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# Preparation and Crystal Structure of a New Reduced Calcium Niobium Oxide: $CaNb_2O_4$

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**Single crystals of a new reduced calcium niobium oxide, $CaNb_2O_4$, were prepared in an evacuated quartz tube at 1100°C. The calcium niobium oxide crystallizes in the orthorhombic space group *Pbcm* with $a = 5.054(1)$, $b = 11.904(1)$, and $c = 5.839(1)$ Å, $Z = 4$, and the final *R* factors are $R = 0.027$ and $R_w = 0.029$ for 799 unique reflections. The crystal structure has the layer built up by edge-sharing of $NbO_6$ trigonal prisms to form infinite metal–metal bondings as seen in $A$NbO$_2$ ($A$ = Li,Na). The $Ca^{2+}$ ion is located at the trigonal prism site in the interlayer. No evidence for superconductivity was found down to 2.0 K.** © 1999 Academic Press

## INTRODUCTION

Many reduced niobium oxides have been reported and most of the strongly reduced ones are characterized by having the $[Nb_6O_{12}]O_6$ cluster with the metal–metal bonding as found in $Rb_{1.51}Nb_{10}O_{15}$ (1), $NaNb_{10}O_{18}$ (2), $Rb_4Al_2Nb_{35}O_{70}$ (3), and $LaNb_7O_{12}$, etc. (4–10). Exceptionally, compounds of $A$NbO$_2$ ($A$ = Li, Na) have a two-dimensional metal–metal bonding network (11, 12), and their deintercalated phases $A_x$NbO$_2$ exhibit the superconductivity below 5.5 K for $A$ = Li (13) and 4.2 K for $A$ = Na (14).

In the course of our investigation to prepare reduced niobium oxides, we found a new reduced calcium niobium oxide, $CaNb_2O_4$, which has a two-dimensional metal–metal bonding network. The crystal structure of the new reduced niobium oxide will be described.

## EXPERIMENTAL

### Sample Preparation

Black single crystals of $CaNb_2O_4$ were obtained as follows. A mixture of $Rb_2CO_3$, $CaCO_3$, and $Nb_2O_5$ with a molar ratio of 1 : 1 : 1 was heated in air at 1000°C for 12 h. The X-ray powder pattern indicated that the product was a mixture of $RbNbO_3$ (15) and $CaNb_2O_6$ (16) with low crystallinity. The product was mixed with Nb powder equimolar to the niobium content in the calcined product. The mixture (1.4 g) and $CaCl_2 \cdot 2H_2O$ (0.5 g) were put into a quartz tube and dehydrated at 300°C for 1 h *in vacuo*. Then the tube was sealed and heated at 1100°C for 12 h. The tube was taken out from the furnace at 800°C to quench to room temperature. The products were washed with distilled water to remove chlorides and dried at 50°C. Samples were identified by X-ray powder diffraction using Cu$K\alpha$ radiation.

### Structure Determination

Single crystal X-ray diffraction data were collected by using a Rigaku AFC-7R four-circle diffractometer with graphite monochromated Mo$K\alpha$ radiation using the $\omega$-$2\theta$ scan technique ($D\omega = (1.63 + 0.30 \tan\theta)°$). The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by using $\psi$ scans. The crystal structure was solved and refined with the computer programs from the TEXSAN crystallographic software package (17). Details of the data collection and refinement are summarized in Table 1. The atomic positions of niobium atoms were determined by the Patterson method and the subsequent Fourier analysis revealed the positions of the calcium and oxygen atoms. The final positional and anisotropic thermal parameters are summarized in Table 2. Selected interatomic distances and angles are listed in Table 3.

## RESULTS AND DISCUSSION

### Sample Preparation

The products obtained under the condition described in the experimental section were contaminated by a small amount of NbO. The reaction without $CaCl_2 \cdot 2H_2O$ did not yield $CaNb_2O_4$, but $CaNb_2O_6$ with the columbite-type structure (16) and unknown phases. When the amount of $CaCl_2 \cdot 2H_2O$ was increased, $Ca_xNb_3O_6$ (18, 19) was obtained. Also, single crystals of $Ca_xNb_3O_6$ were produced

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**TABLE 1**
**Crystal Data and Intensity Collection for $CaNb_2O_4$**

| | |
|---|---|
| Color | Black |
| Size (mm) | $0.05 \times 0.02 \times 0.10$ |
| Crystal system | Orthorhombic |
| Space group | $Pbcm$ (No. 57), $Z = 4$ |
| Lattice parameters (Å) | $a = 5.054(1)$ |
| | $b = 11.904\ (1)$ |
| | $c = 5.839(1)$ |
| Volume (Å$^3$) | 351.2(2) |
| Formula weight | 289.87 |
| Calculated density (g/cm$^3$) | 5.48 |
| Diffractometer | Rigaku AFC-7R |
| Radiation | Graphite monochromated |
| Mo$K\alpha$ | ($\lambda = 0.71069$ Å) |
| Temperature (°C) | 23 |
| $\mu$ (Mo$K\alpha$) (cm$^{-1}$) | 75.40 |
| Maximum $2\theta$ (°) | 90 |
| Scan mode | $\omega$-$2\theta$ |
| Scan speed (°/min) | 16 |
| Number of data collected | 1707 |
| Number of unique data | 799 ($I > 3.00\sigma(I)$) |
| Absorption correction | $\psi$ scans |
| Transmission factors | 0.96–0.99 |
| Refinement method | Full-matrix least-squares on $\lvert F \rvert$ |
| Number of parameters | 41 |
| $R$ | 0.027 |
| $R_w$ | 0.029 |
| Goodness of fit | 1.83 |

**TABLE 2**
**Positional and Anisotropic Thermal Parameters for $CaNb_2O_4$**

| Atom | Site | $x$ | $y$ | $z$ | $B_{eq}$* (Å$^2$)$^a$ |
|---|---|---|---|---|---|
| Nb(1) | 4$d$ | 0.65911(9) | 0.24615(4) | 1/4 | 0.227(6) |
| Nb(2) | 4$c$ | 0.15567(9) | 1/4 | 1/2 | 0.239(6) |
| Ca | 4$d$ | 0.6926(2) | 0.9965(1) | 3/4 | 0.46(1) |
| O(1) | 8$e$ | 0.4929(8) | 0.1381(2) | 0.5058(8) | 0.38(3) |
| O(2) | 4$d$ | 0.9925(9) | 0.1403(3) | 1/4 | 0.40(7) |
| O(3) | 4$d$ | 0.986(1) | 0.3563(3) | 1/4 | 0.44(6) |

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Nb(1) | 0.0023(2) | 0.0028(1) | 0.0035(2) | 0.0002(1) | 0 | 0 |
| Nb(2) | 0.0027(2) | 0.0029(1) | 0.0035(2) | 0 | 0 | 0.0001(1) |
| Ca | 0.0055(3) | 0.0040(3) | 0.0080(3) | 0.0001(4) | 0 | 0 |
| O(1) | 0.0039(8) | 0.0032(7) | 0.0072(9) | −0.0008(9) | −0.0004(8) | −0.0002(9) |
| O(2) | 0.002(2) | 0.004(1) | 0.009(2) | 0.002(1) | 0 | 0 |
| O(3) | 0.004(2) | 0.003(1) | 0.009(2) | −0.001(1) | 0 | 0 |

[a] $B_{eq}^* = (8\pi^2/3)\sum_i \sum_j U_{ij} a_1^* a_j^* a_i a_j$.

**TABLE 3**
**Selected Interatomic Distances (Å) and Angles (°) for $CaNb_2O_4$**

| | | | |
|---|---|---|---|
| | $Nb(1)O_6$ Trigonal Prism | | |
| Nb(1)–O(1) | 2.154(4) × 2 | O(1)–O(1) | 2.666(4) × 2 |
| –O(1) | 2.143(4) × 2 | O(1)–O(1) | 2.85(1) |
| –O(2) | 2.104(4) | O(1)–O(1) | 2.99(1) |
| –O(3) | 2.110(4) | O(1)–O(2) | 2.934(7) × 2 |
| Mean | 2.135 | O(1)–O(3) | 2.931(7) × 2 |
| | | O(2)–O(3) | 2.572(5) |
| O(1)–Nb(1)–O(1) | 82.9(2) | O(1)–Nb(1)–O(1) | 88.4(2) |
| O(1)–Nb(1)–O(1) | 76.7(1) × 2 | O(1)–Nb(1)–O(2) | 54.7(1) × 2 |
| O(1)–Nb(1)–O(3) | 53.6(2) × 2 | O(2)–Nb(1)–O(3) | 75.2(2) |
| | $Nb(2)O_6$ Trigonal Prism | | |
| Nb(2)–O(1) | 2.163(3) × 2 | O(1)–O(1) | 2.666(4) |
| –O(2) | 2.125(3) × 2 | O(1)–O(2) | 2.937(7) × 2 |
| –O(3) | 2.113(3) × 2 | O(1)–O(3) | 2.934(7) × 2 |
| Mean | 2.134 | O(2)–O(3) | 2.572(5) × 2 |
| | | O(2)–O(3) | 2.920(1) × 2 |
| O(1)–Nb(2)–O(1) | 76.1(2) | O(1)–Nb(2)–O(2) | 86.4(2) × 2 |
| O(1)–Nb(2)–O(3) | 86.5(2) × 2 | O(2)–Nb(2)–O(3) | 74.7(1) × 2 |
| O(2)–Nb(2)–O(3) | 87.1(1) × 2 | | |
| | Metal–metal bonding | | |
| Nb(1)–Nb(1) | 2.920(1) | Nb(1)–Nb(2) | 2.903(1) |
| Nb(1)–Nb(2) | 2.934(1) | | |
| Mean | 2.919 | | |
| Nb(1)–Nb(1)–Nb(2) | 60.14(1) × 2 | Nb(1)–Nb(1)–Nb(2) | 59.80(1) × 2 |
| Nb(2)–Nb(1)–Nb(2) | 59.68(2) | Nb(2)–Nb(1)–Nb(2) | 60.36(2) |
| Nb(1)–Nb(2)–Nb(1) | 60.40(2) × 2 | Nb(1)–Nb(2)–Nb(2) | 59.82(1) × 2 |
| Nb(1)–Nb(2)–Nb(1) | 59.71(2) | Nb(1)–Nb(2)–Nb(2) | 60.16(1) |
| | $CaO_6$ trigonal prism | | |
| Ca–O(1) | 2.382(4) × 2 | O(1)–O(1) | 2.85(1) |
| –O(1) | 2.428(4) × 2 | O(1)–O(1) | 2.99(1) |
| –O(2) | 2.276(4) | O(1)–O(1) | 3.289(4) × 2 |
| –O(3) | 2.297(4) | O(1)–O(2) | 2.937(7) × 2 |
| Mean | 2.366 | O(1)–O(3) | 2.873(7) × 2 |
| | | O(2)–O(3) | 3.382(5) |
| Ca–Ca | 3.510(1) | | |
| O(1)–Ca–O(1) | 71.9(2) | O(1)–Ca–O(1) | 86.27(8) × 2 |
| O(1)–Ca–O(1) | 77.7(2) | O(1)–Ca–O(2) | 78.1(1) × 2 |
| O(1)–Ca–O(3) | 74.9(2) × 2 | O(2)–Ca–O(3) | 95.4(1) |

when the molar ratio of Nb metal and $Nb_2O_5$ in the calcined product was 1.5 : 1. The lattice parameters of $Ca_xNb_3O_6$ determined by the four-circle diffractometer were $a = 7.117(2)$, $b = 10.287(2)$, and $c = 6.560(2)$ Å and these values agreed well with those for $Ca_{0.75}Nb_3O_6$ ($a = 7.11291(7)$, $b = 10.2855(1)$, and $c = 6.56264(6)$ Å) (18) and for $Ca_{0.95}Nb_3O_6$ ($a = 7.1156(9)$, $b = 10.286(2)$, and $c = 6.5756(9)$ Å) (19). When $Rb_2CO_3$ was not used, the product was $CaNb_2O_6$ with the columbite-type structure (16). As the color of this compound was black, the noibium might be weakly reduced by oxygen deficiency. Both $RbNbO_3$ and $CaCl_2$ were needed to prepare $CaNb_2O_4$ and were considered to play an important role as mineralizers.

### *Crystal Structure*

The crystal structure of $CaNb_2O_4$ may be described as a layer structure built up by edge-sharing of $NbO_6$ trigonal prisms as shown in Fig. 1. This layer structure is similar to

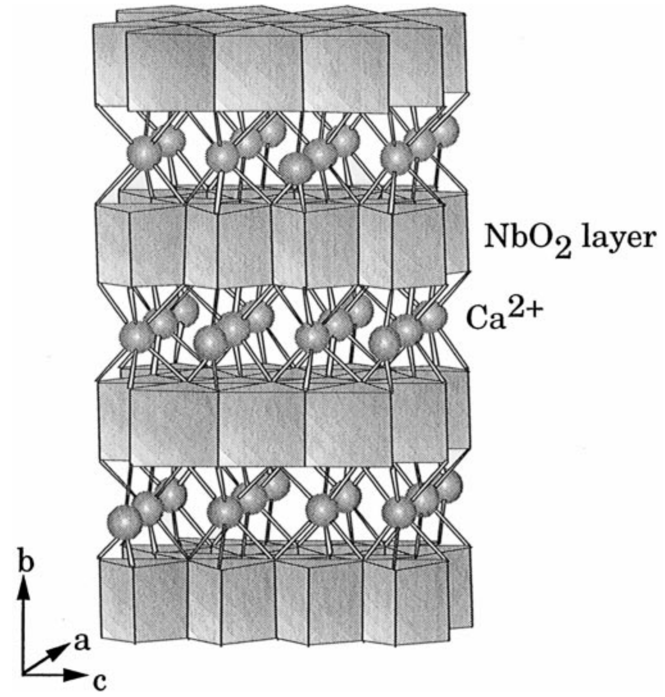

**FIG. 1.** Crystal structure of $CaNb_2O_4$.

that of $ANbO_2$ ($A$ = Li, Na) (11, 12) and the infinite metal–metal bondings are formed in the $(NbO_2)_n$ sheet. However, the stacking of the $(NbO_2)_n$ sheet is different between $ANbO_2$ ($A$ = Li, Na) and $CaNb_2O_4$ as shown in Fig. 2. The stacking of the $(NbO_2)_n$ sheet in $CaNb_2O_4$ can be derived by alternate gliding of the $(NbO_2)_n$ sheet in $ANbO_2$ toward the [1/3 2/3 0] direction. No octahedral site is formed in the interlayer of $CaNb_2O_4$, unlike $ANbO_2$ ($A$ = Li, Na), and the $Ca^{2+}$ ions in the interlayer are sited at the trigonal prism sites as shown in Fig. 3. The interatomic distances of Ca–O ranged from 2.276(4) to 2.428(4) Å and the mean value was 2.366 Å. Trigonal prism coordination of $Ca^{2+}$ ions is observed in $CaM_2O_4$ ($M$ = Ti, Fe, Cr, V), although three additional oxygen atoms are coordinated around the rectangular faces of the trigonal prism. The mean interatomic distances of Ca–O for these compounds, except the additional oxygen atoms, are 2.370 Å for $M$ = Ti (20), 2.417 Å for $M$ = Fe (21), and 2.394 Å for $M$ = Cr (22). These values correspond to the mean interatomic distance of Ca–O in $CaNb_2O_4$.

The Nb–Nb distances ranged from 2.903(1) to 2.934(1) Å and the mean value is 2.919 Å. On the other hand, the Nb–Nb distance in $ANbO_2$ ($A$ = Li, Na) is uniform: 2.908 Å for $A$ = Li and 2.955 Å for $A$ = Na. The interatomic distances of Nb(1)–O range from 2.104(4) to 2.154(4) Å and those of Nb(2)–O from 2.113(3) to 2.163(3) Å, and the mean values are 2.135 and 2.134 Å, respectively. Figure 4 shows the coordination environment of niobium atoms.

Interatomic distances, angles, the thickness of the sheet, $(NbO_2)_n$, and interlayer space, $(AO_2)_n$, are compared among $ANbO_2$ ($A$ = Li, Na) and $CaNb_2O_4$ in Table 4. The

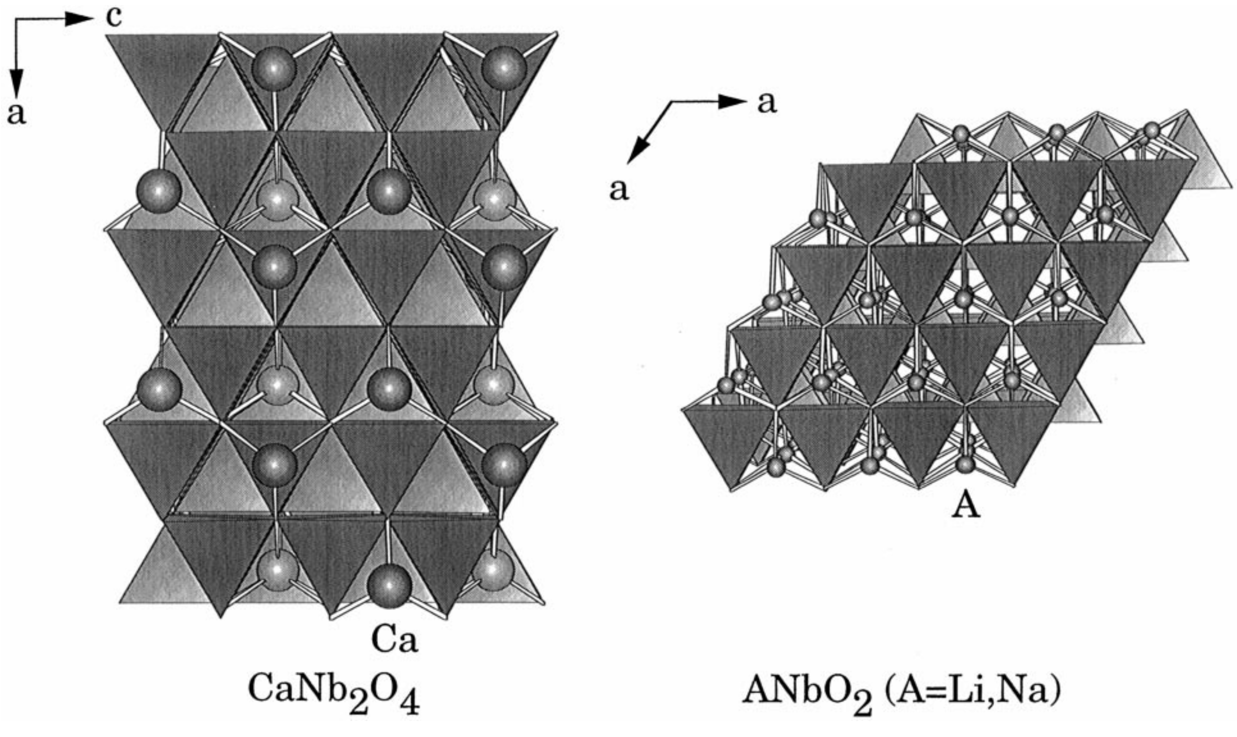

**FIG. 2.** Comparison between crystal structures of $CaNb_2O_4$ and $ANbO_2$ ($A$ = Li, Na).

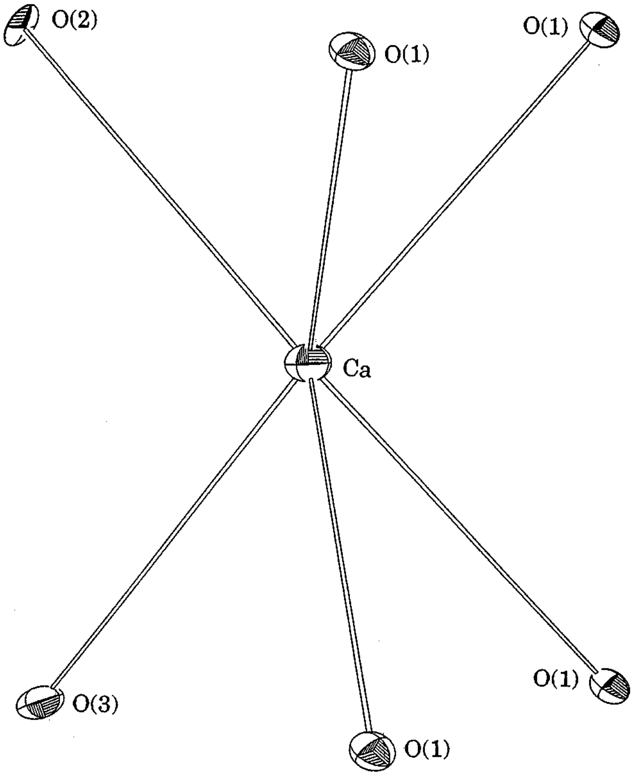

FIG. 3. ORTEP drawing (50% thermal ellipsoids) of coordination environment around calcium atom.

thicknesses of $(NbO_2)_n$ and $(AO_2)_n$ are estimated by the position of oxygen. The values for $ANbO_2$ ($A$ = Li, Na) are calculated from the latest data determined by single crystal X-ray diffraction analysis (23). The Nb–Nb distances (2.908–2.955) found in $ANbO_2$ and $CaNb_2O_4$ are somewhat longer than those (2.7–2.8 Å) in the $[Nb_6O_{12}]O_6$ clusters and that (2.578 Å) for a pair of metal–metal bonding in $Ca_{0.75}Nb_3O_6$ (18). $NaNbO_2$ has the longest Nb–Nb distance among the related compounds, and correspondingly the Nb–O–Nb angle is larger than those of the other two. As a result both values of the Nb–O distance and the thickness of the $(NbO_2)_n$ sheet become smaller than others. The values of these distances for $LiNbO_2$ and $CaNb_2O_4$ are similar to each other. This feature of the $(NbO_2)_n$ sheet in $NaNbO_2$ may be caused by the content of the interlayer space. The alkaline ions in $ANbO_2$ ($A$ = Li, Na) locate at the octahedral sites in the interlayer and the $AO_6$ octahedra in the interlayer are edge-shared each other. The Na–Na distance of 2.955 Å is short when compared with the Ca–Ca distance of 3.510 Å in $CaNb_2O_4$, taking into account that Shannon's ionic radius (24) for $Na^+$ and $Ca^{2+}$ ions with octahedral coordination is 1.02 and 1.00 Å, respectively. Furthermore, the amount of $Na^+$ ions in the interlayer is twice that of $Ca^{2+}$ ions. The repulsion between $Na^+$ ions in the interlayer must extend the O–O distances parallel to the layer. Then the Nb–Nb bonding distance becomes long and the O–O distances perpendicular to the Nb–Nb bonding and the Nb–O distance are shortened. Similar deformation of the $(NbO_2)_n$ sheet, elongation of the Nb–Nb distance accompanied with shortening of the O–O distance perpendicular to the Nb–Nb bonding, was observed in deintercalation of $Li^+$ ions and hence oxidation of the Nb–Nb bonding for $LiNbO_2$ (25).

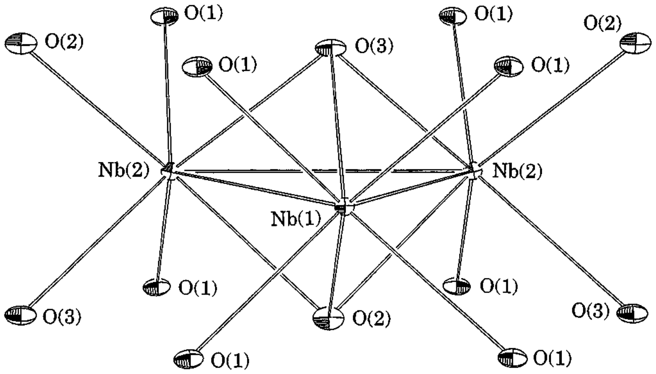

FIG. 4. ORTEP drawing (50% thermal ellipsoids) of coordination environment around niobium atoms.

**TABLE 4**

**Interatomic Distances (Å), Angles (°), and Thickness (Å) of the Sheet and Interlayer Space for $ANbO_2$ ($A$ = Li, Na) and $CaNb_2O_4$**

| Compound | $A$–O | $(AO_2)_n$ | $A$–$A$ | Nb–O | $(NbO_2)_n$ | Nb–Nb | Nb–O–Nb |
|---|---|---|---|---|---|---|---|
| $LiNbO_2$ | 2.121 | 2.594 | 2.908 | 2.136 | 2.640 | 2.908 | 85.8 |
| $NaNbO_2$ | 2.375 | 3.303 | 2.955 | 2.121 | 2.520 | 2.955 | 88.3 |
| $CaNb_2O_4$ | 2.366[a] | 3.320[a] | 3.510 | 2.135[a] | 2.628[a] | 2.919[a] | 86.5[a] |

[a] Mean value.

The magnetic susceptibility of $CaNb_2O_4$ was measured in the temperature range from 2.0 to 300 K. Although the very weak diamagnetism below 5.0 K caused by NbO impurity was observed, no evidence for superconductivity was found. The temperature independent paramagentism was observed and the magnitude of the magnetic susceptibility was on the order of $10^{-4}$ (emu/mol), like $Li_xNbO_2$ (25).

Soft-chemical reaction with $CaNb_2O_4$ and replacement of $Ca^{2+}$ with other metal ions such as rare-earth metals are now under investigation.

## CONCLUSION

A new reduced calcium niobium oxide, $CaNb_2O_4$, was prepared and its crystal structure was determined by using single crystal X-ray diffraction data. This compound has the layer with the infinite Nb–Nb bondings as seen in $A\text{NbO}_2$ ($A = \text{Li, Na}$) and the $Ca^{2+}$ ion is located at the trigonal prism site in the interlayer.

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## REFERENCES

1. N. Kumada, N. Kinomura, R. Wang, and A. W. Sleight, *Mater.Res. Bull.* **29,** 41 (1994).
2. J. Köhler and A. Simon, *Z. Anorg. Allg. Chem.* **572,** 7 (1989).
3. M. J. Geselbracht and A. M. Stacy, *J. Solid State Chem.* **110,** 1 (1989).
4. J. Xu, T. Emge, and M. Greenblatt, *J. Solid State Chem.* **123,** 21 (1996).
5. S. J. Hibble, A. K. Cheetham, J. Köhler, and A. Simon, *J. Less-Common. Metals* **154,** 271 (1989).
6. R. Burnus, J. Köhler, and A. Simon, *Z. Naturforsch* **426,** 536 (1987).
7. G. Svensson, *J. Solid State Chem.* **90,** 249 (1991).
8. G. Svensson and L. Eriksson, *J. Solid State Chem.* **114,** 301 (1991).
9. B. Hessen, S. A. Sunshine, T. Siegrist, A. T. Fiory, and J. V. Waszczak, *Chem. Mater.* **3,** 528 (1991).
10. J. Köhler, R. Tischtau, and A. Simon, *J. Chem. Soc. Dalton Trans.* **1991,** 829 (1991).
11. G. Meyer and R. Hoppe, *Angew. Chem.* **86,** 819 (1974).
12. G. Meyer and R. Hoppe, *Z. Anorg. Allg. Chem.* **424,** 128 (1976).
13. M. J. Geselbracht, Th. J. Richardson, and A. M. Stacy, *Nature* **345,** 324 (1990).
14. M. A. Rzeznik, M. J. Geselbracht, M. S. Thompson, and A. M. Stacy, *Angew. Chem.* **105,** 277 (1993).
15. M. Serafin and R. Hoppe, *J. Less-Common. Metals* **76,** 299 (1989).
16. J. P. Cummings and S. H. Simonsen, *Am. Miner.* **55,** 90 (1970).
17. Molecular Structure Corporation, "TEXSAN," The Woodlands, TX, 1993.
18. S. J. Hibble, A. K. Cheetham, and D. E. Cox, *Inorg. Chem.* **26,** 2839 (1987).
19. P. Alemany, V. G. Zubkov, S. Alvarez, V. P. Zhukov, V. A. Pereliaev, I. Kontsevaya, and A. Tyutyunnik, *J. Solid State Chem.* **105,** 27 (1993).
20. M. P. Rogge, J. H. Caldwell. D. R. Ingram, C. E. Green, M. J. Geselbracht, and T. Siegrist, *J. Solid State Chem.* **141,** 338 (1998).
21. D. F. Becker and J. S. Kasper, *Acta. Cryst.* **10,** 332 (1957).
22. W. Hoekner and B. Mueller, *Z. Naturforsch, B* **31,** 1710 (1976).
23. H. F. Roth, G. Meyer, Z. Hu, and G. Kaindl, *Z. Anorg. Allg. Chem.* **619,** 1369 (1993).
24. R. D. Shannon, *Acta. Cryst. A* **32,** 751 (1976).
25. N. Kumada, S. Muramatsu, F. Muto, N. Kinomura, S. Kikkawa, and M. Koizumi, *J. Solid State Chem.* **73,** 33 (1988).