JOURNAL OF
Materials
CHEMISTRY
Communication

The synthesis and structure of $Tl(Sr_{1.4}La_{2.6})Ni_2O_9$; a direct structural analogue of a superconducting cuprate

Christopher S. Knee and Mark T. Weller*

Department of Chemistry, The University of Southampton, Southampton, UK SO17 1BJ. E-mail: mtw@soton.ac.uk

Received 21st October 1998

The nickelate $Tl(Sr_{1.4}La_{2.6})Ni_2O_9$, synthesised by the reaction of Tl_2O_3, La_2O_3 and $Sr_2Ni_2O_5$, is isostructural with the equivalent superconducting cuprate phase, consisting of layers of apex-sharing, stoichiometric NiO_6 octahedra separated by a TlO layer.

The structural chemistry of complex nickelates has recently regained impetus from its relationship to that of cuprates exhibiting high temperature superconductivity. One area of particular interest has been complex nickel oxides adopting the perovskite and K_2NiF_4 structures *e.g.* $La_{2-x}Sr_xMO_{4\pm\delta}$ (M = Ni, Cu);[1,2] superconductivity has been claimed in the nickelate but this has never been fully substantiated.[2] A few other phases exist with structural analogies in copper and nickel chemistry for example Li_2MO_2[3,4] and '$BaMO_2$'.[5,6] These structural analogues derive from the ability of both copper(II) and nickel(II) to adopt four- (square planar), five- (square pyramidal) and six-fold (octahedron based) coordinations to oxygen though the five- and six-fold geometries are normally more distorted for copper due to the Jahn–Teller effect. More recently the synthesis of $TlSr_2NiO_{4+\delta}$[7,8] has further demonstrated the ability of nickelates to adopt similar structures to cuprates, though in this case the oxygen stoichiometries and distributions differ and no complete NiO_2 layers exist. In this communication we report the synthesis and characterisation of a new layered complex nickel oxide, $Tl(Sr_2La_2)Ni_2O_9$, containing complete NiO_2 layers, which is a direct analogue of a high temperature superconducting phase, $Tl(Ba_{2-x}La_{2+x})Cu_2O_9$, $T_c = 35$ K.[9]

Tl_2O_3, La_2O_3, and $Sr_2Ni_2O_5$, synthesised following the literature method,[10] were mixed in the ratio 1 : 1 : 1 and ground thoroughly. The reactants were pressed into 13 mm diameter pellets under *ca.* 10 tonne cm^{-2} and the pellets so formed sealed inside a gold tube. The capsule was then slowly ramped to 900 °C and fired for 5 h and then allowed to furnace cool. The resulting black powder was examined using a Siemens D5000 diffractometer ($CuK\alpha_1$ radiation) and the pattern obtained was indexed on a tetragonal unit cell with $a \approx 3.8$, $c \approx 30.0$ Å. Weak lines ($I/I_0 < 5\%$), that did not index using this method, were identified as resulting from the impurity phase $Tl_2Sr_4O_7$.

The structure of $Tl(Sr_2La_2)Ni_2O_9$ was refined from X-ray powder diffraction data using the GSAS package.[11] Data were collected in the 2θ range 17–117° over a 17 h period with a step size of 0.02°. The starting structural model was taken from that of $Tl(Ba_{2-x}La_{2+x})Cu_2O_9$,[9] in the space group *I*4/*mmm*. Initial stages of the refinement placed all atoms on these special sites at full occupancy and proceeded with the variation of global parameters such as background and peak profile coefficients and the lattice constants. The contribution from the $Tl_2Sr_4O_7$ impurity was introduced as an additional phase using literature data,[12] and fitted with the refinement of cell constants and phase fraction only. The isotropic temperature factors of the atoms in the main phase were then introduced, and, along with the refinement of atomic positions, resulted in the expected improvement in the least-squares fit. The temperature factor for the thallium atom refined to a larger than expected value and this atom was therefore placed on a new 4-fold site (x,y,0) at quarter occupancy. This displacement refined steadily with $x = y \approx 0.052$, and a concomitant reduction in the thermal parameter to a reasonable value. Attention was then focused on the mixed Sr/La sites, in particular the (0,0,0.2) site, which had an unreasonably low temperature factor. The fractional occupancies of the La and Sr sites were reciprocally linked and allowed to vary from the initial 50 : 50 ratio. The site was found to favour a marked increase in the La content to around 0.8 and the thermal parameter now refined to a larger, more sensible, value. The occupancy of the other Sr/La site (0,0,0.08) was probed in this way however the variation was negligible and the site occupancy factors maintained at 0.5/0.5. The final refined structural parameters are summarised in Table 1 and derived bond lengths given in Table 2. The final fit to the profile is shown in Fig. 1, and Fig. 2 shows the structure of $Tl(Sr_2La_2)Ni_2O_9$.

The refined stoichiometry of $Tl(Sr_{1.4}La_{2.6})Ni_2O_9$ gives a nickel oxidation state of +2.2 with full occupancy of the oxygen sites; no evidence was found in this work of site deficiencies and all refined oxygen atom temperature factors were reasonable. The nickel oxidation state is also dependent on the La : Sr ratio and the slight strontium deficiency with respect to the starting stoichiometry is consistent with the observation of the small level of $Tl_2Sr_4O_7$ impurity. A higher level of lanthanum on the A-sites is also observed in the reported isostructural cuprate, $Tl(Ba_{1.6}La_{2.4})Cu_2O_9$.[9] The effects of different starting ratios of Tl, La and Sr are currently

Table 1 Final refined atomic coordinates for $Tl(Sr_{1.4}La_{2.6})Ni_2O_9$ (e.s.d.s are given in parentheses)

Atom	Site	x	y	z	B/Å^2	n
Tl	8h	0.0517(2)	0.0517(2)	0.0	1.50(18)	0.25
La(1)	4e	0.5	0.5	0.0845(1)	1.82(9)	0.5
Sr(1)	4e	0.5	0.5	0.0845(1)	1.82(9)	0.5
La(2)	4e	0.5	0.5	0.2032(1)	1.19(7)	0.8
Sr(2)	4e	0.5	0.5	0.2032(1)	1.19(7)	0.2
Ni	4e	0.0	0.0	0.1466(3)	1.20(13)	1.0
O(1)	2b	0.5	0.5	0.0	4.1(1)	1.0
O(2)	4e	0.0	0.0	0.0721(8)	3.0(8)	1.0
O(3)	8g	0.5	0.0	0.1439(6)	2.3(4)	1.0
O(4)	4e	0.0	0.0	0.2178(7)	0.5(6)	1.0

Space group *I*4/*mmm*; $a = 3.8062(1)$, $c = 30.0854(6)$ Å; $R_F = 8.50\%$, $\chi^2 = 1.76$.

Table 2 Selected derived bond lengths

Tl–O(1)	2.970(9)	La(2)–O(3) × 4	2.610(1)
Tl–O(1) × 2	2.706(1)	La(2)–O(4) × 5	2.727(4)
Tl–O(1)	2.413(9)	La(2)–O(4) × 1	2.377(8)
Tl–O(2) × 2	2.188(3)	Ni–O(3) × 4	1.905(1)
La(1)–O(1)	2.543(4)	Ni–O(2)	2.24(3)
La(1)–O(2) × 4	2.717(4)	Ni–O(4)	2.14(2)
La(1)–O(3) × 4	2.610(2)		

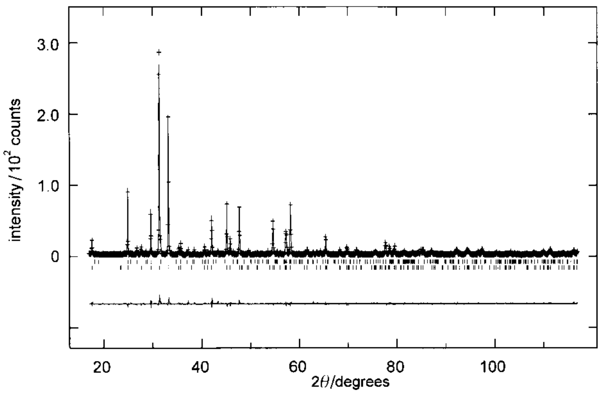

Fig. 1 Final profile fit for $Tl(Sr_{1.4}La_{2.6})Ni_2O_9$. Crosses mark observed intensities, upper continuous line the calculated profile, lower continuous line the difference. Reflections are shown with tick marks for $Tl(Sr_{1.4}La_{2.6})Ni_2O_9$ (lower) and $Tl_2Sr_4O_7$ (upper).

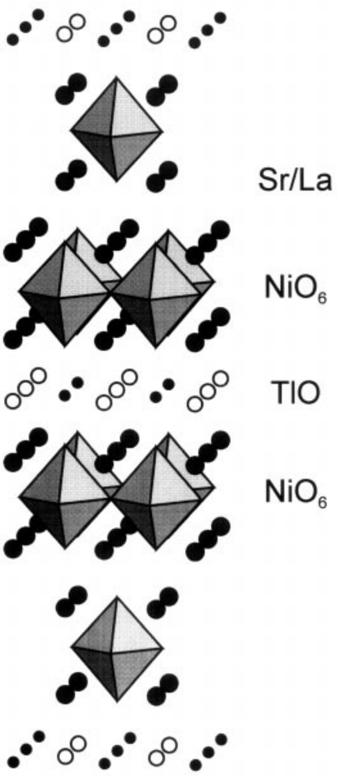

Fig. 2 Structure of $Tl(Sr_2La_2)Ni_2O_9$. The nickel coordination is shown as octahedra, thallium ions are shown as small dark spheres, Sr/La ions as large dark spheres and oxygen as medium light spheres.

being probed but absolute phase purity is difficult to achieve due to loss of thallium from the reactant mixture.

The nickel coordination is an elongated NiO_6 octahedron with an in-plane distance of 1.905(1) Å and two apical bonds of 2.24(3) and 2.14(2) Å. These units are linked by sharing equatorial apices to form infinite layers in the *ab*-plane of stoichiometry NiO_2. There is no evidence of oxygen vacancies in these planes, in contrast to the structurally related 1201 phase $TlSr_2NiO_{4+\delta}$[7,8] in which the asymmetric distribution of oxide vacancies leads to an orthorhombic structure. A TlO layer separates the NiO_6 octahedra. The thallium coordination is complicated by the disorder of the thallium atom, which is a common feature of such single layer thallium materials.[13] The average thallium environment may be most simply viewed as distorted octahedral. The Sr/La sites exhibit 9-fold coordination and the bond lengths are similar to those found in the $(La,Sr)_2NiO_4$ phases with the K_2NiF_4 type structure. Comparison of the nickel and copper coordination in the materials $Tl(Sr_{1.4}La_{2.6})Ni_2O_9$ and $Tl(Ba_{1.6}La_{2.4})Cu_2O_9$ reveal near identical M–O in-plane distances of 1.905(1) and 1.906(1) Å respectively. The apical metal–oxygen environment if more distorted for the cuprate, with two quite different apical distances of 2.63(3) and 2.25(4) Å compared to the more regular 2.24(3) and 2.14(2) Å observed for the nickelate, which may be attributed to Jahn–Teller effects.

The extension of the series of compounds $Tl(Sr_{2-x}Ln_{2+x})Ni_2O_9$, to Ln = Nd–Gd, is being undertaken. The materials show the expected reduction in lattice parameters, *i.e.* for $Tl(Sr_2Gd_2)Ni_2O_9$, $a = 3.7681(1)$, $c = 29.4012(9)$ Å. In conclusion the end member of a new family of layered nickel oxides $Tl(Sr_{1.4}Ln_{2.6})Ni_2O_9$, Ln = La has been synthesised and characterised using powder X-ray diffraction. The electronic and magnetic properties of this material and the structural characterisation of the full range of lanthanide derivatives will be reported in a full paper.

We thank the EPSRC for a studentship for C.S.K.

Notes and references

1 M. James and J. P. Attfield, *J. Mater. Chem.*, 1996, **6**, 57.

2 Z. Kakol, J. Spalek and J. M. Honig, *J. Solid State Chem.*, 1989, **79**, 288.

3 H. Rieck and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1972, **392**, 193.

4 W. Losert and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1970, **379**, 234.

5 M. A. G. Aranda and J. P. Attfield, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1454.

6 R. Gottscall and R. Scollhorn, *Solid State Ionics*, 1993, **59**, 93.

7 C. S. Knee and M. T. Weller, *J. Mater. Chem.*, 1996, **6**, 1449.

8 C. S. Knee and M. T. Weller, The structure of $TlSr_2NiO_{4+\delta}$ by high-resolution powder neutron diffraction, *J. Solid State Chem.*, submitted.

9 C. Martin, A. Maignan, M. Huve, M. Hervieu, C. Michel and B. Raveau, *Physica C*, 1991, **179**, 1.

10 Y. Takeda, T. Hashino, H. Miyamoto, F. Kanamaru, S. Kume and M. Koizumi, *J. Inorg. Nucl. Chem. Lett.*, 1972, **34**, 1599.

11 A. C. Larson and R. B. Von Dreele, MS-H805, Los Alamos National Laboratory, Los Alamos, NM, 87545.

12 R. von Schenck and H. Mueller-Buschbaum, *Z. Anorg. Allg. Chem.*, 1973, **396**, 113.

13 Morosin, E. L. Venturini and D. S. Ginley, *Physica C*, 1991, **183**, 90.

Communication 8/08182D