The binuclear copper(I) cation $[Cu_2(PTP)_2]^{2+}$ represents an unusual, extremely stable copper(I) species, being unaffected in solution and in the solid state on exposure to air for extended periods of time. The formation of such a derivative from both binuclear and mononuclear copper(II) starting materials is remarkable, since it involves major molecular rearrangement, and emphasizes the significance of the redox activity of compounds of this sort. We are in the process of utilizing the unusual redox properties of this type of complex to effect intermolecular redox processes involving just copper(II) species. We have, for example, recently shown that compound III can selectively oxidize a binuclear copper(II) complex of a hexadentate phthalazine ligand, which has an oxidation potential ($E_{1/2}$ = +0.50 V in DMF vs. SCE) in an appropriate range, to form a stable binuclear copper(III) derivative.[27]

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Supplementary Material Available: Tables SI and SIII, listing anisotropic thermal parameters for I and II, and Tables SV and SVI, listing bond length and angle data pertaining to the ligands in I and II (8 pages); Tables SII and SIV, listing observed and calculated structure factors for I and II (41 pages). Ordering information is given on any current masthead page.

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$Ca_{0.75}Nb_3O_6$: A Novel Metal Oxide Containing Niobium–Niobium Bonds. Characterization and Structure Refinement from Synchrotron Powder X-ray Data

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A new mixed-metal oxide, $Ca_{0.75}Nb_3O_6$, has been characterized in the course of our investigations of the Ca–Nb–O system. The space group is *Immm* with cell constants a = 7.113 Å, b = 10.286 Å, and c = 6.563 Å. The structure was refined by using powder X-ray data obtained on the Brookhaven synchrotron. An extremely short Nb–Nb bond of 2.578 Å is present within an Nb_2O_8 unit.

Introduction

Many potentially interesting materials are found only as polycrystalline powders, and the lack of single crystals may preclude further study. In this paper we describe how analytical electron microscopy, combined with powder X-ray diffraction, can prove to be a powerful method for the characterization of polycrystalline materials. We further demonstrate that the high-resolution powder X-ray data obtainable from synchrotron radiation can allow the structural refinement of a novel compound present in a mixture. This methodology is especially appropriate to the investigation of complex phase diagrams of refractory oxides, as in the case considered here.

A large number of ternary oxides of molybdenum are known to contain metal clusters, for example $Zn_2Mo_3O_8$,[2] $NaMo_4O_6$,[3a] $Ba_5(Mo_4O_6)_8$,[3b] and $La_3Mo_4SiO_{14}$,[4] but niobium, which is noted for its formation of octahedral Nb_6 clusters in its lower halides, appears to be less prone to metal–metal bonding in its oxide chemistry. The simple oxides NbO[5] and NbO_2[6] do exhibit metal–metal bonding, but for the lower ternary oxides, cluster formation is only firmly established in the case of $Mg_3Nb_6O_{11}$.[7] It would seem unlikely that the magnesium compound is unique, and we therefore attempted a systematic survey of the lower ternary oxides of niobium with the alkali and alkaline-earth metals.

We have investigated the ternary systems A–Nb–O with A = Ca, Sr, Ba, and K. A compound of composition $Sr_{\sim 0.7}Nb_4O_6$[8] was prepared, which appears to be isomorphous with $Ba_5(Mo_4O_6)_8$[3] and would therefore contain Nb clusters. We have also found isomorphous compounds containing Ba and K. In the Ca–Nb–O system, a new compound, $Ca_{0.75}Nb_3O_6$, was found and the lattice parameters indicated that this compound did not have a molybdenum analogue. The low average oxidation state for niobium made it probable that this compound contained Nb–Nb bonds. A structural investigation using a polycrystalline sample and a synchrotron X-ray source was therefore undertaken. After obtaining the synchrotron data, we learned of the then-unpublished work of Kohler and Simon[9] on $NaNb_3O_5F$ and it appeared likely that this phase was isomorphous with ours. Their structural model, obtained from a single-crystal X-ray study, was used as the basis for our structural refinement.

Experimental Section

Synthesis and Analysis. A mixture of average stoichiometry $CaNb_3O_6$ was prepared from the appropriate mixture of $CaCO_3$, Nb_2O_5, and niobium metal. The carbonate was decomposed by reaction with Nb_2O_5 at 1400 °C, and the product was then ground with the appropriate amount of Nb metal and heated in vacuo in a sealed silica tube at 1250 °C. The product was a black powder.

A small quantity, ~25 mg, of the product was finely ground in an agate mortar and dispersed in ~2 mL of chloroform by an ultrasonic bath. A drop of this dispersion was placed on a 3-mm "Formvar"-coated copper grid and the solvent allowed to evaporate. X-ray microanalysis

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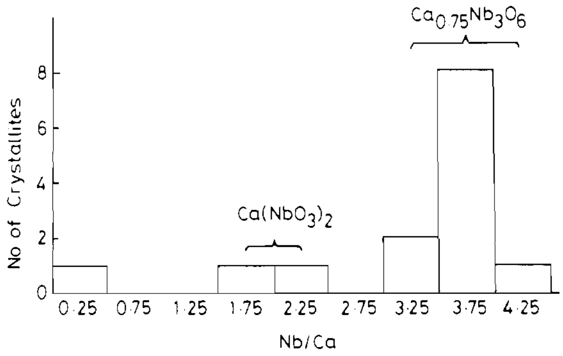

Figure 1. Crystallite distribution in "$CaNb_3O_6$".

was carried out with a JEOL 2000FX electron microscope fitted with a Tracor Northern analysis system employing a solid-state detector with a beryllium window. The compositions of the crystallites were determined by

$$c_{\mathrm{Nb}}/c_{\mathrm{Ca}} = k_{\mathrm{NbCa}} I_{\mathrm{Nb\,K}\alpha}/I_{\mathrm{Ca\,K}\alpha}$$

where c is the concentration of an element, I is the intensity of a characteristic X-ray line, and k is a constant obtained from two standards, $CaNb_2O_6$ and $Ca_2Nb_2O_7$ ($k_{NbCa} = 0.78 \pm 0.03$). This expression is valid in the thin-crystal limit when atomic number, absorption, and fluorescence effects can be ignored.[10] Crystal thickness was monitored from the Nb Lα/Nb Kα ratio. The histogram of crystallite distribution shown in Figure 1 was determined from the analysis of 14 crystals. The average Nb/Ca ratio was found to be 3.70. With use of an ultrathin window detector[11] the approximate oxygen content of the new phase was determined by using the O Kα/Nb Lα ratio ($k_{ONb} = 7.14$). An average value of O/Nb of 2.07 was obtained. These analyses would be consistent with the formula $Ca_{0.75}Nb_3O_6$.

Determination of Unit Cell. A powder X-ray pattern of "$CaNb_3O_6$" was recorded with a Stöe Guinier camera employing Cu K$\bar{\alpha}$ radiation and a curved graphite monochromator. In order to obtain accurate d spacings for autoindexing, an internal calibrant of KCl, $a = 6.2931$ Å,[12] was employed.

NbO and $Ca(NbO_3)_2$ were found in "$CaNb_3O_6$". The reflections due to these phases were removed from the X-ray powder pattern, and the pattern due to the new phase was autoindexed by using the program VISSER.[13] An I-centered orthorhombic cell, $a = 7.122$ Å, $b = 10.289$ Å, and $c = 6.561$ Å, was found, and this was confirmed by electron diffraction when patterns corresponding to the zones [111], [011], and [101] were obtained.

X-ray Structure Refinement. Synchrotron X-ray data were collected on the X13A beam line at Brookhaven National Light Source. X-rays with a wavelength of 1.3222 Å from a Ge(111) crystal monochromator, diffracting in the horizontal plane, impinged on a flat-plate sample; a Ge(220) analyzer crystal and detector measured the scattering in the vertical plane. A full description of the diffractometer is given elsewhere.[14] The sample tray was oscillated by 2° about the θ axis to increase the number of crystallites sampled by the beam. Data were collected from 10 to 60° in 2θ at 0.01° intervals, with a count time of 2 s per step. The incident beam intensity was $\sim 5 \times 10^9$ photons s^{-1}, with the storage ring operating at 2.4 GeV and 55 mA for 10–42.66° and 120 mA for 42.67–60°.

The Rietveld profile method[15] was used for structure refinement. The peak shapes were described by a pseudo-Voight function.[16] The program employed was a modified[17] version of the standard Rietveld/Hewat program.[15,18]

Table I. Profile and Structural Parameters from the Rietveld Analysis of the Synchrotron Data

Profile Parameters

half-width parameters (0.01°)

Gaussian: $U = 166$ (8), $V = -66$ (5), $W = 8.9$ (6)

Lorentzian: $X = 4.3$ (1), $Y = 0$

zero point (0.01°): −0.87 (3)

cell constants: $a = 7.11291$ (7) Å, $b = 10.28551$ (10) Å, $c = 6.56264$ (6) Å

Structural Parameters

overall isotropic temperature factor: 0.20 (7) Å^2

Fractional Atomic Coordinates in *Immm* (No. 71)

atom	sym position	x	y	z	atoms/ unit cell
Nb(1)	4j	0.0000	0.5000	0.3036 (5)	4
Nb(2)	8n	0.2278 (3)	0.2808 (2)	0.5000	8
Ca	4i	0.5000	0.5000	0.238 (2)	3.03 (6)
O(1)	4g	0.5000	0.668 (2)	0.5000	4
O(2)	4h	0.5000	0.678 (2)	0.0000	4
O(3)	16o	0.820 (2)	0.366 (1)	0.232 (1)	16

$R_{nuc}{}^a = 12.5\%$, $R_{prof} = 15.9\%$, $R_{wprof} = 19.5\%$, $R_{expected} = 6.1\%$

[a] R_{nuc} is the reliability factor based on approximate integrated intensities.[15]

Table II. Bond Angles (Å) and Distances (deg) for $CaNb_3O_6$

Nb(1)–Nb(1)	2.578 (7)	Nb(2)–O(2)	1.930 (20)
Nb(1)–Nb(2)	3.061 (4) (×4)	Nb(2)–O(3)	1.992 (20) (×2)
Nb(2)–Nb(2)	3.241 (6)	Nb(2)–O(3)	2.240 (20) (×2)
Nb(2)–Nb(2)	3.357 (6) (×2)	Ca–O(1)	2.432 (24) (×2)
Nb(1)–O(3)	1.941 (20) (×4)	Ca–O(2)	2.415 (24) (×2)
Nb(2)–O(1)	2.008 (20)	Ca–O(3)	2.666 (26) (×4)

Nb(1)–Nb(2)–Nb(1)	49.8	O(3)–Nb(1)–O(3)	152.0
Nb(2)–Nb(1)–Nb(2)	63.9	Nb(2)–O(2)–Nb(2)	114.2
Nb(2)–Nb(1)–Nb(2)	94.9	Nb(2)–O(1)–Nb(2)	149.3
Nb(1)–O(3)–Nb(2)	102.2		

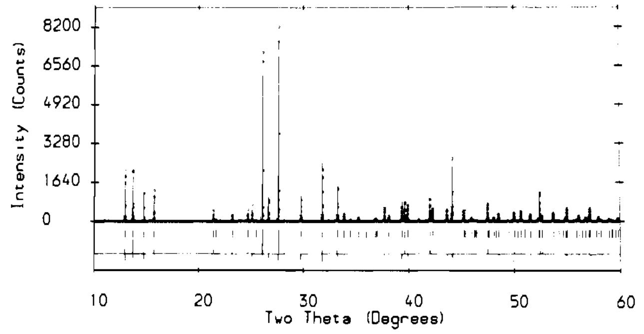

Figure 2. Observed (points), calculated (bold lines), and difference (light lines) diffraction profile for $Ca_{0.75}Nb_3O_6$.

Although the sample of $Ca_{0.75}Nb_3O_6$ used for the collection of synchrotron X-ray data contained NbO_2 as an impurity, the very high resolution of the instrument, fwhm = 0.02° at 20° and 0.06° at 48°, resulted in most of the peaks due to NbO_2 being excluded from the profile refinement. Excluded regions were used to remove remaining tails of NbO_2 peaks; only one peak of $Ca_{0.75}Nb_3O_6$ was lost on this account.

The initial coordinates used were those obtained by Kohler and Simon for $NaNb_3O_5F$. Scattering factors for Ca^{2+}, Nb^{3+}, and O were those from ref 19. A single overall temperature factor was refined. The final coordinates and details of the refinement are shown in Table I, and the observed, calculated, and difference diffraction profile is shown in Figure 2. Some problem with preferred orientation remains as is apparent from the large positive differences for reflections $0kk$. The final R factors are rather large, probably reflecting this remaining discrepancy. Some selected bond lengths and angles are given in Table II.

Results and Discussion

The structure viewed down the z axis is shown in Figure 3 and down x in Figure 4. Layers of NbO_6 octahedra are edge-sharing

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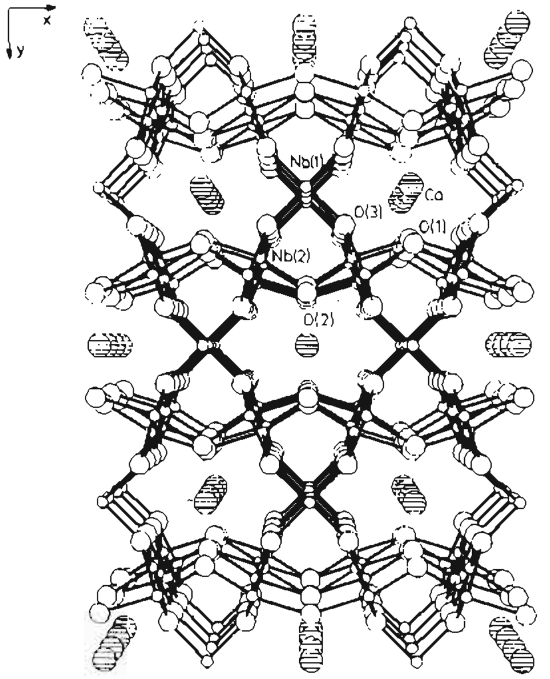

Figure 3. Structure of $Ca_{0.75}Nb_3O_6$ viewed down z (Ca, hatched circles; Nb, small circles; O, large open circles).

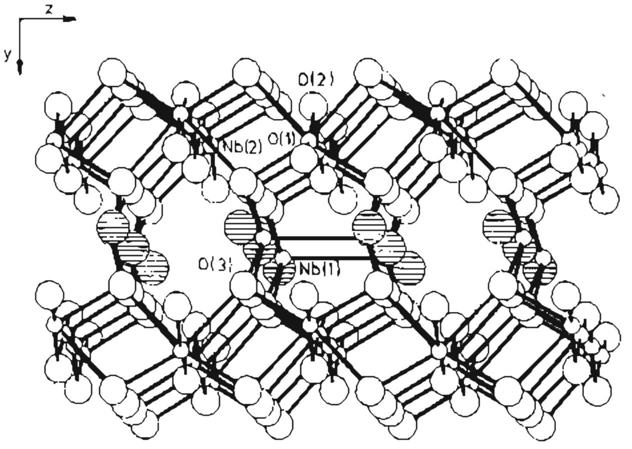

Figure 4. Structure of $Ca_{0.75}Nb_3O_6$ viewed down a (legend as for Figure 3).

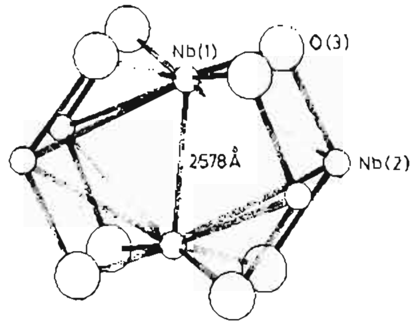

Figure 5. Nb_6 group with the central Nb_2O_8 unit.

down z and corner-sharing along x. These layers are held together by Nb atoms, which are coordinated to four oxygen atoms, and Ca^{2+} ions. The four-coordinate NbO_4 groups form Nb_2 pairs in the z direction with Nb–Nb = 2.578 Å. The structure may also be viewed as being derived from Nb_6 groups (Figure 5); the octahedral Nb_6 group distorted to give a very short 2.578-Å Nb–Nb bond formed from opposite apices of the original octahedron, 8 short edges of 3.061 Å, 2 edges of 3.241 Å, and very long edges of 4.509 Å (cf. NbO with 12 Nb–Nb distances of 2.977 Å).

The Rietveld method has of course been used previously to analyze patterns from biphasic mixtures.[20] But clearly this can be a difficult procedure, and the extra resolution available with synchrotron radiation offers a considerable advantage, allowing impurity peaks to be rejected in the structure refinement. In this case, where our principal interest was in the metal–metal bonding in the oxide, we have been able to locate accurately the Nb atoms with esds in the positional parameters of <0.003 Å. The oxygen positions, though in good agreement with those found by Kohler and Simon, have significantly larger uncertainties (<0.02 Å).

The structural parameters are very similar to those of Kohler and Simon[9] for $NaNb_3O_5F$. The difference in occupancy for the tunnel cations Na and Ca is interesting, and the two formulas, if correct, would mean the compounds were not isoelectronic. This discrepancy could result from an error in the O/F ratio.

Bond-order calculations using the Pauling equation[21], $0.6 \log n = d_1 - d_{\text{obsd}}$, where n is the metal–metal bond order of the bond with length d_{obsd} and d_1 is the bond length of a single bond ($d_1 = 2.708$ Å for niobium), have in the past given good agreement with the number of electrons available for metal–metal bonding in a number of niobium oxides.[21] Taking Nb–Nb contributions of $n > 0.07$ and summing for Nb1 and the two Nb2 atoms in the formula unit $Ca_{0.75}Nb_3O_6$ gives $n = 4.15$, in good agreement with the empirical formula, which would provide 4.5 electrons for Nb–Nb bonding. A similar calculation for $NaNb_3O_5F$ gives 3.68, whereas the empirical formula would give 5 electrons available for Nb–Nb bonding. One possibility is that the number of electrons available for bonding is lower than the empirical formula suggests (the formula $NaNb_3O_6$ would give four electrons for Nb–Nb bonding, in much better agreement with the observed Nb–Nb distances).

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