Structural and Magnetic Properties of Ni doped $SrRuO_3$

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Introduction

$SrRuO_3$ has been the subject of numerous studies since it is the only ferromagnetic metal among 4d transition metal oxide. It has a Curie temperature T_c ~ 165K. [1] It has been established that the Curie temperature is sensitive to chemical substitution and there are reports that Ru-site substitution with 3d metals including Mn^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} significantly decrease T_c. Detailed structural studies have been reported for the Mn and Cu doped oxides and these show a transition to a tetragonal structure as a consequence of orbital ordering associated with the Jahn-Teller cation. Little is known of the analogous Ni doped materials.

Experimental

Polycrystalline samples of $SrRu_{1-x}Ni_xO_3$ were prepared by standard solid-state reaction methods from $SrCO_3$, NiO and Ru metal. Powder neutron diffraction data were recorded on the Echidna diffractometer at ANSTO' s OPAL reactor. Magnetic Properties were measured using a Quantum Design PPMS. X-ray absorption near edge structure data were obtained at beamline 16A1 at the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. Variable temperature powder X-ray data were collected from room temperature to 760^{0}C with 10 ^{0}C step intervals on a PANalytical Xpert-Pro diffractometer.

Results

Powder X-ray and neutron data show that the oxides in the series $SrRu_{1-x}Ni_xO_3$ display an orthorhombic structure in space group Pnma for $x \leq 0.2$.

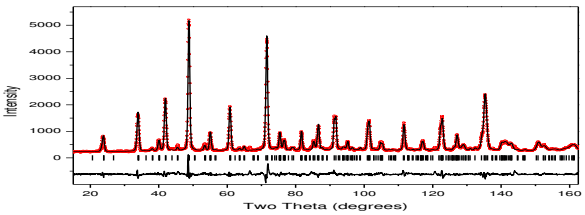


Figure 1: Observed, calculated, and difference neutron diffraction profile recorded at room temperature with λ= 1.6220 Å for $SrRu_{0.8}Ni_{0.2}O_3$.

Table 1: The lattice parameters and atomic positions for $SrRu_{0.8}Ni_{0.2}O_3$ with space group Pnma at room temperature. These value were obtained from the Rietveld refinement of neutron data.

a (Å) : 5.53753	b (Å) :7.84313	c (Å): 5.57156		
	x	y	z	U_{iso} (Å)^2
Sr	0.0094(10)	0.2500(0)	0.5017(6)	2.07
Ru/Ni	0	0	0	1.57
O1	-0.0052(12)	0.25(0)	-0.0480(6)	2.33
O2	0.2709	0.2145(26)	0.23076(35)	2.11
R_p (%) 5.56	R_{wp} (%) 7.49	χ^2 2.462		

Table 2: Selected bond distances in $SrRu_{0.8}Ni_{0.2}O_3$ obtained from neutron diffraction data refinements

Bond	Length (Å)
Sr–O(1)	2.513(4)
Sr–O(1)	2.692(5)
Sr–O(1)	2.871(5)
Sr–O(1)	3.062(4)
Sr–O(2) x 2	2.5754(31)
Sr–O(2) x 2	2.7445(31)
Sr–O(2) x 2	2.7671(29)
Sr–O(2) x 2	3.0365(29)
Ru/Ni–O(1) x 2	1.9795(4)
Ru/Ni–O(2)	1.9812(19)
Ru/Ni–O(2)	1.9745(19)

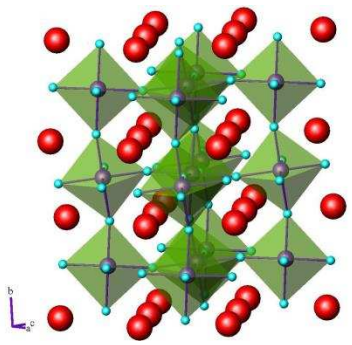


Figure 2: View of the crystal structure of the orthorhombic form of $SrRu_{0.8}Ni_{0.2}O_3$

As shown in Table 2 and Figure 2, the six M-O bond distances in $SrRu_{0.8}Ni_{0.2}O_3$ are all approximately equal and there is no evidence for a measurable tetragonal distortion of the MO_6 octahedra. This contrasts the small Jahn-Teller distortion of the octahedra seen in $SrRu_{0.8}Cu_{0.2}O_3$ where the axial M-O distance is 0.02 Å longer than equatorial distance. The structure shows cooperative tilting of the corner sharing MO_6 octahedra.

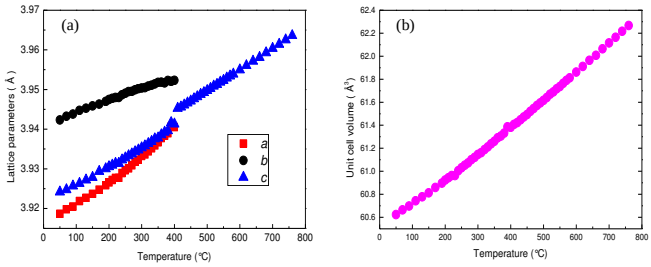
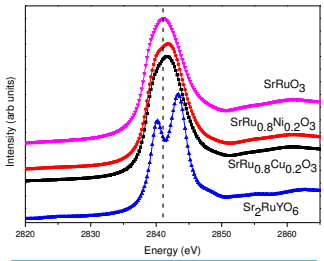


Figure 3: Temperature dependence of the (a) normalized lattice parameters and (b) unit cell volumes for sample $SrRu_{0.8}Ni_{0.2}O_3$, from X-ray diffraction measurements.

Variable temperature powder X-ray diffraction measurements for $SrRu_{0.8}Ni_{0.2}O_3$ illustrated in Figure 3 show:

(1) Abrupt first order Pnma − Pm3m phase transition near 400 ^{0}C.
(2) No evidence for tetragonal intermediate phase. This is in contrast to undoped $SrRuO_3$ that shows the sequence Pnma − Imma − *I 4/mcm* − *Pm3m*.
(3) Normal thermal expansion with no obvious discontinuity at the Pnma − *Pm3m* transition.



The figure also shows the spectra for the Ru^{4+} standard $SrRuO_3$ and Ru^{5+} standard Sr_2RuYO_6. The shift to the higher energy in the Ni and Cu doped samples is indicated by the dotted line and demonstrate partial oxidation of the Ru.

Figure 4. Ruthenium L-edge X-ray absorption spectra for $SrRu_{0.8}Cu_{0.2}O_3$ and $SrRu_{0.8}Ni_{0.2}O_3$.

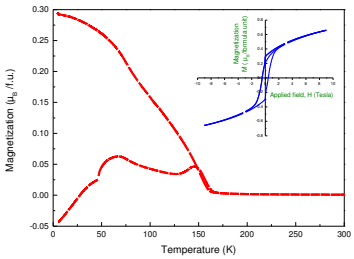


Figure 5. ZFC and FC susceptibility measured at 0.1 T and (inset) isothermal magnetization measured at 5K for $SrRu_{0.8}Ni_{0.2}O_3$

That the sample is ferromagnetic is evident from the divergence in the field cooled and zero-field cooled susceptibilities. The sample shows a broad ferromagnetic transition, with a Curie Temperature of 140.5 K. The broadness of the transition is thought to be due to the disorder induced by doping with Ni. The drop at low temperatures is an artefact of the remnant field in the PPMS. The magnetic moment estimated from a Curie-Weiss fit is 2.52μB. This is in reasonable agreement with the value estimated for the mixed $Ru^{4+}_{0.4}Ru^{5+}_{0.4}Ni^{2+}_{0.2}$ cation distribution of 2.6 μB. The saturation moment estimated from the low temperature magnetisation is 0.6 μ_B/formula unit.

Conclusion

We show $SrRu_{0.8}Ni_{0.2}O_3$ is isostructural with $SrRuO_3$, both being orhorhombic in Pnma, and that Ni doping induces partial oxidation of the Ru from Ru^{4+} to Ru^{5+}. This doping reduces the Curie temperature to 140K compared to 165K in pure $SrRuO_3$. Unexpectedly, heating $SrRu_{0.8}Ni_{0.2}O_3$ induces a first order Pnma − *Pm3m* transition.

References:
[1] J.M. Longo, P. Raccah and J.B. Goodenough 1968 J. Appl. Phys. **39** 1327
[2] B.J. Kennedy, B.A. Hunter 1998 Phys. Rev. B **58**, 653–658

Acknowledgments
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