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Charge-doped nickel oxide, $Y_{1.90}Ca_{0.10}BaNiO_5$

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Ni–O) = 0.001 Å
Disorder in main residue
R factor = 0.016
wR factor = 0.042
Data-to-parameter ratio = 18.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The crystal structure of orthorhombic yttrium calcium barium nickel pentaoxide, $Y_{1.90}Ca_{0.10}BaNiO_5$, a charge-doped quasi-one-dimensional nickel oxide, has been determined from X-ray single-crystal data at room temperature. Ca^{2+} ions replace at random the Y^{3+} ions within the *Immm* crystal structure of the undoped compound, Y_2BaNiO_5.

Comment

The crystal structure of the divalent nickel oxide Y_2BaNiO_5 was first determined from single-crystal diffraction data by Müller-Buschbaum & Schlüter (1990), Amador *et al.* (1990) and Buttrey *et al.* (1990). It has an orthorhombic crystal structure that contains infinite linear chains of flattened NiO_6 octahedra sharing corners along the crystallographic *a* direction. The magnetic properties of this charge-transfer insulator are those of an antiferromagnetic chain compound with a Haldane spin gap (Darriet & Regnault, 1993). Hole doping in Y_2BaNiO_5, which is achieved by substituting Ca^{2+} for Y^{3+}, has attracted considerable attention in recent years, arising from quite interesting electronic and physical properties and possible connections to high-temperature superconductivity (Di Tusa *et al.*, 1994; Janod *et al.*, 2001). X-ray powder diffraction data for $Y_{2-x}Ca_xBaNiO_5$ have been analysed using the Rietveld method (Massarotti *et al.*, 1999) but, as far as we know, no single-crystal structure determination has been published so far.

In this work, we have analyzed a single-crystal of $Y_{2-x}Ca_xBaNiO_5$, prepared by a flux method. The refinement of the single-crystal data confirms that Ca^{2+} ions replace at random the Y^{3+} ions within the *Immm* crystal structure of the undoped compound without any sign of superstructure, in agreement with the results of a previous electron diffraction study (Xu *et al.*, 2000). The refinement of the Ca,Y occupancy factors leads to the composition $x = 0.10$ (1), in agreement with the value determined from our energy-dispersive X-ray elemental analysis, $x = 0.11$ (2). Atomic parameters (positions, ADP's and occupation ratio) are obtained here with s.u.'s much smaller than those reported from powder data (Massarotti *et al.*, 1999). Moreover, the *z* coordinate of the Y/Ca site is very close to those reported for the undoped compound by Müller-Buschbaum & Schlüter (1990) and Amador *et al.* (1990), but significantly different from that obtained by Buttrey *et al.* (1990). Our study seems to highlight the unreliability of the refinement of Buttrey *et al.* (1990) concerning not only the lattice parameters, as already suggested by these authors, but also the *z* coordinate of the Y site.

We thus confirm that substitution of Y^{3+} by Ca^{2+} does not induce significant structural modification around the Y site.

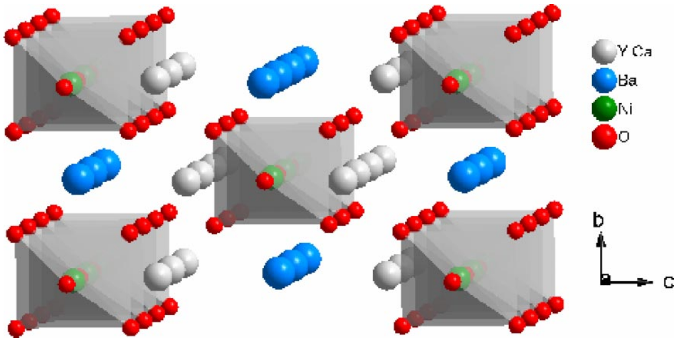

Figure 1
Schematic view of the crystallographic structure of $Y_{1.90}Ca_{0.10}BaNiO_5$ highlighting the existence of linear chains of vertex-sharing NiO_6 octahedra.

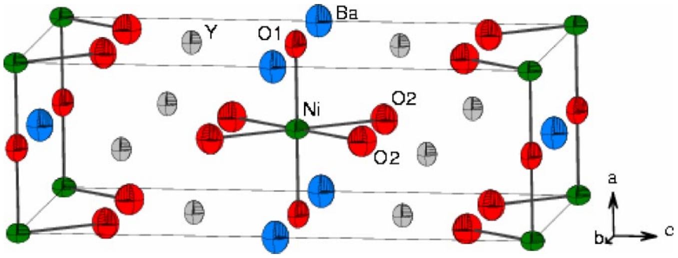

Figure 2
A view of the unit cell of $Y_{1.90}Ca_{0.10}BaNiO_5$. Displacement ellipsoids are drawn here at the 97% probability level. Ni—O bonds of the central NiO_6 octahedra and unit-cell edges are shown.

On the other hand, the Ni–O1 and Ni–O2 distances are found to decrease upon doping in spite of a bigger ionic radius for Ca^{2+}, as suggested earlier (Massarotti *et al.*, 1999). The shortening of both axial Ni—O1 and equatorial Ni—O2 distances is due to the effects of hole doping on the electronic structure close to the Fermi level (Lannuzel *et al.*, 2001).

Experimental

Single crystals of $Y_{1.90}Ca_{0.10}BaNiO_5$ were prepared using a self-flux method, as described by Yokoo *et al.* (1995). We first synthesized a ceramic sample of the parent compound Y_2BaNiO_5 by solid-state reaction from a mixture of NiO, Y_2O_3 and $BaCO_3$ in air. We then added this polycrystalline sample to a mixture of $CaCO_3$, NiO and $BaCO_3$, in a mole ratio of $CaCO_3$:NiO:$BaCO_3$:Y_2O_3 = 1.62:45:45:10. This mixture was then heated at 1723 K for 2 h in a Pt crucible, and slowly cooled (2 K h^{-1}) to room temperature.

Crystal data

$Y_{1.90}Ca_{0.10}BaNiO_5$
$M_r = 449$
Orthorhombic, *Immm*
$a = 3.7527$ (5) Å
$b = 5.7581$ (9) Å
$c = 11.313$ (2) Å
$V = 244.46$ (6) Å^3
$Z = 2$
$D_x = 6.097$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.4$–15.0°
$\mu = 34.10$ mm^{-1}
$T = 293$ K
Thick needle, black
0.16 × 0.02 × 0.02 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: Gaussian (*JANA*2000; Petrícek & Dusek, 2000)
$T_{\min} = 0.420$, $T_{\max} = 0.511$
2650 measured reflections
409 independent reflections
387 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.035$
$\theta_{\max} = 38.0°$
$h = -6 \rightarrow 6$
$k = -9 \rightarrow 9$
$l = -19 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity decay: 0.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.016$
$wR(F^2) = 0.042$
$S = 1.00$
409 reflections
22 parameters
$w = 1/[\sigma^2(I) + 0.001024I^2]$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 1.07$ e Å^{-3}
$\Delta\rho_{\min} = -1.64$ e Å^{-3}
Extinction correction: B—C type 1, Lorentzian isotropic
Extinction coefficient: 0.45 (2)

Table 1
Selected geometric parameters (Å, °).

Y—O1	2.2949 (2)	Ba—O2	2.9287 (12)
Y—O2	2.4107 (10)	Ni—O1^{ii}	1.8764 (3)
Y—O2^{i}	2.2528 (15)	Ni—O2	2.1740 (15)
Ba—O1	2.8791 (5)		
O2—Ni—O2^{iii}	101.04 (5)	O2—Ni—O2^{iv}	78.96 (5)

Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$; (ii) $x-1, y, z$; (iii) $x, y, -z$; (iv) $-x, -y, z$.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992); cell refinement: *CAD*-4-*PC Software*; data reduction: *JANA*2000 (Petrícek & Dusek, 2000); program(s) used to refine structure: *JANA*2000; molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *JANA*2000.

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