ST-synthesized samples annealed in air, the upturn at low temperature appears, the curve becoming similar to that of the air-synthesized sample. In contrast, the magnetic behaviour is not significantly modified by the annealing. Clearly, the modification of the $\rho(T)$ curves in the air-synthesized sample at low temperature, especially the resistivity upturn, originates from oxidization at the grain boundary, the grains of the ceramics remaining unchanged. Moreover, for the air-synthesized samples, the ferromagnetic domain walls at the grain boundary are probably more pinned because of the large number of defects, which cause a larger coercive field.
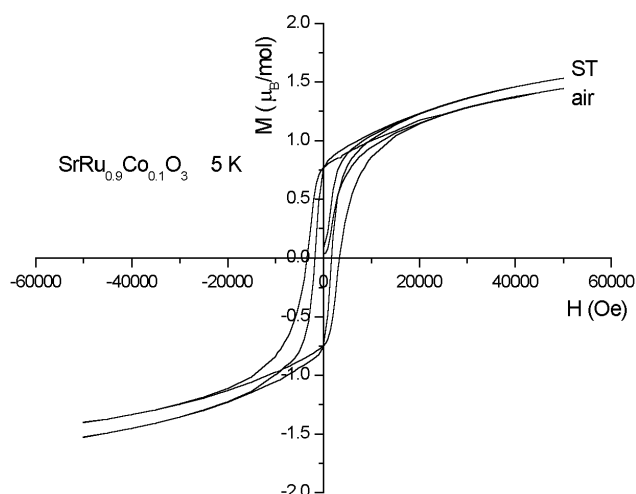
Figure 6. The field dependence of the magnetization of ST- and air-synthesized $SrRu_{0.9}Co_{0.1}O_3$.

4. Conclusions

In conclusion, this study of the doping at the manganese sites of $SrRuO_3$ shows unique behaviour of Cr^{3+}, which has been found to be the only cation that increases the T_C of this compound. Although the origin of this peculiar behaviour is not, to date, fully understood, it is most probable that Cr^{3+}, due to its size being close to that of Ru^{4+} and to its e_g^0 electronic configuration, favours the hybridization with the t_{2g} band of Ru^{4+} and contributes to the broadening of the bandwidth, in contrast to other cations which are bigger and contain e_g electrons. The sensitivity of the transport properties of these ceramics to the atmosphere during synthesis, probably due to oxidization phenomena at the grain boundary, needs further investigation to provide an understanding.

References

[1] Longo J M, Raccah P M and Goodenough J B 1968 *J. Appl. Phys.* **39** 1327
[2] Rao C N R and Raveau B (ed) 1998 *Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides* (Singapore: World Scientific)
[3] Klein L, Dodge J S, Ahn C H, Snyder G J, Geballe T H, Beasley M R and Kapitulnik A 1996 *Phys. Rev. Lett.* **77** 2774
[4] Klein L, Dodge J S, Ahn C H, Reiner J W, Mieville L, Geballe T H, Beasley M R and Kapitulnik A 1996 *J. Phys.: Condens. Matter* **9** 10 111
[5] Kostic P 1998 *Phys. Rev. Lett.* **81** 2498
[6] Kats Y, Klein L, Reiner J W, Geballe T H, Beasley M R and Kapitulnik A 2001 *Phys. Rev.* B **63** 54 435
[7] Shepard M, Henning P F, Cao G and Crow J E 1998 *J. Appl. Phys.* **83** 6989
[8] Dodge J S, Kulatov E, Ohta H, Uspenskii Y and Halilov S 1999 *Phys. Rev.* B **60** R6987
[9] Martin C, Maignan A, Hervieu M, Autret C, Raveau B and Khomskii D I 2001 *Phys. Rev.* B **63** 174402
[10] Maignan A, Martin C, Hervieu M and Raveau B 2001 *Solid State Commun.* **117** 377
[11] Jones C W, Battle P D, Lightfoot P and Harrison W T 1989 *Acta Crystallogr.* C **45** 365
[12] Shikano M, Huang T K, Inaguma Y, Itoh M and Nakamura T 1994 *Solid State Commun.* **90** 115
[13] Lopez de la Torre M A, Sefrioui Z, Arias D, Varela M, Villegas J E, Ballestros C, Leon C and Santamaria J 2001 *Phys. Rev.* B **63** 52 403
[14] Rodriguez-Carjaval J 1993 *Physica* B **192** 55