

Preparation and Characterization of New Ternary Compounds in the System BaO-TiO₂-Al₂O₃

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Three new ternary compounds, BaTi₅Al₂O₁₄, BaTiAl₆O₁₂, and Ba₃TiAl₁₀O₂₀ have been identified in the system BaO-TiO₂-Al₂O₃ and were characterized by X-ray powder diffraction. BaTi₅Al₂O₁₄ has a tetragonal unit-cell with $a = 7.025 \text{ \AA}$, $c = 10.156 \text{ \AA}$, and $Z = 2$. The compound melts incongruently at 1500°C. BaTiAl₆O₁₂ also has a tetragonal unit-cell with $a = 10.07 \text{ \AA}$, $c = 9.107 \text{ \AA}$, and $Z = 4$. The compound melts incongruently at 1560°C. Ba₃TiAl₁₀O₂₀ has an orthorhombic unit-cell with $a = 14.854 \text{ \AA}$, $b = 11.356 \text{ \AA}$, $c = 4.986 \text{ \AA}$, and $Z = 2$. The compound dissociates in the solid state at 1440°C to yield BaTiAl₆O₁₂ and BaAl₂O₄.

I. Introduction

As part of a continuing study of phase relationships in the alkaline earth-transition metal oxide systems, subsolidus phase equilibria in the system BaO-TiO₂-Al₂O₃ have been investigated. A preliminary examination of several mixtures by X-ray diffraction has revealed that a number of hitherto unknown compounds exist in the ternary system. In a previous communication (1), we reported the X-ray data for one of these compounds having a probable composition BaO·4TiO₂·Al₂O₃. Further study of subsolidus compatibility relations in the system, however, indicated that the compound reported earlier has a chemical composition corresponding to a slightly different BaO:TiO₂:Al₂O₃ ratio. Thus, it is apparent that the inconsistency observed on the chemical composition for this compound should be resolved and the

stability relations of various compounds occurring in the system BaO-TiO₂-Al₂O₃ should be established.

The work reported in this paper is concerned with the identification and characterization of a number of new barium-titanium-aluminum oxides and their stability relations in the ternary system BaO-TiO₂-Al₂O₃.

II. Experimental

The compounds were prepared by solid-state reaction of analytical-grade barium carbonate (BDH Chemicals), titanium dioxide (99.5% pure, Koch-Light) and α -Al₂O₃ (highly pure, BDH Chemicals). Stoichiometric compositions of the powdered materials were mixed thoroughly under alcohol, dried in an oven and pressed into pellets, which were wrapped in Pt-envelopes

and fired at 1000°C for 10–15 hr to decompose the carbonate. The calcined samples were fired in air at higher temperatures for longer periods with intermittent cooling, crushing, mixing, and pressing to ensure homogeneity and to attain equilibrium. The fired samples were examined by X-ray powder diffraction. X-ray powder patterns were obtained in a Guinier-type focussing camera using Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), which served for routine phase identification. For precision lattice parameter measurements, however, a Geiger-counter diffractometer was used. The scanning rate was $\frac{1}{8}^\circ 2\theta/\text{min}$. The diffractometer was calibrated with the known peaks of pure gold ($a_0 = 4.0786 \text{ \AA}$). The interplanar spacings for the compounds were indexed with the aid of the method suggested by Ito (2) using a series of computer programs written by Haendler and Cooney (3). The selection between the possible unit-cells conforming to the original data was made on the basis of the best agreement between the measured and calculated densities, at lowest possible cell-parameters and highest symmetry. The powder patterns of both $\text{BaTi}_5\text{Al}_2\text{O}_{14}$ and $\text{BaTiAl}_6\text{O}_{12}$ also have been indexed by the aid of graphical method using a complete Hull–Davey chart. The unit-cell parameters obtained for these two compounds were in good agreement with those obtained by the computer method. Unit-cell dimensions were refined by a least-squares computer program and were estimated to be accurate to at least ± 2 in the last decimal place listed.

Reported intensities were derived from the relative peak heights.

Reflected-light microscopy was used extensively throughout the phase analysis and to determine the correct compositions of the compounds. Melting behavior of the compounds was investigated by a heating microscope (Leitz–Wetzlar, West Germany) equipped with a furnace capable of operating to a maximum temperature of 1750°C. The samples were heated up to the melting temperature at a rate of 2°C/min and the melting was observed through an eyepiece focused on the sample. The melted samples were examined by X-ray diffraction and petrographic methods. Density of the compounds was determined by pycnometric method using hexane as the immersion liquid.

III. Results and Discussion

The three ternary compounds identified in the system $\text{BaO–TiO}_2\text{–Al}_2\text{O}_3$ include $\text{BaO}\cdot 5\text{TiO}_2\cdot \text{Al}_2\text{O}_3$, $\text{BaO}\cdot \text{TiO}_2\cdot 3\text{Al}_2\text{O}_3$, and $3\text{BaO}\cdot \text{TiO}_2\cdot 5\text{Al}_2\text{O}_3$. Their existence has been suspected during subsolidus phase equilibria studies in the ternary system when X-ray powder diffraction patterns of several samples showed the presence of many unidentified d -lines. The chemical formula has been assigned to the compounds after examining several compositions by X-ray powder diffraction and by reflected-light microscopy. Among several compositions examined, the chemical formula was chosen as the correct one when

TABLE I
X-RAY CRYSTALLOGRAPHIC DATA FOR THE TERNARY COMPOUNDS

	$\text{BaTi}_5\text{Al}_2\text{O}_{14}$	$\text{BaTiAl}_6\text{O}_{12}$	$\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$
Symmetry	Tetragonal	Tetragonal	Orthorhombic
Cell dimensions	$a = 7.025 \text{ \AA}$ $c = 10.156 \text{ \AA}$	$a = 10.070 \text{ \AA}$ $c = 9.107 \text{ \AA}$	$a = 14.854 \text{ \AA}$ $b = 11.356 \text{ \AA}$ $c = 4.986 \text{ \AA}$
Cell volume	501.2049 \AA^3	923.4944 \AA^3	841.0485 \AA^3
Cell content	2	4	2
Density (measured)	$4.32 \pm 0.02 \text{ g/cm}^3$	$3.84 \pm 0.02 \text{ g/cm}^3$	$4.13 \pm 0.02 \text{ g/cm}^3$
Density (calculated)	4.338 g/cm^3	3.876 g/cm^3	4.144 g/cm^3

(i) X-ray powder diffraction pattern of a composition was found to be distinctly different from those for the starting materials and for the binary compounds known to exist in the system BaO–TiO₂–Al₂O₃ or mixtures thereof, and (ii) petrographic examinations showed only a single-phase microstructure. The X-ray and petrographic results were further corroborated by the fact that the compositions assigned for the compounds were found to lie exactly on the binary joins in the ternary system.

The crystallographic data presented for the compounds were based entirely on powder data. No single crystal data were available to confirm the data reported herein. The *d*-spacings for the compounds were chosen from the *2θ* values of three X-ray diffraction tracings obtained for each compound. The sharpness of the diffraction peaks and the clear separation of the *Kα* doublet at higher angles are characteristic of homogeneous and well

crystallized materials. A very satisfactory refinement was obtained from the powder data. The observed and calculated density values were found to be in good agreement. The X-ray crystallographic data for the compounds are summarized in Table I.

(a) BaTi₅Al₂O₁₄

The existence of this compound in the ternary system BaO–TiO₂–Al₂O₃ can be demonstrated by the presence of its characteristic X-ray pattern of the samples containing high proportions of TiO₂. The interplanar spacings for the compound with the corresponding indices are given in Table II. The powder pattern can be indexed satisfactorily on the basis of a tetragonal unit-cell with *a* = 7.025 Å and *c* = 10.156 Å. Two formula weights per unit cell lead to a calculated density of 4.338 g/cm³ as compared with the measured density 4.32 g/cm³. Petrographic and X-ray analysis of the melted sample

TABLE II
X-RAY POWDER DIFFRACTION DATA FOR BaTi₅Al₂O₁₄

<i>hkl</i> ^a	<i>d</i> _{calc.}	<i>d</i> _{obs.}	<i>I</i> / <i>I</i> ₀	<i>hkl</i> ^a	<i>d</i> _{calc.}	<i>d</i> _{obs.}	<i>I</i> / <i>I</i> ₀
1 1 0	4.967	4.97	10	0 3 5	1.534	1.54	5
0 2 0	3.512	3.51	25	2 4 2	1.500	1.51	5
1 2 0	3.141	3.14	100	1 2 6	1.490	1.49	5
1 1 3	2.797	2.80	15	0 0 7	1.451	1.46	10
1 2 2	2.671	2.66	5	2 4 3	1.425	1.43	10
0 2 3	2.437	2.44	50	3 4 0	1.405	1.41	5
0 3 0	2.341	2.34	15	0 5 0			
1 3 0	2.221	2.22	30	3 4 1	1.392	1.400	5
1 3 1	2.170	2.19	35	0 5 1			
2 2 3	2.002	2.00	15	0 3 6	1.372	1.372	15
2 3 0	1.948	1.95	15	2 4 4	1.336	1.335	5
2 3 1	1.913	1.91	5	0 4 5	1.328	1.326	10
1 3 3	1.857	1.86	30	2 5 0	1.304	1.306	10
0 2 5	1.758	1.76	10	3 3 5	1.283	1.280	5
1 2 5	1.705	1.71	10	2 5 2	1.263	1.261	8
1 4 0				1.704	1.232	1.234	5
2 3 3	1.688	1.69	5	4 4 2	1.206	1.206	5
1 3 4	1.672	1.67	5	3 3 6	1.183	1.183	5
3 3 0	1.655	1.66	20	4 4 3	1.166	1.167	5
3 3 1	1.634	1.63	5	2 5 4	1.160	1.160	5
1 1 6	1.602	1.61	5	1 6 0	1.155	1.155	5
0 4 3	1.559	1.56	35	1 6 1	1.147	1.147	5

^a Indexed on the basis of a tetragonal unit-cell with *a* = 7.025 Å and *c* = 10.156 Å.

showed that the compound melts incongruently to yield Al_2TiO_5 and a liquid. The melting point of the compound as determined by the heating microscope as well as by metallographic examination was found to be about 1500°C . DTA runs made on the compound in a Linseis apparatus using $\alpha\text{-Al}_2\text{O}_3$ as a reference material indicated that the compound melts incongruently at $1495 \pm 5^\circ\text{C}$. The X-ray pattern of the melted sample showed the presence of Al_2TiO_5 .

(b) $\text{BaTiAl}_6\text{O}_{12}$

Petrographic and X-ray examinations of a sintered mixture containing stoichiometric composition $\text{BaO}:\text{TiO}_2:3\text{Al}_2\text{O}_3$ showed the presence of only one phase, which was stable at the subsolidus temperatures. The compound also can be prepared from appropriate proportions of BaTiO_3 and Al_2O_3 heated to 1400°C . In both cases, the same X-ray diffraction pattern was obtained, which can be

TABLE III
X-RAY POWDER DIFFRACTION DATA FOR $\text{BaTiAl}_6\text{O}_{12}$

hkl^a	$d_{\text{calc.}}$	$d_{\text{obs.}}$	I/I_0	hkl^a	$d_{\text{calc.}}$	$d_{\text{obs.}}$	I/I_0
0 1 1	6.754	6.75	35	3 5 0	1.727	1.73	5
1 1 1	5.609	5.61	5	3 5 1	1.696	1.70	5
0 0 2	4.553	4.55	15	0 4 4	1.688	1.69	5
2 1 1	4.036	4.03	8	1 2 5	1.688		
1 1 2	3.836	3.82	15	0 6 0	1.678	1.68	5
2 2 0	3.560	3.56	8	3 4 3	1.678		
0 2 2	3.377	3.43	70	1 6 0	1.655	1.65	12
2 2 1	3.316	3.31	50	1 5 3	1.655		
0 3 1	3.149	3.15	100	2 4 4	1.601	1.60	8
1 3 1	3.006	2.99	5	2 5 3	1.592	1.59	10
0 1 3	2.906	2.90	5	1 3 5	1.581	1.58	10
2 2 2	2.804	2.80	45	4 5 0	1.572	1.57	5
2 3 0	2.793			1 6 2	1.556	1.56	30
0 3 2	2.702	2.69	5	4 5 1	1.549	1.55	20
0 2 3	2.599	2.59	75	4 4 3	1.535	1.53	20
0 4 0	2.517	2.52	15	4 5 2	1.486	1.49	5
0 4 1	2.426	2.42	20	1 4 5	1.460	1.46	5
1 4 1	2.359	2.34	10	1 6 3	1.453	1.45	5
3 3 1	2.296	2.29	10	0 2 6	1.453		
0 0 4	2.276	2.26	25	0 7 0	1.438	1.44	15
2 4 0	2.251	2.25	25	1 2 6	1.438		
2 4 1	2.186	2.19	10	3 6 2	1.425	1.43	20
1 4 2	2.152	2.14	10	4 6 0	1.396	1.40	10
3 3 2	2.104	2.09	8	4 5 3	1.396		
1 2 4	2.032	2.03	8	4 6 1	1.380	1.381	5
0 5 0	2.014	2.01	10	1 3 6	1.370	1.369	5
3 4 1	1.966	1.97	20	1 7 2	1.359	1.357	10
0 5 1				3 6 3	1.345	1.345	5
2 2 4	1.918	1.92	25	1 6 4	1.339	1.339	10
2 5 0	1.870	1.87	5	1 5 5	1.338		
3 3 3	1.869			4 6 2	1.335	1.336	10
2 4 3	1.808	1.80	40	4 5 4	1.294	1.295	20
0 1 5	1.792	1.79	40	5 6 1	1.276	1.277	5
4 4 0	1.780	1.77	12	4 6 3	1.268	1.268	10
4 4 1	1.747	1.75	12	5 6 2	1.240	1.241	5

^a Indexed on the basis of a tetragonal unit-cell with $a = 10.07 \text{ \AA}$ and $c = 9.107 \text{ \AA}$.

TABLE IV
X-RAY POWDER DIFFRACTION DATA FOR Ba₃TiAl₁₀O₂₀

<i>hkl</i> ^a	<i>d</i> _{calc.}	<i>d</i> _{obs.}	<i>I</i> / <i>I</i> ₀	<i>hkl</i> ^a	<i>d</i> _{calc.}	<i>d</i> _{obs.}	<i>I</i> / <i>I</i> ₀
0 2 0	5.678	5.67	50	7 4 1	1.609	1.61	20
0 0 1	4.986	4.99	3	2 1 3	1.605	1.60	20
1 0 1	4.726	4.72	3	6 5 1	1.586	1.59	10
0 1 1	4.565	4.56	35	9 0 1	1.567	1.57	3
2 0 1	4.139	4.13	12	8 4 0	1.554	1.55	3
2 1 1	3.890	3.90	3	9 1 1	1.552		
4 0 0	3.713	3.71	5	0 7 1	1.542	1.54	5
1 3 0	3.668	3.67	5	0 3 3	1.522	1.52	8
1 2 1	3.633	3.63	3	5 6 1	1.520		
4 1 0	3.529	3.53	5	0 6 2	1.507	1.51	20
3 0 1	3.513	3.51	5	6 4 2	1.494	1.49	10
4 2 0	3.108	3.11	75	2 6 2	1.477	1.48	5
3 3 0	3.007	3.01	100	3 6 2	1.442	1.44	5
5 0 0	2.971	2.97	50	9 4 0	1.427	1.43	12
4 1 1	2.881	2.90	35	4 7 1	1.424	1.42	12
5 1 0	2.874	2.87	35	0 8 0	1.419	1.41	15
0 4 0	2.839	2.84	15	9 4 1	1.372	1.372	3
2 3 1	2.793	2.79	25	6 7 0	1.357	1.357	5
5 1 1	2.490	2.49	45	5 3 3	1.354	1.355	5
1 4 1	2.433	2.43	5	2 8 1	1.343	1.342	3
1 1 2	2.403	2.40	3	4 8 0	1.326	1.327	5
0 5 0	2.271	2.27	3	7 5 2	1.316	1.316	5
1 2 2	2.256	2.26	15	5 4 3	1.291	1.290	10
3 4 1	2.208	2.21	25	9 5 1	1.289		
2 5 0	2.172	2.17	10	4 8 1	1.281	1.282	3
7 1 0	2.080	2.09	40	4 7 2	1.277	1.277	3
0 5 1	2.067	2.07	40	0 9 0	1.262	1.263	5
7 2 0	1.987	1.99	3	5 8 1	1.240	1.240	3
7 0 1	1.952	1.95	8	9 4 2	1.238	1.238	3
4 5 0	1.937	1.93	6	8 0 3	1.238		
5 0 2	1.910	1.91	5	1 1 4	1.234	1.234	5
5 4 1	1.898	1.90	5	0 8 2	1.233		
0 6 0	1.892	1.89	20	2 6 3	1.231	1.231	5
1 4 2	1.858	1.86	15	6 8 0	1.231		
7 3 0	1.851	1.85	12	0 9 1	1.223	1.224	3
7 2 1	1.846	1.84	8	6 8 1	1.195	1.195	3
5 2 2	1.810	1.81	10	6 7 2	1.191	1.191	5
1 6 1	1.757	1.76	3	4 0 4	1.181	1.181	5
6 4 1	1.747	1.74	5	4 1 4	1.175	1.174	5
4 6 0	1.686	1.69	10	2 3 4	1.169	1.169	3
4 4 2	1.672	1.67	5	9 1 3	1.165	1.164	5
8 2 1	1.663	1.66	5	4 9 1	1.162	1.162	5
0 1 3	1.644	1.64	3	0 4 4	1.141	1.141	5
7 0 2	1.616	1.62	18				

^a Indexed on the basis of an orthorhombic unit-cell with $a = 14.854 \text{ \AA}$, $b = 11.356 \text{ \AA}$, and $c = 4.986 \text{ \AA}$.

indexed on the basis of a tetragonal unit-cell with $a = 10.070 \text{ \AA}$ and $c = 9.107 \text{ \AA}$. For unit-cell contents of a two-formula unit the cal-

culated density is 3.876 g/cm^3 , which agrees well with the measured density of 3.84 g/cm^3 . The interplanar spacings for this compound

with the corresponding indices are given in Table III. The compound was found to melt incongruently at a temperature about 1560°C to yield $\text{BaAl}_{19}\text{O}_{39}$ and a liquid.

(c) $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$

The existence of a phase of this composition has been observed by the presence of its distinct and characteristic X-ray pattern. The powder pattern can be indexed satisfactorily on the basis of an orthorhombic unit-cell with $a = 14.854 \text{ \AA}$, $b = 11.356 \text{ \AA}$, and $c = 4.986 \text{ \AA}$. The calculated density, 4.144 g/cm^3 , is in good agreement with that of the measured density, 4.13 g/cm^3 . The interplanar spacings of the compound with the corresponding indices are given in Table IV. The crystal structure of $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$ was found to be similar to that of $\text{Pb}_3\text{SiAl}_{10}\text{O}_{20}$ and $\text{Pb}_3\text{GeAl}_{10}\text{O}_{20}$ reported earlier by Vinek et al. (4) who have proposed a pseudo-orthorhombic monoclinic unit-cell for both the compounds. The compound $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$ is not stable up to the solidus temperature but dissociates in the solid state to BaAl_2O_4 and $\text{BaTiAl}_6\text{O}_{12}$. The maximum temperature of stability of this compound as determined by X-ray diffraction appeared to be 1440°C. Above this temperature the presence of both BaAl_2O_4 and $\text{BaTiAl}_6\text{O}_{12}$ could be detected. Petrographic examination of annealed samples showed that at least partial dissociation had occurred at temperatures above 1450°C as evident by the appearance of the characteristic grey phase of BaAl_2O_4 , the amount of which was increased with increasing temperature or on extended heat-treatment at the dissociation temperature.

The symmetry and the unit-cell parameters for the three compounds reported in this paper were based on the computer calculation of the powder data and do not necessarily ensure the inherent correctness that could be obtained from single crystal data. Single crystals were difficult to obtain because two of the compounds, namely, $\text{BaTi}_5\text{Al}_2\text{O}_{14}$ and $\text{BaTiAl}_6\text{O}_{12}$, melt incongruently while the third compound, $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$, undergoes a solid-state dissociation at subsolidus temperatures. Although an excellent agreement was observed between the $d_{\text{obs.}}$ and $d_{\text{calc.}}$ at all interplanar spacings reported and between the calculated and measured density for all the compounds, it may be possible that the proposed unit-cells represent only an approximation to the correct symmetry. This point can be resolved only when single crystal data are available for these compounds.

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