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A New Synthetic Route to Pseudo-Brookite-Type $CaTi_2O_4$

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A new synthetic route to the reduced calcium titanate $CaTi_2O_4$ has been discovered. Single crystals of $CaTi_2O_4$ were grown by the reduction of $CaTiO_3$ with Ti metal powder in a $CaCl_2$ flux under flowing nitrogen at 1000°C. The pseudo-brookite-type structure of $CaTi_2O_4$ was redetermined from single crystal X-ray diffraction data and refined to an *R* value of 0.016. $CaTi_2O_4$ crystallizes in the orthorhombic space group *Bbmm*: $a = 9.718(4)$ Å, $b = 9.960(4)$ Å, and $c = 3.140(2)$ Å with four formula units per unit cell. The structure is built up from edge-sharing chains of TiO_6 octahedra that condense to form one-dimensional tunnels in which the calcium atoms are located. This new synthetic route provides a simple method of obtaining high quality samples of $CaTi_2O_4$ for further study. © 1998 Academic Press

INTRODUCTION

The discovery of high temperature superconductivity in 1986 renewed an interest in understanding structure-property relationships in various classes of mixed metal oxides. The class of oxides that we have been investigating includes the ternary reduced titanates. Two notable members of this class are the superconductors, $SrTiO_{3-x}$ ($T_c \sim 0.5$ K) (1, 2) and $Li_{1+x}Ti_{2-x}O_4$ ($T_c \sim 13$ K) (3, 4). While many interesting examples of new reduced titanates have been reported recently in the literature (5–8), the electronic and magnetic properties of these compounds are often unknown. One obstacle to obtaining this information lies in the difficult synthetic routes that are reported for these materials. We have been investigating alternative synthetic routes to ternary reduced titanates that can easily yield high quality samples for further study.

One such titanate that we have focused on is $CaTi_2O_4$, which was first prepared and structurally characterized in 1956 by Bertaut and Blum (9). The electronic and magnetic properties of this Ti(III) oxide are still unknown. Crystals of $CaTi_2O_4$ were originally grown by electrolysis of TiO_2 at Pt electrodes in molten $CaCl_2$. Electrolysis was also used by Bright *et al.* a few years later to grow crystals of $CaTi_2O_4$ starting from $CaTiO_3$ in molten $CaCl_2$ (10). However, neither of these previous reports provide detailed experimental information and attempts to repeat this work in our lab have been unsuccessful (11, 12). We report here a new and simple route to high quality crystals of $CaTi_2O_4$ that can be used for further study. A preliminary account of this work was published previously (13). Given the advances in crystallography since the original structure was reported over 40 years ago, we have also redetermined the crystal structure of $CaTi_2O_4$ and obtained an excellent refinement of the structural model, the results of which are reported below.

EXPERIMENTAL

Titanium metal powder (Cerac, −325 mesh, 99.5%), $CaTiO_3$ (Aldrich, −325 mesh, 99+%), and TiO (Cerac, −325 mesh, 99.9%) were all used as received from the supplier. Reagent grade anhydrous $CaCl_2$ was subjected to further drying by heating at 150°C under vacuum for 6–12 h. A Lindberg tube furnace equipped for flow of an inert atmosphere was used for all the reactions described below. The tube furnace was fitted with a mullite processing tube (74 × 78mm, ID × OD), which was sealed at both ends with stainless steel Universal Seals (Vesuvius McDanel), drilled and tapped for gas inlet and outlet ports.

In a typical reaction to form $CaTi_2O_4$, equimolar quantities of Ti metal powder and $CaTiO_3$ (typically 0.185 g (3.86 mmol) Ti and 0.525 g (3.86 mmol) $CaTiO_3$) were ground together with 6.00 g (54.1 mmol) dried $CaCl_2$ in a nitrogen-filled glove bag. The mixture was poured into an alumina combustion boat ($l \times w \times h$: 94 mm × 19 mm × 12 mm), and a barrier layer of approximately 3.00 g (27.0 mmol) pure $CaCl_2$ was added on top of the reaction mixture to prevent the surface reaction of titanium with N_2 gas at high temperatures. The reaction boat was then removed from the glove bag and quickly inserted into a tube furnace through which nitrogen or argon gas was flowing. After purging the tube furnace with inert gas for 15 min, the temperature was raised from 200°C to 1000°C at 20°/min,

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held at 1000°C for 6 h, and then cooled to 700°C at 2°/min. The furnace was then turned off and allowed to cool to 200°C at the maximum rate (approximately 5°/min). At this point, the reaction boat was removed and submerged in a beaker of deionized water. The water in the beaker was slowly stirred to dissolve the $CaCl_2$ flux, and the black solid product was isolated by suction filtration. The predominant phase in the product was $CaTi_2O_4$, identified by X-ray powder diffraction.

Variations on the ideal reaction described above were carried out in attempts to prepare single-phase $CaTi_2O_4$. The concentration of the reactants in the molten salt flux was varied, as well as the molar ratio of $CaTiO_3$ to Ti metal. Reactions of $CaTiO_3$ and TiO in molten $CaCl_2$ were also investigated. In all of these cases, the general procedure was similar to the one described above.

To investigate the effect of reaction time on the formation of products, a stainless steel wire harness was wrapped snugly around the reaction boat and fed through a T-junction located at the gas inlet port. After a specified time at 1000°C, the reaction was quenched by quickly pulling the reaction boat to the cool end of the furnace ($\sim$330°C) under a positive flow of nitrogen. At this point, the flow rate of nitrogen was increased to expedite cooling of the reaction boat. The products of these quenched reactions were isolated in the standard manner.

Since the reactions did not lead to single-phase $CaTi_2O_4$, we developed methods to separate the products and obtain highly purified samples of $CaTi_2O_4$ crystals. Unreacted $CaTiO_3$, present as a fine beige powder, was removed by resuspending the solid products in a large test tube of deionized water. The test tube was sonicated in an ultrasonic cleaner for 30 s and then allowed to stand for 30 s, during which time the larger crystals of $CaTi_2O_4$ settled to the bottom of the test tube. The supernatant, containing the fine $CaTiO_3$ powder in suspension, was then decanted into another beaker. This process was repeated several times until the supernatant over the $CaTi_2O_4$ crystals was clear. Examining the remaining insoluble products under a low magnification microscope (1–7 × magnification) revealed the predominant bluish-black crystalline needles of $CaTi_2O_4$, as well as golden polycrystalline clumps of TiO. The TiO impurities were separated from the $CaTi_2O_4$ crystals by passing the mixture through a 325 mesh (44 μm) stainless steel sieve. The smaller particles of TiO and the smallest crystals of $CaTi_2O_4$ passed through the sieve, leaving fairly pure samples of larger $CaTi_2O_4$ crystals behind. The final stages of purification were carried out by a simple but effective method. A very small amount of the sample to be purified was sprinkled over a piece of weighing paper. The paper was then held in a vertical position and gently tapped. This dislodged the impurities as well as some $CaTi_2O_4$ but, due to an electrostatic attraction, a significant amount of $CaTi_2O_4$ crystals remained on the weighing paper. The purified crystals were then removed from the weighing paper with a spatula. This process was repeated until no impurities could be visually detected under a low magnification microscope. The purity of samples was confirmed by X-ray powder diffraction.

TABLE 1
Crystallographic Data and Experimental Parameters at 23°C for $CaTi_2O_4$

$a = 9.718(4)$ Å	Crystal size: $0.04 \times 0.01 \times 0.14$ mm
$b = 9.960(4)$ Å	$\lambda = 0.70932$ Å
$c = 3.140(2)$ Å	ρ(calc) = 4.368 g cm^{-3}
$\alpha = \beta = \gamma = 90°$	μ(calc) = 6.69 mm^{-1}
$V = 303.9(3)$ Å^3	$R_F = 0.016$
$Z = 4$	$R_w = 0.018$
FW = 199.88	GOF = 0.21
Space group: *B bmm*	

X-ray powder diffraction data were obtained on a Scintag XDS 2000 diffractometer using copper K_α radiation. For the refinement of lattice parameters, silicon powder was added to diffraction samples as an internal standard. A purified sample of $CaTi_2O_4$ was checked for superconductivity by measuring the magnetic susceptibility at 1.8 K using a Quantum Design SQUID magnetometer in an applied field of approximately 20 G.

Single-crystal intensity data were collected on a Nonius diffractometer at 23°C using the omega scan mode. Unit cell dimensions, $a = 9.718(4)$ Å, $b = 9.960(4)$ Å, and $c = 3.140(2)$ Å, were obtained from 31 reflections with $50° \leq 2\theta \leq 60°$. Other relevant crystal parameters are summarized in Table 1.

Intensities for 3139 reflections were measured ($0 \leq h \leq 15$, $0 \leq k \leq 15$, $0 \leq l \leq 4$, $2\theta < 70°$). A Gaussian integration absorption correction was applied to all measured reflections. The structure was refined in the orthorhombic space group *Bbmm*. Averaging yielded 394 unique reflections. The original structural model proposed by Bertaut and Blum (9) provided the starting point for the refinement. All atoms were subsequently refined with anisotropic thermal parameters. The final atom positions are listed in Table 2 and anisotropic thermal parameters are listed in Table 3. The final residuals for 26 variables refined against the 287 significant reflections with $I_{net} > 2.5\,\sigma(I_{net})$ were $R = 0.016$ and $R_w = 0.018$. A list of the values of F_0 and F_c is available as supplementary material.[2]

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[2] See NAPS document No. 05487 for 6 pages of supplementary material. This is not a multi-article document. Order from NAPS c/o Microfiche Publications, 248 Hempstead Turnpike, West Hempstead, New York 11552. Remit in advance in U.S. funds only $15.00 for photocopies or $5.00 for microfiche. There is a $25.00 invoicing charge on all orders filled before payment. Outside U.S. & Canada add postage of $4.50 for the first 20 pages and $1.00 for each ten pages of material thereafter, or $5.00 for the first microfiche and $1.00 for each fiche thereafter.

TABLE 2
Atomic Positional Parameters and Isotropic Temperature Factors for $CaTi_2O_4$

Atom	x	y	z	B_{iso} (Å^2)
Ca	0.38164(7)	0.250	0.000	0.45(2)
Ti	0.12705(5)	0.06454(4)	0.000	0.327(14)
O1	0.500	0.000	0.000	0.52(8)
O2	0.0593(3)	0.250	0.000	0.44(8)
O3	0.23025(18)	− 0.10611(18)	0.000	0.37(5)

RESULTS AND DISCUSSION

Synthesis

Combining equimolar quantities of $CaTiO_3$ and Ti metal powder in a $CaCl_2$ flux at 1000°C led to the formation of bluish-black crystalline needles (~ 1-mm long) of $CaTi_2O_4$. The successful isolation of $CaTi_2O_4$ depended critically on the method used to dry the $CaCl_2$ prior to the reaction. When the reaction was carried out in $CaCl_2$ that had been dried overnight in an oven at 130°C, a dark gray powder was obtained. The X-ray diffraction pattern of this powder identified $CaTiO_3$ as the major product. If instead, the $CaCl_2$ was dried overnight under vacuum at 150°C, $CaTi_2O_4$ was the major product identifiable in the X-ray diffraction pattern. This new synthetic route provides a straightforward method of preparing large samples of crystalline $CaTi_2O_4$.

The molten salt flux provides an effective reaction medium for the preparation of $CaTi_2O_4$. The solid state reaction of equimolar quantities of $CaTiO_3$ and Ti metal, sealed in an evacuated quartz tube and treated to the same firing conditions at 1000°C, led to recovery of the starting materials as indicated by powder X-ray diffraction. Although the molten salt flux is a necessary component, the exact role that the flux plays in the reaction is not clear. When a mixture of $CaTiO_3$ and Ti metal was placed between two layers of pure $CaCl_2$, rather than mixing the reactants with the $CaCl_2$ prior to reaction, no $CaTi_2O_4$ was isolated. Furthermore, after reaction, the products were not dispersed throughout the frozen salt matrix but remained in the same physical location as the initial reactants. Clearly, thoroughly mixing the flux and reactants prior to melting is essential for the synthesis of $CaTi_2O_4$.

TABLE 3
Anisotropic Temperature Factors (×100) for $CaTi_2O_4$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca	0.65(3)	0.66(3)	0.42(3)	0.0	0.0	0.0
Ti	0.437(16)	0.445(17)	0.363(18)	0.082(17)	0.0	0.0
O1	0.58(9)	1.00(11)	0.39(11)	− 0.24(9)	0.0	0.0
O2	0.54(9)	0.47(10)	0.65(11)	0.0	0.0	0.0
O3	0.51(6)	0.43(7)	0.45(8)	− 0.04(6)	0.0	0.0

The molten salt flux route provides a simple method for preparing $CaTi_2O_4$; however, the stoichiometry of the reactants dictates that the product of the reaction is not single-phase. The two most common impurities were $CaTiO_3$ and TiO. The presence of TiO is not surprising since the combination of equimolar amounts of Ti^{IV} and Ti^0 should lead to an average valence of Ti^{II} in the products. Attempts to adjust the stoichiometry of the reactants to produce an average valence of Ti^{III} in the products did not yield any $CaTi_2O_4$. This was most likely due to the uncontrolled oxidation of Ti metal by small amounts of water remaining in the salt flux. Our results suggest that once the Ti metal is oxidized to TiO, the reaction halts. Although the reaction of $CaTiO_3$ and TiO should lead cleanly to $CaTi_2O_4$, we have verified experimentally that this reaction does not proceed in molten $CaCl_2$ at 1000°C. An excess of Ti metal, specifically equimolar amounts of $CaTiO_3$ and Ti, is required to form significant amounts of $CaTi_2O_4$ under our conditions.

In our efforts to optimize the conditions for preparing $CaTi_2O_4$, we have investigated the effects of time and temperature on the molten salt reaction of $CaTiO_3$ and Ti metal. A reaction temperature of 1000°C appears to be optimal in molten $CaCl_2$, since reactions carried out at 880°C and at 950°C failed to produce any $CaTi_2O_4$. To explore the effect of reaction time, we conducted a series of quenching experiments in which the reaction boat was fired at 1000°C for a designated amount of time and then quickly moved to a region of the furnace where the temperature was ~330°C (m.p. $CaCl_2$ = 782°C). We estimate that the reaction mixture cooled from 1000°C to 330°C in approximately 5 min. When the temperature of the reaction boat was raised to 1000°C followed by an immediate quench, powder X-ray diffraction revealed that the products consisted of $CaTiO_3$, Ti metal, and TiO. The presence of TiO confirms the rapid uncontrolled oxidation of Ti metal at elevated temperatures. Quenching the reaction mixture after 15 min at 1000°C resulted in the same products identifiable in the X-ray diffraction pattern. However, we were able to visually identify bluish-black crystalline needles of $CaTi_2O_4$ under an optical microscope. Similar results were found after a reaction time of 30 min at 1000°C. After 60 min at 1000°C, the fraction of crystalline needles in the products was visibly larger and $CaTi_2O_4$ was also identifiable in the diffraction pattern. Our typical reactions, carried out for 6 h at 1000°C, produced $CaTi_2O_4$ as the major product. These results confirm that the growth of well-formed $CaTi_2O_4$ crystals occurs fairly rapidly in molten $CaCl_2$ and that shorter reaction times (≤ 6 h) are desirable to minimize any uncontrolled oxidation of the product.

Characterization

Although we have not been able to produce single-phase samples of $CaTi_2O_4$ directly by this new synthetic route, we have been able to prepare pure samples by physical separation techniques (see Experimental). In this reaction, $CaTi_2O_4$ typically formed as crystalline needles with an average length of 0.5–1.5 mm, whereas the $CaTiO_3$ and TiO impurities were polycrystalline powders. This difference in morphology was the primary basis for the separations. The success of the purification techniques was measured by the phase purity of the X-ray powder diffraction patterns. The X-ray diffraction pattern of a typical sample of purified $CaTi_2O_4$ is shown in Fig. 1, along with the simulated diffraction pattern calculated from the single crystal structure of $CaTi_2O_4$. All of the reflections in the experimental diffraction pattern can be assigned to $CaTi_2O_4$, and the refined lattice parameters ($a = 9.744(3)$ Å, $b = 9.989(3)$ Å, $c = 3.149(1)$ Å) agree well with those previously reported in the literature (9, 10).

Due to the similarity in composition of $CaTi_2O_4$ to the superconducting lithium titanate, $Li_{1+x}Ti_{2-x}O_4$ ($T_c \sim$ 13 K) (3, 4), we were very interested in characterizing the properties of $CaTi_2O_4$. Measurements of the magnetic susceptibility indicated that $CaTi_2O_4$ is paramagnetic from room temperature down to 1.8 K. Thus, $CaTi_2O_4$ does not superconduct at these temperatures. Of course, it is important to point out that the structure of $CaTi_2O_4$ is very different from the spinel structure of $LiTi_2O_4$ and that $LiTi_2O_4$ contains mixed-valent Ti(III)/Ti(IV), whereas $CaTi_2O_4$ contains Ti(III). Whether one or both of these differences is significant is unclear; however, we believe that the answer to this question would provide valuable insight to the search for new superconducting titanium oxides. We are currently carrying out a more extensive analysis of the magnetic properties of $CaTi_2O_4$ from 5–700 K.

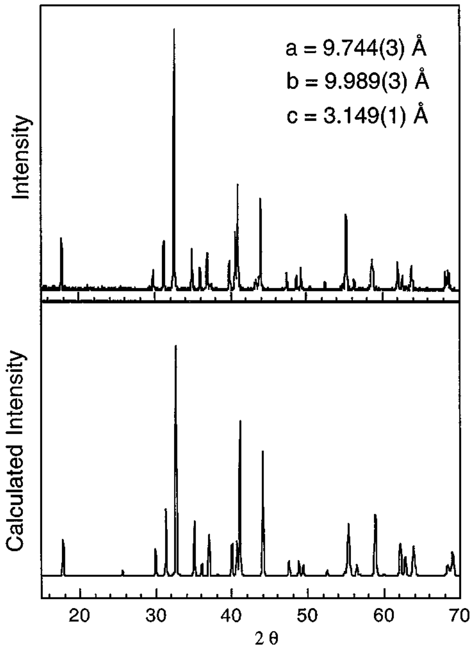

FIG. 1. X-ray powder diffraction pattern of a sample of $CaTi_2O_4$ purified by physical separation techniques (top) and the calculated X-ray diffraction pattern (bottom) based on the structural model refined from single crystal diffraction data.

Single Crystal Diffraction

In 1956, Bertaut and Blum (9) were unable to synthesize enough $CaTi_2O_4$ to carry out any chemical analysis. Therefore, the single crystal structure was solved without any knowledge of the chemical formula, a significant achievement for that time. In the final stage of refinement, single thermal parameters were used for each of the atoms, resulting in an R value of 0.16. Given this level of refinement, we decided to redetermine the crystal structure of $CaTi_2O_4$ with a crystal grown by our new synthetic route.

The results of our single crystal structure determination confirmed the structural model for $CaTi_2O_4$ first proposed by Bertaut and Blum (9). Our refinement, including anisotropic thermal parameters for all of the atoms, resulted in a final R value of 0.016, an order of magnitude better than the previous work. The structure of $CaTi_2O_4$, shown in Fig. 2, is built up from double rutile chains of edge-sharing TiO_6 octahedra. Parallel double rutile chains also share edges to form puckered layers of TiO_6 octahedra that lie perpendicular to the b axis. These layers stack up along the b direction; each layer is connected to its mirror image by corner-sharing. This condensation of double rutile chains

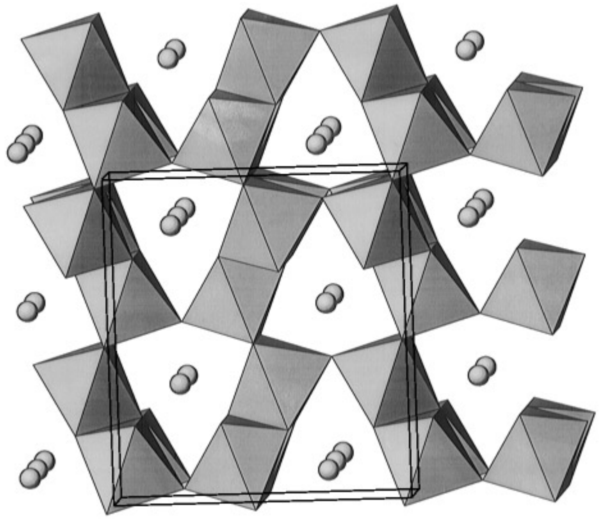

FIG. 2. The structure of $CaTi_2O_4$, viewed along the c direction. The shaded polyhedra represent TiO_6 octahedra, and calcium atoms located in one-dimensional tunnels are represented by circles.

TABLE 4
Selected Interatomic Distances (Å) and Bond Angles (°) for $CaTi_2O_4$

Ti–O1 (×2)	2.0982(9)	O1–Ti–O1	96.88 (4)
Ti–O2	1.961 (1)	O1–Ti–O2 (×2)	95.21 (5)
Ti–O3	1.974 (2)	O1–Ti–O3 (×2)	83.77 (5)
Ti–O3 (×2)	2.135 (1)	O1–Ti–O3 (×2)	92.01 (4)
Ca–O1 (×2)	2.743 (1)	O2–Ti–O3 (×2)	92.04 (7)
Ca–O2	3.133 (3)	O3–Ti–O3	94.66 (8)
Ca–O2 (×2)	2.333 (2)	O3–Ti–O3 (×2)	80.62 (6)
Ca–O3 (×4)	2.388 (2)	O1–Ti–O3 (×2)	172.63 (5)
Ti–Ti	2.784 (1)	O2–Ti–O3	169.09 (9)
Ti–Ti	3.135 (1)	O2–Ca–O3 (×4)	83.94 (6)
Ti–Ti	3.140 (2)	O3–Ca–O3 (×2)	73.77 (6)

results in one-dimensional tunnels running along the *c* direction in which the calcium atoms are located. The anisotropic, one-dimensional tunnel structure is reflected in the morphology of the $CaTi_2O_4$ crystals; the crystal needle axis corresponds to the *c* axis.

The coordination geometries around the calcium and titanium atoms can be described as trigonal prismatic and octahedral, respectively, although the polyhedra are distorted. Selected bond distances and bond angles are listed in Table 4. There are six short Ca–O bond lengths that define the trigonal prism, two at 2.333(2) Å and four at 2.388(2) Å. In addition, there are three longer contacts to oxygen atoms, capping the rectangular faces of the trigonal prism, two at 2.743(1) Å and one at the very long distance of 3.133(3) Å. The distorted octahedral geometry around the titanium atom is characterized by bond lengths ranging from 1.961(1) to 2.135(1) Å and bond angles severely distorted from the ideal values (for example, O3–Ti–O3 = 80.62(6)°, ideal angle = 90°).

CONCLUSION

We have discovered a new synthetic route to $CaTi_2O_4$ in molten $CaCl_2$. While this route does not lead directly to single-phase samples, $CaTi_2O_4$ grows as well-formed crystalline needles, which can be easily separated from the other products. Therefore, large quantities of crystalline $CaTi_2O_4$ can easily be prepared for further study. We are currently investigating the electrical and magnetic properties of $CaTi_2O_4$, as well as its chemical reactivity.

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