

A Reduced Neodymium Titanate with a New Intergrowth Structure Type

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Single crystals of a new reduced neodymium titanate, $\text{Nd}_3\text{Ti}_4\text{O}_{12}$, have been obtained by slow cooling of a reduced Nd–Ti–O ceramic precursor in a molten neodymium borate flux under high vacuum. Single crystal X-ray diffraction (space group $Pcmn$, $a = 5.420(1) \text{ \AA}$, $b = 7.610(1) \text{ \AA}$, $c = 22.015(5) \text{ \AA}$, $Z = 4$, Pearson symbol $oP76$) showed that the structure of $\text{Nd}_3\text{Ti}_4\text{O}_{12}$ is built from an arrangement of corner-sharing and edge-sharing TiO_6 -octahedra that can be considered as a regular intergrowth of the GdFeO_3 and CaTa_2O_6 structure types. The material is nonmetallic ($R(25^\circ\text{C}) = 35 \text{ \Omega cm}$) which may arise due to the localization of the Ti 3d-electrons in the edge-sharing pairs of TiO_6 -octahedra (short Ti–Ti distance of $2.760(3) \text{ \AA}$). © 1993 Academic Press, Inc.

Introduction

The Ti(III) rare earth ternary oxides LnTiO_3 ($\text{Ln} = \text{La, Nd, Sm, Gd}$) are known to have a distorted orthorhombic perovskite structure of the GdFeO_3 -type (1). Apart from the defect perovskite series $\text{La}_{2/3+x}\text{TiO}_3$ (2), few other rare-earth containing reduced ternary titanates are known. Recently we prepared a new reduced La–Ti–O compound, $\text{La}_{1.33}\text{Ti}_8\text{O}_{16}$ with the hollandite structure, from a LaTiO_3 ceramic and a lanthanum borate flux (3). We also investigated the use of ceramic precursors with lower rare earth content. A significant difference in behavior between the La–Ti–O and Nd–Ti–O systems is observed in that case. Here we present the synthesis and crystal structure of a new reduced neodymium titanate, $\text{Nd}_3\text{Ti}_4\text{O}_{12}$, with a structure derived from intergrowth of the GdFeO_3 and CaTa_2O_6 structure types. Similar attempts to prepare a La–Ti–O analogue only produced crystals of the $\text{La}_{2/3+x}\text{TiO}_3$ defect perovskite.

Ordered intergrowth of two different structure types has been observed in a num-

ber of systems, frequently giving rise to homologous series with varying sizes of the blocks corresponding to the two structure types. Well known examples are the Ruddlesden–Popper series, with SrTiO_3 and SrO layer intergrowth (4), and the intergrowth of BaZnF_4 and GdFeO_3 structure types in the Ca–Na–Nb–O and Ca–La–Ti–O systems (5). It is conceivable that intergrowth of the GdFeO_3 and CaTa_2O_6 structure types can also give rise to a homologous series.

Experimental

Sample Preparation

Ceramic titanate precursors with nominal composition “ $\text{Ln}_{0.33}\text{Ti}_2\text{O}_4$ ” were prepared from pressed pellets of Ln_2O_3 , Ti_2O_3 (Alfa), and TiO_2 (Aldrich) in the appropriate stoichiometry (9 mmole Ti/pellet). As mineralizer $\text{Ln}_2\text{O}_3 \cdot 3\text{B}_2\text{O}_3$ was added in the molar ratio of Nd:Ti: $\text{B}_2\text{O}_3 = 1.3:1.0:1.7$. The pellets were wrapped in Mo-foil and heated *in vacuo* to 1200°C for 24 hr. X-ray powder diffraction showed that they consisted

mainly of Ti_2O_3 and $\text{Ln}_{2/3+x}\text{TiO}_3$ -type perovskites.

Borates $\text{Ln}_2\text{O}_3 \cdot 3\text{B}_2\text{O}_3$ were prepared from $\text{La}(\text{OH})_3$ (Alfa) or Nd_2O_3 (Aldrich) with B_2O_3 (Fisher) in the appropriate ratio. The mixtures were heated at 950°C in alumina crucibles for 24 hr. Lanthanide sesquioxides were fired at 1000°C in air for 12 hr before use.

Mixtures of ceramic precursors of nominal composition " $\text{Ln}_{1/3}\text{Ti}_2\text{O}_4$ " ($\text{Ln} = \text{La}, \text{Nd}$) and $\text{Ln}_2\text{O}_3 \cdot 3\text{B}_2\text{O}_3$ in 1:3 weight ratio were placed in Mo-foil cups with Mo-foil lids. They were heated *in vacuo* (in a Centorr high-vacuum furnace) to 400°C to remove adsorbed water, and then to 1250°C (1 hr, 10^{-6} – 10^{-7} Torr). The mixtures were then cooled to 1140°C at $8^\circ\text{C}/\text{hr}$. The heater was subsequently turned off, allowing the sample to reach room temperature in approximately 1.5 hr. The mixtures were soaked in warm concentrated aqueous KOH for 12 hr, after which the products were mechanically broken up. For $\text{Ln} = \text{Nd}$ the product mixture consisted of dark blue crystalline aggregates showing in places well-developed rectangular crystal faces, together with small crystals of Ti_2O_3 and a pink transparent crystalline flux. The blue product was determined by single crystal X-ray diffraction on several cleaved crystal fragments to be a new orthorhombic Nd-titanate, $\text{Nd}_3\text{Ti}_4\text{O}_{12}$. For $\text{Ln} = \text{La}$, a dark crystalline mass with jagged edges but with locally well-developed crystals with square faces had formed, together with small crystals of Ti_2O_3 and a colorless crystalline flux. X-ray diffraction on crystals and cleaved crystal fragments showed the dark crystalline product to be an ordered defect perovskite of the type $\text{La}_{2/3+x}\text{TiO}_3$.

A dc four-point resistivity measurement was performed on a single crystal of $\text{Nd}_3\text{Ti}_4\text{O}_{12}$. Silver wires were connected (with Ag/epoxy) to evaporated Au–Ge/Au strip contacts on the crystal.

Structure Determinations

The crystals were measured at 23°C on an Enraf–Nonius CAD-4 diffractometer using

graphite-monochromatized $\text{MoK}\alpha$ radiation and the NRCCAD program package (6). All calculations were carried out on an Alliant FX/80 computer, using the NRCVAX structure package (7). Lattice parameters were determined from the absolute 2θ values of reflections at a high angle ($\text{Nd}_3\text{Ti}_4\text{O}_{12}$: 30 reflections with $49^\circ < 2\theta < 58^\circ$, $\text{La}_{1/3+x}\text{TiO}_3$: 28 reflections with $50^\circ < 2\theta < 56^\circ$). The metal atom positions for $\text{Nd}_3\text{Ti}_4\text{O}_{12}$ were obtained by direct methods. A Gaussian absorption correction was applied. Anisotropic temperature factors for all atoms were included in the refinement. Crystallographic data are listed in Table I, atomic coordinates and isotropic thermal parameters in Table II.*

Crystals of $\text{La}_{2/3+x}\text{TiO}_3$ appeared to be primitive cubic with $a = 7.7837(3) \text{ \AA}$. It is likely that the material is actually a tetragonal defect perovskite with $c = 2a$ as described earlier for $\text{La}_{2/3}\text{TiO}_{2.954}$ (8). This also corresponds well with powder X-ray diffraction on crushed crystals. The doubling in all three dimensions as observed by single crystal X-ray diffraction is likely to be produced by twinning. From the observed cell parameter and comparison with the data for $\text{La}_{2/3+x}\text{TiO}_3$ of Kestigan and Ward (2), the composition of the crystals can be derived by interpolation to be approximately $\text{La}_{0.73}\text{TiO}_3$ ($x \approx 0.06$).

Description of the Structure

The structure of $\text{Nd}_3\text{Ti}_4\text{O}_{12}$ is shown in Fig. 1, projected along the b -axis. Pertinent

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TABLE I
CRYSTALLOGRAPHIC DATA FOR $\text{Nd}_3\text{Ti}_4\text{O}_{12}$

Formula	$\text{Nd}_3\text{Ti}_4\text{O}_{12}$
Space group	$Pcmn$
Crystal size (mm)	$0.12 \times 0.18 \times 0.12$
a (Å) (at 23°C)	5.4203(8)
b (Å)	7.6104(9)
c (Å)	22.105(5)
V (Å ³)	908.1(3)
Z	4
D_c (g/cm ³)	5.971
μ (MoK α , cm ⁻¹)	202.8
Minimum transmission	0.1079
Maximum transmission	0.2513
Scan type	$\omega/2\theta$
Reflections measured	2168
Independent reflections	2099
Observed reflections ($I > 2.5\sigma(I)$)	1670
Refined parameters	98
R	0.040
R_w ($w = 1/\sigma^2(F_o)$)	0.056
Extinction length (μm)	0.29(1)

interatomic distances are listed in Table III. The framework of the structure is formed by TiO_6 octahedra, arranged in puckered single and double ReO_3 -type chains running in the direction of the b -axis. The $\text{Ti}(1)\text{O}_6$ -octahedra make up the single chains, and share only corners with the neighboring octahedra. The $\text{Ti}(2)\text{O}_6$ -octahedra form the double chains as edge-sharing pairs, which

TABLE II
ATOMIC POSITIONAL PARAMETERS AND ISOTROPIC TEMPERATURE FACTORS FOR $\text{Nd}_3\text{Ti}_4\text{O}_{12}$

	x	y	z	B_{iso} (Å ²)
Nd(1)	0.93871(15)	0.25	0.19959(3)	0.464(20)
Nd(2)	0.45551(14)	0.75	0.02782(3)	0.471(19)
Nd(3)	0.92754(14)	0.75	0.17866(3)	0.394(18)
Ti(1)	0.4390(3)	0.49921(20)	0.17863(7)	0.38(4)
Ti(2)	0.9516(3)	0.48936(21)	0.06143(7)	0.43(4)
O(1)	0.2465(14)	0.4624(9)	0.0122(3)	0.53(19)
O(2)	0.6351(14)	0.5593(10)	0.1147(3)	0.69(21)
O(3)	0.7090(13)	0.5367(9)	0.2378(3)	0.48(19)
O(4)	0.1223(13)	0.4708(9)	0.1421(3)	0.43(19)
O(5)	0.4976(22)	0.25	0.1869(5)	0.9(4)
O(6)	0.3578(22)	0.75	0.1954(5)	0.7(3)
O(7)	0.8410(23)	0.25	0.0642(5)	0.8(3)
O(8)	0.0321(21)	0.75	0.0699(4)	0.5(3)

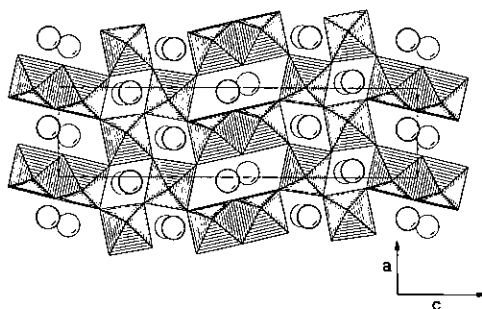


FIG. 1. Polyhedral representation of the structure of $\text{Nd}_3\text{Ti}_4\text{O}_{12}$, projected along the b -axis. Ti-O polyhedra are hatched; Nd-atoms are represented as circles.

share corners in the ac -plane with the $\text{Ti}(1)$ -octahedra. The structure can be described as a regular intergrowth of two known structure types: the GdFeO_3 -structure, which is an orthorhombic distortion of the perovskite structure (MO_6 -octahedra that are corner-sharing in three dimensions) (9) and the CaTa_2O_6 -structure, with M_2O_{10} -groups of edge-sharing octahedra linked together by corner sharing (10). All three independent Nd-atoms are located in eight-coordinate distorted bicapped-trigonal prismatic sites, as is also observed for the A-cation in the GdFeO_3 and CaTa_2O_6 structure types. The Nd(2)-atom, located between the puckered double ReO_3 -type chains, has a slightly

TABLE III
SELECTED INTERATOMIC DISTANCES (Å) FOR $\text{Nd}_3\text{Ti}_4\text{O}_{12}$ WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Ti(1)	-O(2)	1.822(7)	Ti(2)	-O(1)	1.942(7)	
	-O(3)	1.980(7)			1.979(7)	
		2.239(7)		-O(2)	2.145(7)	
	-O(4)	1.908(7)		-O(4)	2.007(7)	
	-O(5)	1.932(3)		-O(7)	1.919(4)	
	-O(6)	1.993(4)		-O(8)	2.040(3)	
Nd(1)	-O(3)	2.585(7)	2 ×	Nd(2)	-O(1)	2.449(7)
		2.649(7)	2 ×			2.489(7)
	-O(4)	2.328(7)	2 ×		-O(2)	2.591(7)
	-O(5)	2.411(1)			-O(7)	2.59(1)
	-O(6)	2.35(1)			-O(8)	2.47(1)
Nd(3)	-O(2)	2.570(8)	2 ×	Ti(2)	-Ti(2)	2.760(3)
	-O(3)	2.395(7)	2 ×			
	-O(4)	2.506(7)	2 ×			
	-O(6)	2.36(1)				
	-O(8)	2.461(9)				

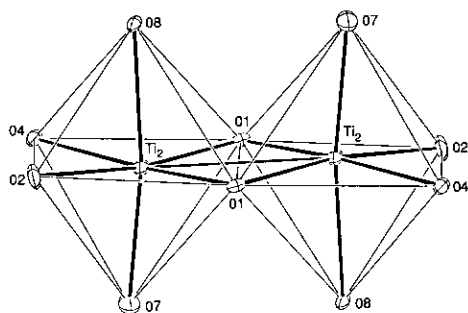


FIG. 2. ORTEP representation of the Ti_2O_{10} group in $\text{Nd}_3\text{Ti}_4\text{O}_{12}$. Thermal ellipsoids represented at the 50% probability level.

larger and more regular coordination sphere than the other Nd-atoms (average $\text{Nd}(2)\text{-O} = 2.515 \text{ \AA}$, with maximum deviations of -0.066 and $+0.076 \text{ \AA}$, for $\text{Nd}(1)$ 2.486 \AA and $+0.163/-0.158 \text{ \AA}$, for $\text{Nd}(3)$ 2.470 \AA and $+0.100/-0.110 \text{ \AA}$ respectively).

The average Ti–O distances in $\text{Nd}_3\text{Ti}_4\text{O}_{12}$ are 1.979 \AA for Ti(1) and 2.005 \AA for Ti(2) respectively. The average Ti–O distance for Ti(1) in the GdFeO_3 type block is significantly smaller than that observed in NdTiO_3 (2.022 \AA (I)). It is close to the value for $\text{Ti}^{4+}\text{-O}$ in rutiles (1.97 \AA). The coordination geometry around Ti(1) is also considerably more distorted, with sharp O–Ti–O angles ranging from 80.3° to 94.4° (in NdTiO_3 from 89.0° to 90.3° (I)). One notable feature in the structure is the distortion in the Ti_2O_{10} -groups. The Ti(2)-atoms are displaced from the center of the octahedra towards each other rather than away from each other (as might be expected from Coulomb repulsion). The geometry of this group is shown in Fig. 2. The Ti(2)–Ti(2) distance of $2.760(3) \text{ \AA}$ is quite short for a Ti–Ti distance in a pair of edge-shared octahedra. An interesting comparison can be made with the recently published crystal structure of the Ti(4+) compound $\text{Nd}_4\text{Ti}_9\text{O}_{24}$ in which edge-shared Ti_2O_{10} -pairs are also present (II). The average Ti–O distance in these groups are smaller than for Ti(2) in $\text{Nd}_3\text{Ti}_4\text{O}_{12}$, and typical for Ti(4+) ($1.973/1.978 \text{ \AA}$). However, the Ti–Ti distance in

the pairs (2.963 \AA) is 0.20 \AA longer than in $\text{Nd}_3\text{Ti}_4\text{O}_{12}$. The stoichiometry of $\text{Nd}_3\text{Ti}_4\text{O}_{12}$ obtained from X-ray diffraction indicates an average Ti oxidation state of $3.75+$; i.e., there is one $3d$ -electron per Ti_2O_{10} -pair. These $3d$ -electrons are possibly localized in orbitals associated with the Ti(2)–Ti(2) pairing. This would imply nonmetallic behavior of the material, at least at or below the temperature at which the structure was determined (23°C). At high temperatures a first-order transition to a metallic state may be anticipated. A low-temperature four-point resistivity measurement on a single crystal showed nonmetallic behavior (Fig. 3) with a room-temperature resistivity of 35 \Omega cm . Due to the small size of the crystal, only the conductivity along the b -axis could be measured. Anisotropy in the conductivity was expected due to the low symmetry of the crystal structure, but unfortunately could not be measured. Degradation of the very small contacts made data collection unreliable above room temperature. The $\ln(\rho)$ vs $1/T$ plot is nonlinear, suggesting that the material does not behave as an intrinsic semiconductor. The high-temperature data give an activation energy of 0.26 eV , but the fit is valid only over a rather small temperature range. A second fit, based on a hopping mechanism for the conduction with a $\rho \propto \rho_0$

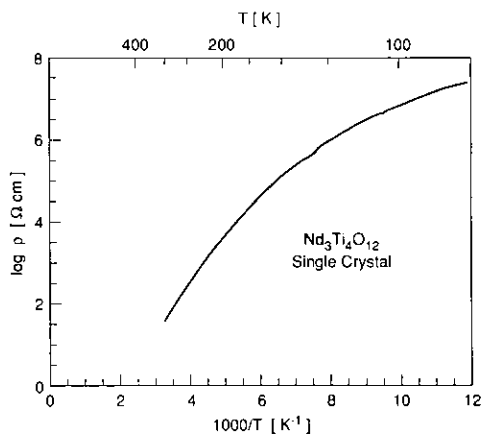


FIG. 3. Plot of $\log(\text{resistivity})$ vs $1000/T$ from a dc resistivity measurement on a $\text{Nd}_3\text{Ti}_4\text{O}_{12}$ single crystal.

$\exp(T_0/T)^{1/4}$, gives a critical temperature of $T_0 = 1.24 \times 10^6$ K. This fit extends over a larger temperature range, but at low temperature, the deviations are very pronounced. Further experiments would be needed to elucidate the mechanism of conductivity.

Discussion

It is observed that recrystallization of ceramics with nominal composition $Ln_{0.33}Ti_2O_4$ from $Ln_2O_3 \cdot 3B_2O_3$ fluxes ($Ln = La, Nd$) leads to two crystalline products: Ti_2O_3 and a ternary compound that is only partially reduced. The difference in ionic radius between La and Nd is relatively small (1.32 Å for La^{3+} , 1.26 Å for Nd^{3+} in eight-coordination (12)). However, this difference, under otherwise identical conditions, causes a drastic change in the structure of the ternary product, being an ordered defect perovskite for the La–Ti–O system and $Nd_3Ti_4O_{12}$ with the intergrowth structure as described above for the Nd–Ti–O system. This suggests a delicate dependence of the thermodynamics of these ternaries on the size of the A-cation. Also notable is the apparent absence of the $La_{1.33}Ti_8O_{16}$ hollandite phase that was obtained earlier from a more La-rich mixture (3). This can correspond with our findings in the Sr–Nb–O system that the occurrence of disproportionation reactions in ternary borate flux media is strongly dependent on the concentration of the common ion between the flux and the ternary transition metal oxide system (13).

Although currently $Nd_3Ti_4O_{12}$ is the only member of the ordered $GdFeO_3/CaTa_2O_6$ intergrowth type synthesized, it is possible to predict the existence of a homologous series based on this intergrowth principle. The general formula of such a series would be $Nd_{1+n}Ti_{2+n}O_{6+3n}$, of which $Nd_3Ti_4O_{12}$ is the $n = 2$ member. It is based on $GdFeO_3$ -blocks expanding in the c -direction between the edge-sharing pairs of octahedra of the

$CaTa_2O_6$ structure. The end members in the Nd–Ti–O system would be defined by $n = 1$ ($Nd_2Ti_3O_9, Ti^{4+}$) and $n = \infty$ ($NdTiO_3, Ti^{3+}$). The $n = \text{even}$ and $n = \text{odd}$ members differ in the orientation of the edge-sharing pairs relative to each other. In the $n = \text{even}$ members, sequential Ti_2O_{10} -blocks along the c -direction will be shifted over $a/2$, and canted in the opposite direction within the ac -plane (as in $Nd_3Ti_4O_{12}$). In the $n = \text{odd}$ members these blocks would not be shifted, and would have the same canting direction. Presently we are exploring the possibility of accessing members of this series by ceramic routes. Initial efforts were directed to prepare related Ti^{4+} ceramics, e.g., with composition $CaNd_2Ti_4O_{12}$ or $Nd_3Ti_3AlO_{12}$. As yet, these attempts have met with little success, yielding tetragonal defect perovskite type species as main products.

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