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A New Mixed-Metal Titanate. The Synthesis and Characterization of $Ba_2NiTi_5O_{13}$

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The new mixed-metal titanate $Ba_2NiTi_5O_{13}$, **1** was obtained in a crystalline form by heating a mixture of $BaCO_3$, $NiCO_3$, and TiO_2 at 1375 °C for 48 h. Compound **1** was characterized by single-crystal X-ray diffraction analysis. Magnetic susceptibility measurements reveal an effective magnetic moment at 5 K of 2.70 μ_B per nickel atom, 3.2 μ_B at 300 K. This is consistent with that of a Ni^{2+} ion in an octahedral environment. The temperature-dependent susceptibility in the temperature range 5–300 K was fitted to a modified Curie–Weiss expression, $\chi = C/(T - \theta_p) + \text{TIP}$, where $C = 0.948(3)$ emu K/mol, $\theta_p = -0.5(1)$ K, and $\text{TIP} = 1.20(1) \times 10^{-3}$ emu/mol. Crystal data for **1**: space group = $C2/m$, $a = 15.090(1)$ Å, $b = 3.9119(4)$ Å, $c = 9.1141(6)$ Å, $\beta = 98.500(6)°$, $Z = 2$, 846 reflections, $R = 0.032$.

Introduction

Alkali and alkaline-earth titanates have attracted attention for their use in ion-exchange processes,[2] for ceramic capacitors,[3] applications as dielectric resonators in microwave oscillators and bandpass filters,[3,4] and for their nonlinear optical properties.[5] The nonstoichiometric mixed metal titanate $La_{1-x}Ba_xTiO_3$ has been shown to exhibit unusual electrical and magnetic properties.[6] Alkali titanates exhibit a range of layered, corrugated layered, and tunnel-type structures in the solid state.[7] It occurred to us that it might be possible to prepare transition-metal-substituted titanates by replacing one or more of the Ti^{4+} ions in alkali titanates structures with transition-metal ions in lower oxidation states if one could simultaneously replace the alkali ions with alkaline earth ions in the 2^+ oxidation state. Such transition-metal-containing titanates might exhibit interesting magnetic properties due to the presence of the unpaired electrons on the transition metal ions. Our first successful demonstration of this concept is the synthesis of the new nickel containing titanate $Ba_2NiTi_5O_{13}$, **1**, which is described in this report.

Experimental Section

The reagents $BaCO_3$ (99.98%) and TiO_2 (99.9%) were purchased from Aldrich. $NiCO_3$ (98%) was purchased from J. T. Baker. These reagents were used without further purification. The reaction mixture was heated in a Lindberg Model 51333 oven in an atmosphere of air. Diffraction measurements were made on a Rigaku AFC6S automatic diffractometer by using graphite-monochromated Mo Kα radiation. Magnetic susceptibility measurements were performed on a Quantum Design SQUID magnetometer. Electron microprobe analysis was performed at the University of South Carolina by using a Cameca SX-50 electron microprobe analyzer with wavelength dispersion.

Synthesis and Characterization of $Ba_2NiTi_5O_{13}$. A mixture consisting of 0.791 g (4.01 mmol) of $BaCO_3$, 0.475 g (4.00 mmol) of $NiCO_3$, and 0.640 g (8.01 mmol) of TiO_2 was ground thoroughly in a mortar and then transferred to a platinum crucible. The platinum crucible was placed in the oven and heated to 1375 °C for 48 h. After this period, the oven was cooled slowly (approximately 1 °C/min) to 1000 °C and then allowed to cool rapidly to room temperature. The sample was removed from the oven at room temperature. Analysis: metal composition Ba/Ni/Ti % calcd 35.2/7.5/30.7 (% found 32.9/7.2/32.4).

Crystallographic Analyses. Single crystals of **1** suitable for X-ray diffraction analysis were obtained from the crucibles in which the preparations were carried out. A transparent light green crystal was cleaved from the bulk sample with a scalpel. The crystal used for the intensity measurements was mounted in a thin-walled glass capillary. The unit cell was determined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analysis are listed in Table 1. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Lorentz polarization (Lp) and absorption corrections (empirical) were applied to all data. Neutral atom scattering factors were calculated by the standard procedures.[8a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[8b] Crystals of compound **1** belong to the monoclinic crystal system. The pattern of systematic absences observed in the data is consistent with either of the space groups $C2/m$, $C2$, or Cm. The centrosymmetric space group $C2/m$ was selected as the starting point and was confirmed by the successful solution and refinement

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(8) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol IV, (a) Table 2.2B, pp 99–101, (b) Table 2.3.1, pp 149–150.

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Table 1. Crystal Data for $Ba_2NiTi_5O_{13}$

formula	$Ba_2NiTi_5O_{13}$
formula wt	780.85
crystal system	monoclinic
lattice parameters	
a (Å)	15.090(1)
b (Å)	3.9119(4)
c (Å)	9.1141(6)
β (deg)	98.500(6)
V (Å^3)	532.10(7)
space group	*C2/m* (#12)
Z	2
ρ_{calc} (g/cm^3)	4.87
μ(Mo Kα) (cm^{-1})	126.3
temp (°C)	20
$2\theta_{max}$ (deg)	60.0
no. of obs ($I > 3\sigma$)	846
no. of variables	67
GOF	2.69
residuals:[a] R; R_w	0.032; 0.043
abs cor (based on 3 azimuthal ψ scans)	empirical
transmission coeff max/min	1.00/0.62
largest peak in final diff map (e$^-$/Å^3)	2.40

[a] $R = \Sigma_{hkl}(||F_{obs}| - |F_{calc}||/\Sigma_{hkl}|F_{obs}|$; $R_w = [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|^2)/\Sigma_{hkl}wF_{obs}{}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; GOF $= [\Sigma_{hkl}(|F_{obs}| - |F_{calc}|/\sigma(F_{obs})]/(n_{data} - {}_{nvari})$.

Table 2. Positional Parameters and B(eq) for $Ba_2NiTi_5O_{13}$, 1

atom	x	y	z	B(eq)
Ba	0.44914(02)	0	0.22810(04)	0.90(2)
Ni(1)[a]	0.1688	0	0.4397	0.4
Ni(2)[a]	0.1208	0	0.0951	0.7
Ni(3)[a]	0.7581	0	0.2320	0.4
Ti(1)[a]	0.16881(07)	0	0.43973(12)	0.45(4)
Ti(2)[a]	0.12084(07)	0	0.09506(13)	0.75(4)
Ti(3)[a]	0.75806(07)	0	0.23199(12)	0.38(3)
O(1)	0.2994(03)	0	0.5680(05)	0.6(1)
O(2)	0.0714(03)	0	0.3005(05)	0.8(1)
O(3)	0	0	0	0.9(2)
O(4)	0.2388(03)	0	0.2432(05)	0.7(1)
O(5)	0.1283(03)	0	0.6172(05)	1.0(2)
O(6)	0.6327(03)	0	0.1121(05)	0.9(2)
O(7)	0.8321(03)	0	0.0842(05)	0.8(2)

[a] Ni occupancy 0.1666, Ti occupancy 0.8334.

of the structure. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. Full-matrix least-squares refinements minimized the function $\Sigma_{hkl}w(|F_o| - |F_c|)^2$, *where* $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o{}^2)/2F_o$, *and* $\sigma(F_o{}^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$. All atoms were refined with anisotropic thermal parameters.

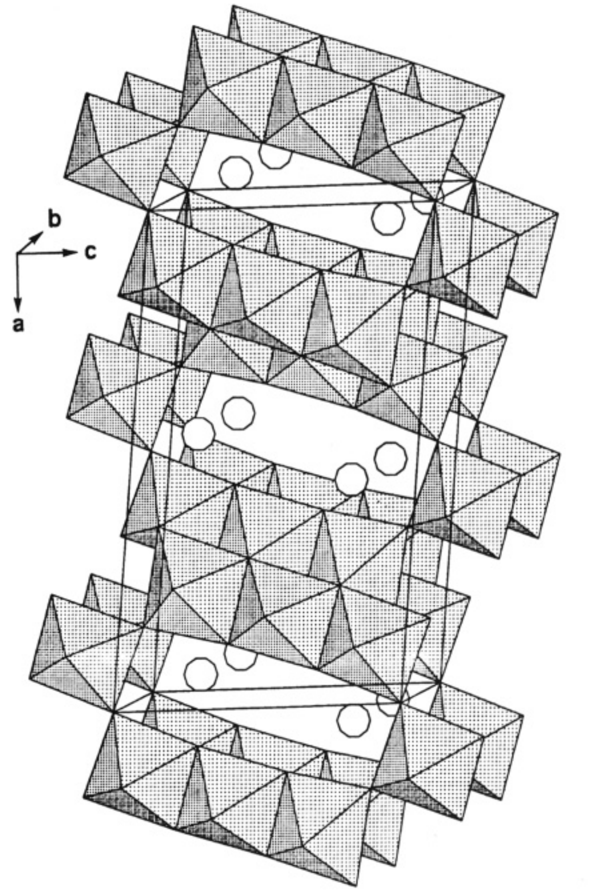

Figure 1. Projection of the solid-state structure of $Ba_2NiTi_5O_{13}$ in the *ac* plane showing the connections of $(Ni,Ti)O_6$ octahedra and the channels of barium ions running parallel to the *b* axis. The connectivities to the barium atoms represented as circles are not shown in the figure.

Table 3. Intramolecular Distances for $Ba_2NiTi_5O_{13}$, 1[a]

atom	atom	distance	atom	atom	distance
Ba	M(1)	4.0797(4)	M(1)	O(2)	1.794(5)
Ba	M(1′)	4.2133(4)	M(1)	O(4)	2.210(5)
Ba	M(2)	3.5969(4)	M(1)	O(5)	1.811(5)
Ba	M(2′)	3.5632(4)	M(2)	O(2)	2.116(5)
Ba	M(3)	3.4887(4)	M(2)	O(3)	1.8997(1)
Ba	O(2)	2.703(3)	M(2)	O(4)	2.069(4)
Ba	O(3)	3.0345(3)	M(2)	O(6)	1.9682(6)
Ba	O(4)	3.197(4)	M(2)	O(6′)	1.9682(6)
Ba	O(5)	2.769(3)	M(2)	O(7)	1.875(5)
Ba	O(6)	3.108(5)	M(3)	O(1)	2.131(5)
Ba	O(6)	3.164(5)	M(3)	O(4)	1.9822(7)
Ba	O(7)	2.825(3)	M(3)	O(4′)	1.9822(7)
M(1)	O(1)	2.137(4)	M(3)	O(5)	2.033(5)
M(1)	O(1′)	2.018(1)	M(3)	O(6)	2.040(5)
M(1)	O(1″)	2.018(1)	M(3)	O(7)	1.873(5)

[a] All sites, M, contain Ti/Ni in a 5/1 ratio. Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Results and Discussion

The new mixed-metal titanate $Ba_2NiTi_5O_{13}$, **1**, was obtained in crystalline form by a heating mixture of $BaCO_3$, $NiCO_3$, and TiO_2 at 1375 °C for 48 h. Compound **1** was characterized by single-crystal X-ray diffraction analysis. The crystal is isomorphous to the related known compounds $Na_2Ti_6O_{13}$ and $Rb_2Ti_6O_{13}$ that have been structurally characterized previously.[9] A projection of the crystallographic unit cell in the *ac* plane is shown in Figure 1. Final atomic positional parameters for **1** are listed in Table 2. Selected bond distances and angles are listed in Tables 3 and 4. All transition-metal ions occupy sites surrounded by six oxide ions in an octahedral environment. These sites are represented by the octahedral shapes in the figure and the metal atoms lie in the center of the octahedron. The transition-metal ions occupy three different sites in the crystal and nickel and titanium ions are randomly distributed among them. The population refinements showed no significant deviations from an equal distribution of 0.1667 nickel in each of the three metal sites. In the *ac* plane the octahedra are linked into groups of three through the sharing of adjacent pairs of oxide ions. Two of the metal ions in this group are symmetry related. These groups are cross linked at each end by sharing oxide ions at the corners of the octahedron of the metal ion in the third site. This results in the formation of cavities of three octahedra in length and one octahedron

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Table 4. Intermolecular Bond Angles for $Ba_2NiTi_5O_{13}$, 1[a]

atom	atom	atom	angle	atom	atom	atom	angle
O(2)	Ba	O(2′)	92.7(1)	O(2)	M(1)	O(5)	106.4(2)
O(2)	Ba	O(3)	57.9(1)	O(4)	M(1)	O(5)	171.3(2)
O(2)	Ba	O(4)	129.47(8)	O(2)	M(2)	O(3)	87.9(1)
O(2)	Ba	O(5)	135.3(1)	O(2)	M(2)	O(4)	78.7(2)
O(2)	Ba	O(6)	58.2(1)	O(2)	M(2)	O(6)	88.3(1)
O(2)	Ba	O(7)	166.3(1)	O(2)	M(2)	O(7)	178.4(2)
O(3)	Ba	O(3′)	80.27(1)	O(3)	M(2)	O(4)	166.6(1)
O(3)	Ba	O(4)	112.50(6)	O(3)	M(2)	O(6)	96.1(1)
O(3)	Ba	O(5)	94.31(4)	O(3)	M(2)	O(7)	93.7(1)
O(3)	Ba	O(6)	55.26(5)	O(4)	M(2)	O(6)	83.6(1)
O(3)	Ba	O(7)	55.92(9)	O(4)	M(2)	O(7)	99.7(2)
O(4)	Ba	O(5)	116.4(1)	O(6)	M(2)	O(6′)	122.9(1)
O(4)	Ba	O(6)	162.8(1)	O(6)	M(2)	O(7)	92.4(1)
O(4)	Ba	O(7)	57.6(1)	O(1)	M(3)	O(4)	120.0(1)
O(5)	Ba	O(5′)	98.80(8)	O(1)	M(3)	O(5)	101.87(7)
O(5)	Ba	O(6)	149.45(6)	O(1)	M(3)	O(6)	119.0(1)
O(5)	Ba	O(7)	108.75(8)	O(1)	M(3)	O(7)	167.5(1)
O(6)	Ba	O(6′)	84.6(1)	O(4)	M(3)	O(4′)	161.3(3)
O(6)	Ba	O(7)	111.7(1)	O(4)	M(3)	O(5)	94.6(1)
O(1)	M(1)	O(1′)	79.3(1)	O(4)	M(3)	O(6)	84.0(1)
O(1)	M(1)	O(2)	168.4(2)	O(4)	M(3)	O(7)	98.3(1)
O(1)	M(1)	O(4)	86.0(2)	O(5)	M(3)	O(6)	175.39(8)
O(1)	M(1)	O(5)	85.2(2)	O(5)	M(3)	O(7)	88.76(9)
O(2)	M(1)	O(4)	82.3(2)	O(6)	M(3)	O(7)	102.7(2)

[a] All sites, M, contain Ti/Ni in a 5/1 ratio. Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

in width. These cavities are occupied by two symmetry related barium ions that lie side by side and combine with the other barium ions to form channels that run parallel to the *b* axis. Each barium ion has eight near oxide neighbors <3.04 Å arranged in the shape of a distorted cube and three additional oxide neighbors at slightly longer distances, 3.104(7), 3.166(6), and 3.196(6) Å. The barium ions are positioned most closely to the metal sites (2) and (3): Ba···Ni(2) = 3.564(1) and 3.595(1) Å, Ba···Ni(3) = 3.489(1) Å, Ba···Ni(1) = 4.0757(4) Å and 4.2090(5) Å.

Magnetic susceptibility measurements of **1** were performed in the temperature range 5–300 K. Charge balance suggests that the nickel ion should have a 2+ oxidation state. The effective magnetic moment, μ_{eff}, at 5 K equals 2.70 μ_B per nickel atom and 3.20 μ_B per nickel atom at 300 K. This is similar to what is typically observed for d^8 Ni^{2+} in the related material $BaNiO_2$[10] and in Ni(II) complexes having two unpaired electrons.[11] Figure 2 shows a plot of the temperature dependence of the inverse susceptibility $1/\chi$ in the temperature range 5–300 K. There is a continuous increase of the magnetic moment as the temperature increases. The observations were found to fit a modified Curie–Weiss law (see Figure 2):

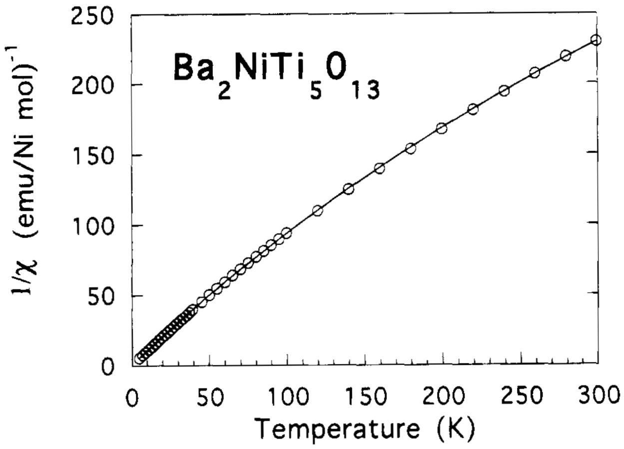

Figure 2. Plot of the inverse of the magnetic susceptibility of a polycrystalline sample of $Ba_2NiTi_5O_{13}$ measured at 5 kOe in the temperature range 5–300 K. The line shows the best fit; see text.

$$\chi = C/(T - \theta_p) + \text{TIP}$$

where $C = 0.948(3)$ emu K/mol, $\theta_p = -0.5(1)$ K, and TIP $= 1.20(1) \times 10^{-3}$ emu/mol (TIP = temperature-independent magnetism). Nickel(II) ions have a $^3A_{2g}$ ground state which can mix with the higher lying $^3T_{2g}$ state and therefore can be expected to possess a significant TIP term.[12]

Compound **1** can be viewed as a derivative of the structurally related compounds $Na_2Ti_6O_{13}$ and $Rb_2Ti_6O_{13}$ formed by the replacement of the two singly charged alkali ions with two doubly charged barium ions and replacement of one of the six Ti^{4+} ions with a Ni^{2+} ion. It seems reasonable to expect that families of related alkaline earth mixed-metal titanates of the general formula $M_2M'Ti_5O_{13}$, M′ = 2^+ ion, or even $M_2M'_2Ti_4O_{13}$, M′ = 3^+ ion, could be prepared by employing other transition metal ions M′ and other dipositive alkaline earth ions, M, for the barium ion.

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Supporting Information Available: Table of anisotropic thermal parameters is available for the structural analysis (1 page); tables of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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