

New barium manganese titanates prepared under reducing conditions

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Dedicated to Martha Greenblatt

Abstract

We report the synthesis and initial characterization of $\text{BaMnTi}_5\text{O}_{12}$, the first example of an oxide displaying an interesting tripled hollandite-type structure. Shiny black crystals which crystallize in the monoclinic space group, $P2_1/n$, with $a = 9.921(3) \text{ \AA}$, $b = 8.8716(22) \text{ \AA}$, $c = 10.309(3) \text{ \AA}$, and $\beta = 91.24(3)^\circ$, were grown from a borate-based melt in vacuo. The structure contains layers made up of edge-shared pairs of TiO_6 octahedra forming a hollandite framework. The Ba^{2+} ions occupy large high coordination number channel sites. Oxidation states of the transition metal ions are such that a charge balance of one half barium ion per three framework units with an ideal stoichiometry $\text{Ba}_{0.5}\text{M}_3\text{O}_6$, produces the tripling. In addition, crystals of $\text{Ba}_2\text{MnTi}_5\text{O}_{13}$, monoclinic, space group $C2/m$, $a = 15.075(1) \text{ \AA}$, $b = 3.9470(2) \text{ \AA}$, $c = 9.0985(5) \text{ \AA}$, and $\beta = 98.23(1)^\circ$, which is isostructural with the mineral jeppeite, $\text{K}_2\text{Ti}_6\text{O}_{13}$, were also grown. © 2002 Éditions scientifiques et médicales Elsevier SAS. All rights reserved.

1. Introduction

A variety of interesting structural features as well as electronic properties are seen in reduced ternary oxides of titanium. Among the early oxide superconductors is the spinel titanate, $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$, with a relatively high T_c near 13 K. The titanates of the large alkali ions, K, Rb and Cs, have tunnel structures related to the hollandite structure, while more complicated tunnel structures have been observed in the reduced Na–Ti–O compounds, $\text{Na}_2\text{Ti}_4\text{O}_9$ and $\text{Na}_{1.7}\text{Ti}_6\text{O}_{11}$. Hessen et al. had earlier shown that borate fluxes were useful to produce single crystals of reduced ternary titanates because of their low volatilities which allows their use under high-vacuum conditions [1]. Here we have examined the pseudo-ternary system Ba–Mn–Ti–O under reducing conditions. The Mn^{2+} is a spin 5/2 ion which forms the classic antiferromagnetic insulator, MnO [2]. We find a new phase of composition $\text{BaMnTi}_5\text{O}_{12}$ grown using a borate flux. This phase displays an interesting tripling of the hollandite structure. When we move to a more barium-rich portion of the phase diagram, we obtain crystals with stoichiometry, $\text{Ba}_2\text{MnTi}_5\text{O}_{13}$, which are isostructural with the mineral jeppeite, $\text{K}_2\text{Ti}_6\text{O}_{13}$ [3]. The jeppeite structure is a shear-

related structure based on the perovskite structure. Adding one additional BaO unit to a stoichiometry which adopts a hollandite-type structure moves the material to an entirely different packing situation. The structure adopted for a given stoichiometry depends less on favored structural motifs than on achieving a suitable charge balance.

2. Experimental

2.1. Sample preparation

Black, euhedral crystals of typical size 0.5 mm were grown from a borate-based melt corresponding to the composition 25 mol % BaO (as BaCO_3 , Johnson Matthey Puratronic, 99.997%), 12.5 mol % Ti_2O_3 (Alfa, 99.9%), and 25 mol % MnO (Alfa, 99.9%). The reagents were ground together using an agate mortar and pestle, then placed in a hand formed Mo-foil cup with an Mo-foil lid and heated in vacuo (in a Centorr high-vacuum furnace) to 400°C to remove absorbed water, then heated to 1100°C in 2 hours, soaked at this temperature for 2 hours, and, finally, slowly cooled at a rate of 5°C h^{-1} to 800°C . Single crystals were selected from the resulting product using a microscope.

A homogeneous powder of the Ba–Mn–Ti–O compound was prepared by grinding together a stoichiometric mixture in an agate mortar and pestle, then firing at 1000°C for 12 h

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Table 1
Crystal data for BaMnTi₅O₁₂ (triple hollandite-type) and Ba₂MnTi₅O₁₃ (jeppeite-type)

Formula	BaMnTi ₅ O ₁₂	Ba ₂ MnTi ₅ O ₁₃
Formula weight	623.76	777.09
Space group	P2/n (Nr. 13)	C2/m (Nr. 12)
Crystal size (mm ³)	0.03 × 0.08 × 0.08	0.08 × 0.20 × 0.05
<i>a</i> (Å)	9.921(3)	15.0750(10)
<i>b</i> (Å)	8.9139(22)	3.94700(20)
<i>c</i> (Å)	10.309(3)	9.0985(5)
β (deg)	91.24(3)	98.228(8)
<i>V</i> (Å ³)	911.5(4)	535.80(5)
<i>Z</i>	4	2
<i>D_c</i> (g cm ⁻³)	4.546	4.817
μ (Mo <i>Kα</i>) (cm ⁻¹)	97.3	119.0
Diffractometer	Enraf–Nonius CAD4	Enraf–Nonius CAD4
λ (Å)	0.70930 (graphite-monochromatized Mo <i>Kα</i>)	0.70930 (graphite-monochromatized Mo <i>Kα</i>)
Temperature	23 °C	23 °C
$2\theta_{\max}$ (deg)	70	70
Data collected	12761	1337
Scan type	ω	ω
Independent reflections	3978	1285
Reflections (<i>I</i> > 2.5 σ (<i>I</i>))	2053	1168
<i>R</i>	0.064	0.030
<i>R_w</i> (<i>w</i> = 1/ σ^2 (<i>F_o</i>))	0.053	0.027

in vacuo in an Al₂O₃ crucible. The resulting powder was reground then heated to 1050 °C for 12 hours as before. At the end of the second reaction, the material was a uniform shiny black powder.

2.2. Structure determination

Crystals were measured at 23 °C on an Enraf–Nonius CAD-4 diffractometer using graphite monochromatized Mo *K α* radiation and the NRCCAD program package [4]. All calculations were carried out on a Digital AlphaStation using the NRCVAX structure package [5]. Lattice parameters were determined from the absolute 2θ values of reflections at high angle, 25 reflections with $60 < 2\theta < 65^\circ$. A Gaussian integration absorption correction was applied to all measured intensities. The initial barium atom positions were determined using the Patterson method. The titanium and manganese atoms were located in ensuing Fourier maps, and the oxygen positions were obtained from difference maps. Anisotropic temperature factors for all atoms were included in the final refinements. Crystallographic data are listed in Table 1, atomic coordinates and isotropic thermal parameters in Table 2, and selected bond lengths in Table 3.

The phase BaMnTi₅O₁₂ crystallizes in the monoclinic space group, P2/n, with *a* = 9.921(3) Å, *b* = 8.8716(22) Å, and *c* = 10.309(3) Å, and β = 91.24(3)°. The unique *b*-axis is the tripled hollandite “short” axis, with pseudo-tetragonal symmetry.

This unit cell corresponds well to the powder X-ray diffraction pattern for stoichiometric ceramic material as shown in Table 4. Powder diffraction data was collected using a Phillips PW1720 diffractometer. We note that the powder

pattern shows some evidence for preferential orientation that is to be expected due to the highly anisotropic nature of the structure; measured and calculated intensities differ for a few reflections.

3. Description of the structure

3.1. BaMnTi₅O₁₂

The BaMnTi₅O₁₂ structure is a triple hollandite-type structure, with the titanium/manganese octahedra forming the familiar hollandite framework (see Fig. 1a). In each unit cell, there are two channels, both occupied by one barium atom each. The barium atoms are located in the first and last layer of the standard hollandite [6], giving a distance of 8.8716 Å between barium located in the same channels. This type of cation ordering has not been observed previously. However, a five-fold stacked hollandite was observed in Ba_{1.2}Mg_{1.2}Ti_{6.8}O₁₆, where the barium atoms in the channel are separated by 5.476 Å [7]. Since the hollandite-type structure with disordered barium is common for titanium and manganese based systems, it is expected that the structure will also occur in mixed phases. However, no apparent ordering of the manganese on any particular octahedral site could be inferred from the X-ray structure determination, indicating that manganese is randomly distributed over all the possible titanium sites. The stoichiometry, as determined from semiquantitative EDX measurements is consistent with the assumption of Ti⁴⁺ and Mn²⁺. A reducing atmosphere is therefore needed to maintain the lower valence state of Mn. In contrast, in the manganese-based hollandite

Table 2

Atomic parameters x , y , z and B_{iso} for $\text{BaMnTi}_5\text{O}_{12}$ and $\text{Ba}_2\text{MnTi}_5\text{O}_{13}$. E.S.Ds. refer to the last digit printed

	x	y	z	B_{iso}
BaMnTi₅O₁₂				
Ba1	1/4	0.86774(14)	1/4	1.20(6)
Ba2	1/4	0.30586(14)	1/4	1.01(6)
Ti/Mn1	0.9024(3)	0.7518(5)	0.08619(23)	0.34(10)
Ti/Mn2	0.5817(3)	0.2445(4)	0.10390(23)	0.27(9)
Ti/Mn3	0.89900(20)	0.4157(5)	0.08150(18)	0.38(7)
Ti/Mn4	0.57575(21)	0.5793(5)	0.10732(18)	0.40(8)
Ti/Mn5	0.58484(20)	0.9142(5)	0.09996(18)	0.44(8)
Ti/Mn6	0.90746(20)	0.0807(5)	0.09022(18)	0.39(8)
O1	0.0994(7)	0.4144(18)	0.0444(7)	0.35(11)
O2	0.0993(10)	0.7463(17)	0.0443(9)	0.37(15)
O3	0.1024(8)	0.0797(18)	0.0473(7)	0.45(12)
O4	0.9277(7)	0.5819(19)	0.2082(7)	0.42(11)
O5	0.7095(8)	0.4191(21)	0.0985(7)	0.54(12)
O6	0.4455(7)	0.4172(20)	0.0905(7)	0.34(11)
O7	0.9357(10)	0.2566(19)	0.2089(9)	0.54(16)
O8	0.4430(8)	0.0817(21)	0.0918(7)	0.43(12)
O9	0.7098(10)	0.7470(20)	0.0945(9)	0.65(16)
O10	0.7123(8)	0.0822(22)	0.0982(7)	0.68(12)
O11	0.4465(10)	0.7491(20)	0.0912(9)	0.61(16)
O12	0.9360(8)	0.9160(21)	0.2123(7)	0.57(12)
Ba₂MnTi₅O₁₃				
Ba1	0.448916(25)	0	0.22439(4)	0.781(12)
Ti/Mn1	0.12143(7)	0	0.09879(10)	0.62(4)
Ti/Mn2	0.16889(7)	0	0.44343(10)	0.41(3)
Ti/Mn3	0.24685(7)	0	−0.22311(10)	0.45(4)
O1	0.7004(3)	0	0.4302(4)	0.63(13)
O2	0.8715(3)	0	0.3825(4)	0.84(14)
O3	0.2403(3)	0	0.2462(4)	0.70(14)
O4	0.0718(3)	0	0.2998(4)	0.80(14)
O5	0.8297(3)	0	0.0825(4)	0.93(15)
O6	0	0	0	1.03(21)
O7	0.6269(3)	0	0.1111(4)	0.92(15)

B_{iso} is the mean of the principal axes of the thermal ellipsoid.

$\text{BaMn}_8\text{O}_{16}$ [8], manganese is mostly tetravalent, with an average valence of 3.75.

The superstructure leading to the tripling of the unit cell parameter b parallel to the channels arises from the ordering of the barium atoms. The substructure has a unit cell parameter of 2.957 Å in the direction along the channel, close to the values observed for other titanium-based hollandites.

Bond valence sum calculations [9] indicate that for $\text{BaMnTi}_5\text{O}_{12}$, the Ti4 and Ti5 sites are fully occupied by titanium, whereas the other transition metal sites are mixed titanium/manganese. Furthermore, the barium sites show a slightly reduced valence. This might be attributed to the large channels where the barium is located, with a corresponding lower coordination number and greater bonding distances.

3.2. $\text{Ba}_2\text{MnTi}_5\text{O}_{13}$

The new phase $\text{Ba}_2\text{MnTi}_5\text{O}_{13}$ is structurally related to the hollandite-type phases, and is isostructural to the mineral jeppeite [3], and $\text{Ba}_2\text{Fe}_2\text{Ti}_4\text{O}_{13}$ [10] (see Fig. 1b). The

structure consists of rows of three edge-sharing octahedra connecting to another row beneath by edge-sharing. The rows connect to each other via corner-sharing, producing channels that accept two barium atoms, spaced 5.031 Å apart and 3.947 Å apart along the channels. The barium atoms are coordinated by only 10 oxygen atoms, at distances ranging from 2.794 to 3.102 Å.

It should be noted that bond valence sum calculations indicate that barium is under compression, with a calculated charge of 2.253, instead of 2.0. In contrast, the titanium bond valence sums indicate that Ti2 site is almost entirely occupied by titanium. This site is the central titanium of the chain of three octahedra, whereas the flanking transition metal sites have mixed titanium–manganese occupancy.

4. Discussion

Recently, Vanderah et al. have examined the pseudo-ternary system Ba–Fe–Ti–O prepared under ambient air atmosphere [10] and have found a large number of new phases. Some of these phases are of possible interest either as dielec-

Table 3

Selected bond distances for BaMnTi₅O₁₂ and selected interatomic distances in Ba₂MnTi₅O₁₃ (jeppeite-type) in (Å)

BaMnTi ₅ O ₁₂		
Ba1–O2	2.787(10)	2x
–O3	3.154(11)	2x
–O8	3.178(11)	2x
–O10	3.645(8)	2x
–O11	2.782(12)	2x
–O12	3.160(8)	2x
Ba2–O1	2.743(9)	2x
–O3	3.231(11)	2x
–O6	2.754(9)	2x
–O7	3.169(10)	2x
–O8	3.233(13)	2x
–O9	3.613(10)	2x
Ti/Mn1–O1	2.001(13)	
–O2	2.011(10)	
–O3	2.036(13)	
–O4	1.981(13)	
–O9	1.914(11)	
–O12	1.982(13)	
Ti/Mn3–O1	2.033(8)	
–O1	1.995(13)	
–O2	1.941(13)	
–O4	1.992(13)	
–O5	1.892(8)	
–O7	1.961(13)	
TiMn5–O8	2.052(14)	
–O8	1.991(8)	
–O9	1.940(14)	
–O10	1.960(15)	
–O11	2.013(14)	
–O12	1.951(8)	
Ti/Mn2–O5	2.009(13)	
–O6	2.051(14)	
–O7	1.944(10)	
–O8	2.002(14)	
–O10	1.943(14)	
–O11	2.025(10)	
Ti/Mn4–O4	1.903(8)	
–O5	1.953(14)	
–O6	1.944(14)	
–O6	2.045(8)	
–O9	2.007(14)	
–O11	1.988(14)	
Ti/Mn6–O2	2.074(13)	
–O3	1.994(8)	
–O3	2.015(13)	
–O7	2.004(14)	
–O10	1.940(9)	
–O12	1.950(14)	
Ba ₂ MnTi ₅ O ₁₃		
Ba–O2	2.794(3)	2x
–O4	2.726(3)	2x
–O5	2.851(3)	2x
–O6	3.018(3)	2x
–O7	3.008(5)	
–O7	3.102(4)	
Ti/Mn1–O3	2.079(4)	
–O4	2.073(4)	
–O5	1.901(4)	

Table 3 (Continued)

–O6	1.920(4)	
–O7	1.978(4)	2x
Ti/Mn2–O1	2.037(2)	2x
–O1	2.135(4)	
–O2	1.776(4)	
–O3	2.221(4)	
–O4	1.817(4)	
Ti/Mn3–O1	2.148(4)	
–O2	2.132(4)	
–O3	1.997(3)	2x
–O5	1.841(4)	
–O7	2.027(4)	

Table 4

Powder diffraction pattern for BaMnTi₅O₁₂

<i>h</i>	<i>k</i>	<i>l</i>	2θ (Å)	<i>d</i>	<i>I</i> / <i>I</i> ₀
1	1	3	21.92	4.051	19
–1	2	6	30.58	2.921	45
3	0	0	31.30	2.855	100
0	0	9	37.02	2.426	1
–2	4	3	38.50	2.336	28

tric or magnetic materials for potential applications in wireless technologies. The substitution of manganese in place of iron requires control over the manganese valence. To produce phases that might have interesting magnetic properties, divalent manganese, with a $^6S_{5/2}$ state, is desirable, giving a large spin-only moment. However, in general, divalent manganese needs to be prepared under reducing conditions to prevent the formation of Mn³⁺ or Mn⁴⁺. In the case where titanium ions are also found in the material, reduction from Ti⁴⁺ to Ti³⁺ is quite difficult, so that a vacuum atmosphere was deemed sufficient to maintain Mn²⁺ while not reducing Ti⁴⁺. We have succeeded in growing two new phases, a triple hollandite, and a jeppeite-related phase, that differ by the amount of barium oxide. The general stoichiometry of the phases may be expressed as $l(\text{BaO}) + m(\text{MnO}) + n(\text{TiO}_2)$, with the first one being the $l = 1, m = 1, n = 5$, and the second phase being the $l = 2, m = 1, n = 5$ member. Other stoichiometries may exist, for example, BaMnTiO₄ (1, 1, 1), BaMnTi₂O₆ (1, 1, 2), BaMn₂Ti₂O₇ (1, 2, 2), BaMn₂Ti₄O₁₁ (1, 2, 4), Ba₂MnTi₂O₇ (2, 1, 2), etc. to mentioned just a few. Within these examples, homologous series may exist. The synthesis of such phases requires finding reducing conditions that stabilize Mn²⁺, while not producing Ti³⁺. Stronger reducing conditions may yield phases where titanium is in a mixed-valent regime, coexisting with Mn²⁺.

Analogously, similar phases might be expected for materials in which magnesium ions take the place of the Mn²⁺ ions. Such phases are possible because Mg²⁺ also prefers an octahedral environment and has a size that is similar to the Mn²⁺ ion [11]. However, careful control of reducing conditions would not be necessary for Ba–Mg–Ti–O phases.

It is interesting to note that the triple hollandite phase differs from the jeppeite-type phase by the addition of just

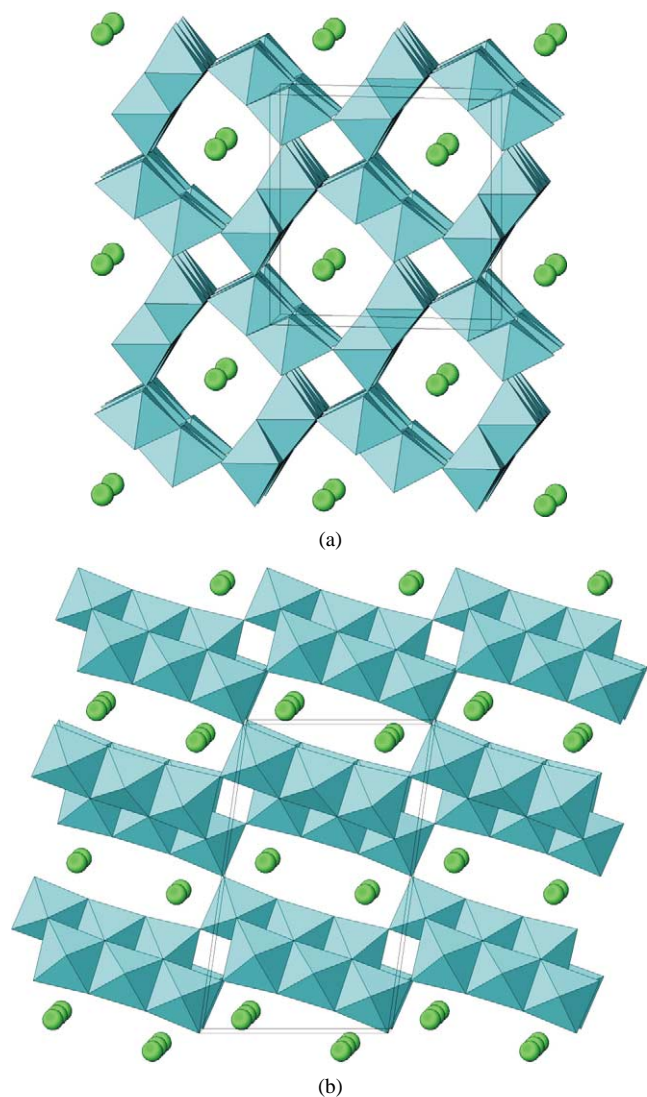


Fig. 1. (a) View of the $\text{BaMnTi}_5\text{O}_{12}$ triple hollandite-type structure down the b -axis showing stacked layers made up of pairs of edge-shared $(\text{Ti}/\text{Mn})\text{O}_6$ octahedra. The circles represent barium atoms [12]. (b) View of the $\text{Ba}_2\text{MnTi}_5\text{O}_{13}$ jeppelite-type structure down the short b -axis, showing the corner connected units of six edge-sharing octahedra [12].

one more BaO unit. However, the additional BaO is not accommodated in a hollandite-type arrangement. Rather, the material adopts a jeppelite-type structure that also contains channels, but has closer barium contacts, for a higher concentration of barium. Furthermore, both the hollandite-type and jeppelite-type occur in the barium–titanium–oxygen system, with reduced titanium valence.

Because these phases contain low concentrations of manganese, paramagnetic behavior is expected. Since the main magnetic coupling mechanism in MnO is super-

exchange, antiferromagnetic interactions are likely to occur. Investigations of the magnetic properties of these phases are anticipated.

5. Conclusions

Two new reduced phases in the Ba–Mn–Ti–O system were synthesized and structurally characterized. In the case of $\text{BaMnTi}_5\text{O}_{12}$, a triple hollandite-type structure was found with the barium atoms ordered in the channels. Tripled hollandites have been observed previously in the Ba–Fe–Ti–O system, but no structural information was reported. The closely related $\text{Ba}_2\text{MnTi}_5\text{O}_{13}$ phase crystallizes in the jeppelite-type, with the barium located in elongated channels. We suggest the possibility of a homologous series, which would produce a large number of new phases with potentially interesting magnetic properties.

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