Redetermination of Co$_4$Nb$_2$O$_9$ by single-crystal X-ray methods

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A high-precision structure of tetracobalt diniobium nonaoxide, Co$_4$Nb$_2$O$_9$, is presented, based on X-ray single-crystal data. The space group and cation distribution previously obtained from powder data [Bertaut, Corliss, Forrat, Aleonard & Pauthenet (1961). *J. Phys. Chem. Solids*, **21**, 234–251] are confirmed.

Comment

The title compound, Co$_4$Nb$_2$O$_9$, (I), was shown to be an ordered corundum derivative on the basis of X-ray and neutron powder diffraction (Bertaut *et al.*, 1961). We obtained single crystals of this material by a novel lithium deintercalation reaction (see *Experimental*) and we now present a precise structural characterization based on X-ray single-crystal data (Fig. 1).

Co$_4$Nb$_2$O$_9$ may be described as a hexagonal close-packed array of oxide-anion layers with two-thirds of the octahedral sites filled with Co and Nb in an ordered 2:1 ratio. One sheet is built up of hexagonal rings of Co2O$_6$ octahedra centred on the threefold axis, by sharing edges (Fig. 2, layer A). The neighbouring sheet contains similar hexagonal rings located along the $\overline{3}$ axis, *i.e.* with alternating edge-sharing Co1O$_6$ and Nb1O$_6$ octahedra (Fig. 2, layer B). The whole structure is based on isolated face-sharing pairs of [NbO$_6$]$_2$ octahedra and corner-connected face-sharing pairs of [CoO$_6$]$_2$ octahedra (Fig. 3).

Both the CoO$_6$ and the NbO$_6$ octahedra present distorted geometries. The Co1—O distances range from 2.022 (2) to 2.247 (3) Å (Table 1) and the *trans* O—Co1—O angles are all 159.21 (11)°, perhaps due to the location of this ion in the Nb-containing B sheets. Atom Co2, lying in the A layer, is less
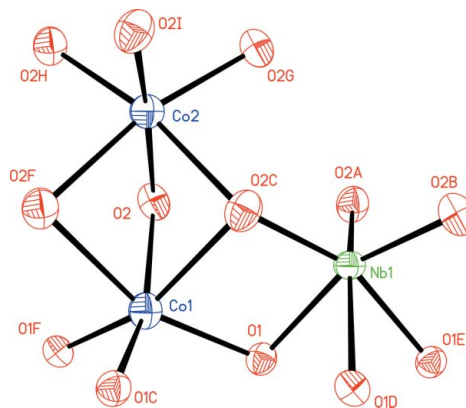
Figure 1
A part of the structure of (I), viewed along [001], showing the octahedral environments of all the cations. Displacement ellipsoids are drawn at the 90% probability level. Symmetry codes: (A) $-x + y - 1, -x, z$; (B) $x, y - 1, z$; (C) $-y + 1, x - y + 1, z$; (D) $-x + y, -x, z$; (E) $-y, x - y, z$; (F) $-x + y, -x + 1, z$; (G) $-x, -y + 1, -z$; (H) $x - y + 1, x + 1, -z$; (I) $y, -x + y, -z$.
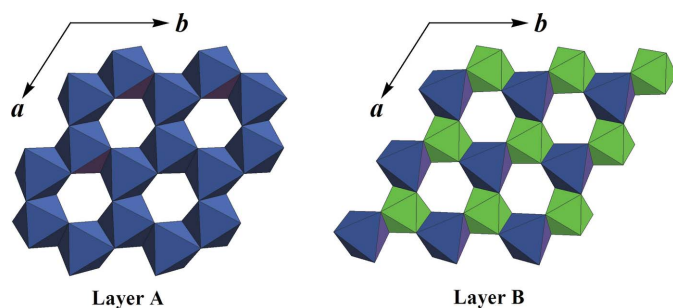
Figure 2
Layers A (left side) and B (right side) in the structure of (I), viewed along axis [001] of the trigonal cell. Blue octahedra represent [CoO$_6$] and green octahedra [NbO$_6$].
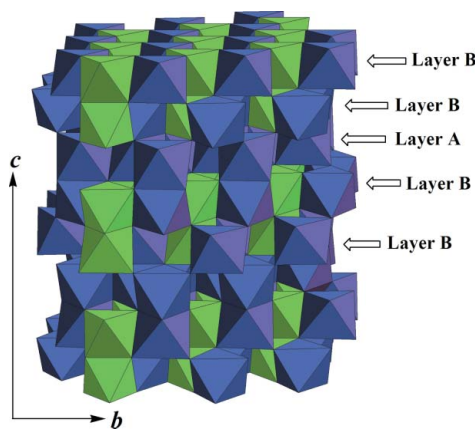

Figure 3
Complete structure of (I), described as an array of octahedra and viewed along [100]. Colour key as in Fig. 2.

distorted, with Co2—O bond lengths in the range 2.083 (3)–2.155 (3) Å. Finally, the NbO$_6$ polyhedron has far from ideal octahedral geometry, with Nb1—O bond lengths ranging from 1.892 (3) to 2.131 (3) Å and O—Nb1—O *trans* angles of 159.50 (13)°. The O atoms are four-coordinated by two Co and two Nb (O1) and by three Co and one Nb (O2). These results compare with the refinement by Bertaut *et al.* (1961) based on 36 indexed powder diffraction peaks: Co1—O and Co2—O bond lengths ranged from 1.98 to 2.25 and 2.08 to 2.26 Å, respectively, and Nb—O bond lengths were found in the range 1.82–2.21 Å (s.u. values were not determined).

Bond valence sums (Brown, 2002) computed using *softBV* (Adams, 2004) are as follows: 4.91 for Nb1 and 2.01 for both Co1 and Co2. It is thus clear that no mixed-valence species are present in (I).

Experimental

During a systematic study of the ternary system Li$_2$O–Nb$_2$O$_5$–CoO we obtained the complex oxide Li$_3$Co$_2$NbO$_6$, which crystallized as cubic and orthorhombic polymorphs (Vega-González, 2002). The orthorhombic polymorph of this polycrystalline material, treated at 1273 K under air for three months, yielded single crystals of the oxides CoNb$_2$O$_6$ (Weitzel, 1976) and Co$_4$Nb$_2$O$_9$. We propose the following delithiation mechanism to rationalize the formation of these phases:

$$2Li_3Co_2NbO_6 \rightarrow CoNb_2O_6 + 3CoO + 3Li_2O,$$

$$2Li_3Co_2NbO_6 \rightarrow Co_4Nb_2O_9 + 3Li_2O.$$
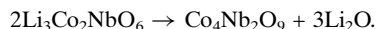
A powder diffraction characterization of the product of the reaction revealed a composition of 2 CoNb$_2$O$_6$:1 Co$_4$Nb$_2$O$_9$. This composition could imply the participation of a third reaction:

$$CoNb_2O_6 + 3CoO \rightarrow Co_4Nb_2O_9.$$

This hypothesis is supported by the fact that no trace of CoO is observed in the product. The products may be identified by their colours: dark blue for CoNb$_2$O$_6$ and violet for (I).

Crystal data

Co$_4$Nb$_2$O$_9$	$D_x = 5.728$ Mg m^{-3}
$M_r = 565.54$	Mo $K\alpha$ radiation
Trigonal, $P\bar{3}c1$	$\mu = 13.29$ mm^{-1}
$a = 5.1736$ (3) Å	$T = 297$ (1) K
$c = 14.1457$ (11) Å	Block, violet
$V = 327.90$ (4) Å^3	$0.12 \times 0.07 \times 0.05$ mm
$Z = 2$	

Data collection

Bruker $P4$ diffractometer	262 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.076$
Absorption correction: ψ scan	$\theta_{max} = 30.0°$
($XSCANS$; Siemens, 1996)	2 standard reflections
$T_{min} = 0.272$, $T_{max} = 0.510$	every 48 reflections
1234 measured reflections	intensity decay: 1.5%
328 independent reflections	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.031$	$\Delta\rho_{max} = 0.95$ e Å^{-3}
$wR(F^2) = 0.079$	$\Delta\rho_{min} = -0.80$ e Å^{-3}
$S = 1.28$	Extinction correction: *SHELXTL-Plus*
328 reflections	Extinction coefficient: 0.0107 (11)
25 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.0148P)^2 + 2.3726P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected bond lengths (Å).

Nb1—O2^i	1.892 (3)	Co1—O2	2.247 (3)
Nb1—O1	2.131 (3)	Co2—O2^{ii}	2.083 (3)
Co1—O1	2.022 (2)	Co2—O2	2.155 (3)

Symmetry codes: (i) $x, y - 1, z$; (ii) $y, -x + y, -z$.

Additional pseudo-symmetry 6 and *m* are detected by *ADDSYM* (Le Page, 1987; Spek, 2003), suggesting space group $P6_3/mcm$ rather than $P\bar{3}c1$. The diffraction pattern also seems to fit this symmetry, since the extinction for a 6_3 axis is unambiguously observed. However, the full data are not consistent with Laue class 6/*mmm* (hexagonal system, $R_{int} = 0.563$ before absorption correction), while Laue class $\bar{3}m1$ is consistent with the diffraction data (trigonal system, $R_{int} = 0.152$ before absorption correction). Finally, Wilson statistics, $\langle E^2 - 1 \rangle = 1.12$, consistent with a hypercentric distribution, suggest a centrosymmetric space group, a feature previously mentioned by Bertaut *et al.* (1961), who were unable to detect a piezoelectric effect for this material.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *CaRIne Crys-*

tallography (Boudias & Monceau, 1998); software used to prepare material for publication: *SHELXTL-Plus*.

References

Adams, St. (2004). *softBV*. Release 0.96 (February 2004). Available at http://kristall.uni-mki.gwdg.de/softbv/index.html.

Bertaut, E. F., Corliss, L., Forrat, F., Aleonard, R. & Pauthenet, R. (1961). *J. Phys. Chem. Solids*, **21**, 234–251.

Boudias, C. & Monceau, D. (1998). *CaRIne Crystallography*. Release 3.1. DIVERGENT S.A., Compiègne, France.

Brown, I. D. (2002). *The Chemical Bond in Inorganic Chemistry – The Bond Valence Model*. IUCr monographs on Crystallography, 12. Oxford University Press.

Le Page, Y. (1987). *J. Appl. Cryst.* **20**, 264–269.

Sheldrick, G. M. (1998). *SHELXTL-Plus*. Release 5.10. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1996). *XSCANS*. Version 2.21. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Vega-González, M. (2002). MSc thesis, Universidad Nacional Autónoma de México.

Weitzel, H. (1976). *Z. Kristallogr.* **144**, 238–258.