

## Subsolidus Equilibria in the System BaO-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>

J. P. GUHA

*Institute Jožef-Stefan, University of Ljubljana, Jamova 39,  
61000 Ljubljana, Yugoslavia*

Received October 20, 1978; in revised form July 24, 1979

The subsolidus phase equilibrium relations in the system BaO-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> have been investigated using conventional solid state reaction techniques and X-ray powder diffraction. The existence of three known ternary compounds, BaTi<sub>5</sub>Al<sub>2</sub>O<sub>14</sub>, BaTiAl<sub>6</sub>O<sub>12</sub>, and Ba<sub>3</sub>TiAl<sub>10</sub>O<sub>20</sub>, was confirmed and their stability relations were studied. Various tie-lines existing between the ternary compounds and the binary titanates and aluminates of barium were established and a subsolidus phase diagram showing the phase assemblages compatible at 1200°C is presented.

### Introduction

Alumina is one of the major impurities introduced in BaTiO<sub>3</sub>-based electronic ceramics during processing and its presence in increased quantity has been associated with inferior electrical properties (1-3). Several workers (4, 5) reported that BaTiO<sub>3</sub> reacts with Al<sub>2</sub>O<sub>3</sub> to form undesirable phases which remain in the grain boundaries as separate phases and form liquid at a considerably lower temperature. As a result, the use of Al<sub>2</sub>O<sub>3</sub> as a container material for firing BaTiO<sub>3</sub>-based electronic ceramics has been drastically limited.

Although the harmful effects of Al<sub>2</sub>O<sub>3</sub> on BaTiO<sub>3</sub>-based dielectric and ferroelectric ceramics were recognized a long time ago, the nature of the reaction involved between these two oxides and the products which form at different temperatures are not known. Thus understanding of solid state reactions between BaTiO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> and knowledge of phase compatibility in the system BaO-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> are of considerable technical importance. The present

investigation was undertaken to identify various ternary compounds and to establish the subsolidus equilibria existing in the system BaO-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>.

Data on phase relations in the system BaO-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> previously reported in the literature are limited to the subordinate binary joins and some data on compound formation within the ternary system are known. The binary system BaO-TiO<sub>2</sub> has been investigated by several workers and contradictory data were reported on the formation and stability of the compounds existing in the system. The first comprehensive phase diagram for the system was reported by Rase and Roy (6), who identified five compounds, namely, Ba<sub>2</sub>TiO<sub>4</sub>, BaTiO<sub>3</sub>, BaTi<sub>2</sub>O<sub>5</sub>, BaTi<sub>3</sub>O<sub>7</sub>, and BaTi<sub>4</sub>O<sub>9</sub>. According to these workers, BaTi<sub>2</sub>O<sub>5</sub> is difficult to form at solid state but can be readily obtained by cooling from the melt. The compound appears to have a stability minimum at 1210°C and melts incongruently at 1322°C. Subsequent studies by Jonker and Kwestroo (7) indicated that two more compounds, Ba<sub>2</sub>Ti<sub>5</sub>O<sub>12</sub> and Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>, exist in the

system. These workers could not prepare  $\text{BaTi}_2\text{O}_5$  in the solid state and suggested that the compound is metastable, forming only in the presence of liquid phase. Tillmanns and Baur (8) and Tillmanns (9) have grown single crystals of two new compounds and assigned their formulas as  $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$  and  $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ , respectively. Negas *et al.* (10), who investigated the subsolidus equilibria in the  $\text{BaTiO}_3$ - $\text{TiO}_2$  subsystem, observed that the correct formula for the compounds previously designated as  $\text{BaTi}_3\text{O}_7$  by Rase and Roy (6) and  $\text{Ba}_2\text{Ti}_5\text{O}_{12}$  by Jonker and Kwestroo (7) are  $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$  and  $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ , respectively. These workers could not obtain  $\text{BaTi}_2\text{O}_5$ , even in small quantities, in the solid state but observed that the compound forms readily when cooled from the melt. The existence of the compound  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  previously reported by Jonker and Kwestroo (7) was confirmed by O'Bryan *et al.* (11) and the  $d$ -values for the compound were presented. O'Bryan and Thomson (12) studied the phase equilibria in the  $\text{TiO}_2$ -rich region of the system  $\text{BaO}$ - $\text{TiO}_2$  and their results agree well with those of Negas *et al.* (10) with respect to the identity of the compounds but differ in regard to stability and melting temperatures of the various phases existing in the system. Tillmanns (13, 14) further reported the existence of two new compounds in the  $\text{TiO}_2$ -rich region of the system and assigned their formulas as  $\text{BaTi}_5\text{O}_{11}$  and  $\text{BaTi}_6\text{O}_{13}$ , respectively. In a recent publication, O'Bryan and Thomson (15) reported the  $d$ -values for  $\text{BaTi}_5\text{O}_{11}$  prepared by solid state reaction of a stoichiometric mixture containing  $\text{BaCO}_3$  and  $\text{TiO}_2$  at  $1100^\circ\text{C}$ .

Compound formation and phase equilibrium relations in the binary system  $\text{BaO}$ - $\text{Al}_2\text{O}_3$  have been investigated by several workers and the existence of a number of barium aluminates was established. One early work in the system was by Wartenberg and Reusch (16), who identified the compound  $\text{BaAl}_2\text{O}_4$  and presented part of

the liquidus curve for the system. Wallmark and Westgren (17) reported the crystallographic data for  $\text{BaAl}_2\text{O}_4$  and  $\text{BaAl}_{12}\text{O}_{19}$ . Carlson *et al.* (18) examined the entire system and reported the existence of yet another compound,  $\text{Ba}_3\text{Al}_2\text{O}_6$ . Toropov and Galachov (19) proposed a phase diagram for the system  $\text{BaO}$ - $\text{Al}_2\text{O}_3$  apparently based on melting point data. The diagram was later revised by Purt (20), who confirmed the existence of three barium aluminates and reported the crystallographic data for  $\text{Ba}_3\text{Al}_2\text{O}_6$ . Solid state reactions in the system  $\text{BaO}$ - $\text{Al}_2\text{O}_3$  were also studied by Planz and Müller-Hesse (21) and X-ray powder diffraction data for the barium aluminates were presented. Subsolidus equilibria in the high  $\text{BaO}$  portion of the system were investigated by Appendino (22) and five new phases were identified by X-ray diffraction. These are  $4\text{BaO}\cdot\text{Al}_2\text{O}_3$ ,  $5\text{BaO}\cdot\text{Al}_2\text{O}_3$ ,  $7\text{BaO}\cdot\text{Al}_2\text{O}_3$ ,  $8\text{BaO}\cdot\text{Al}_2\text{O}_3$ , and  $10\text{BaO}\cdot\text{Al}_2\text{O}_3$ . Haberey *et al.* (23) investigated the high  $\text{Al}_2\text{O}_3$  region of the system and reported that the compound  $\text{BaAl}_{12}\text{O}_{19}$  does not exist. They found instead two very similar compounds having chemical compositions of  $\text{BaO}\cdot 4.6\text{Al}_2\text{O}_3$  and  $\text{BaO}\cdot 6.6\text{Al}_2\text{O}_3$  and presented the indexed powder patterns for both.

The system  $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$  was investigated by Lang *et al.* (24), who reported that only one compound  $\text{Al}_2\text{TiO}_5$  exists in the system. The compound undergoes a polymorphic transformation from a low-temperature  $\beta$ -form to a high-temperature  $\alpha$ -form at  $1820^\circ\text{C}$ . These workers also observed that although  $\text{Al}_2\text{TiO}_5$  can be readily preserved at room temperature by quenching, an area of instability exists for the compound in the temperature range from about  $750$  to  $1300^\circ\text{C}$  in which  $\text{Al}_2\text{TiO}_5$  disproportionates to  $\alpha$ - $\text{Al}_2\text{O}_3$  and rutile.

The phase equilibrium diagram for the system  $\text{BaO}$ - $\text{TiO}_2$ - $\text{Al}_2\text{O}_3$  has not been reported in the literature, but some data on the compound formation within the system

are available. Guha *et al.* (25) have identified three ternary compounds, BaTi<sub>5</sub>Al<sub>2</sub>O<sub>14</sub>, BaTiAl<sub>6</sub>O<sub>12</sub>, and Ba<sub>3</sub>TiAl<sub>10</sub>O<sub>20</sub>, in the system and reported the X-ray powder data for the compounds. According to these workers, BaTi<sub>5</sub>Al<sub>2</sub>O<sub>14</sub> and BaTiAl<sub>6</sub>O<sub>12</sub> melt incongruently and Ba<sub>3</sub>TiAl<sub>10</sub>O<sub>20</sub> dissociates in the solid state to BaTiAl<sub>6</sub>O<sub>12</sub> and BaAl<sub>2</sub>O<sub>4</sub>. No further data on the ternary system are reported in the literature.

### Experimental Procedure

The starting materials used were analytical reagent-grade BaCO<sub>3</sub> (BDH Chemicals), TiO<sub>2</sub> (99.9% purity, A. D. Mackay Inc., New York), and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (BDH Chemicals). Mixtures containing appropriate proportions of the dried materials were weighed to the nearest milligram, mixed together under acetone in an agate mortar, dried in an oven, and pressed into cylindrical pellets which were wrapped in Pt foils and heated initially at 1000°C in air for 10 hr to decompose the carbonate. The samples were then heated to higher temperatures for prolonged periods with intermittent cooling, crushing, mixing, and pressing to promote homogeneity and to attain equilibrium. Temperatures were measured by a calibrated Pt-Pt/10% Rh thermocouple placed adjacent to the sample inside the furnace and assumed to be correct within  $\pm 5^\circ\text{C}$ . Most of the bulk compositions were duplicated using several different sets of reactants. Frequently, one or more of the crystalline barium titanates and aluminates, and the ternary compounds, were used as starting materials. These were prepared in 25-g batches by solid state reaction of the constituents. Occasional checks were made by following weight changes of the samples before and after firing to ensure that no significant loss occurred by volatilization. After the end of heat treatment at the desired temperatures, the pellets were quenched in air and the equilibrium phases were analyzed by X-ray powder diffraction. Equilibrium

was considered to have been attained when X-ray diffraction patterns of successively fired samples showed no further change. X-Ray powder photographs used for routine phase identification were obtained in a Guinier-de-Wolff focusing camera (Enraf-Nonius, Delft, Netherlands) with Ni-filtered CuK $\alpha$  radiation. For precision lattice-parameter measurements, a Geiger-counter diffractometer (Siemens Corp., Karlsruhe, West Germany) was used at a scanning rate of  $1/4^\circ 2\theta/\text{min}$ . The diffractometer was calibrated against the known peaks of pure Au ( $a_0 = 4.0786 \text{ \AA}$ ). An effort was made to characterize the phases in the fired samples by reflecting-light microscopy but the method was not very effective in examining the comparatively fine-grained structure of the sintered samples.

### Results and Discussion

Data on phase equilibrium relations in the three subordinate binary joins BaO-TiO<sub>2</sub>, BaO-Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> previously reported in the literature appear to have adequately characterized the various binary compounds and their polymorphs. In the present investigation, only the salient features related to the formation and stability of the binary compounds which have direct relevance to the subsolidus compatibility relations of the ternary system BaO-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> were examined.

In the system BaO-TiO<sub>2</sub>, the existence of the compounds Ba<sub>6</sub>Ti<sub>17</sub>O<sub>40</sub>, Ba<sub>4</sub>Ti<sub>13</sub>O<sub>30</sub>, and Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> was confirmed but no evidence could be obtained to show that the compounds BaTi<sub>5</sub>O<sub>11</sub> and BaTi<sub>6</sub>O<sub>13</sub> occur as stable phases at the subsolidus temperatures. Both Ba<sub>6</sub>Ti<sub>17</sub>O<sub>40</sub> and Ba<sub>4</sub>Ti<sub>13</sub>O<sub>30</sub> were found to melt incongruently at 1335 and 1357°C, respectively. These temperatures are in good agreement with those reported by Negas *et al.* (10). However, the temperature at which Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> dissociates to give BaTi<sub>4</sub>O<sub>9</sub> and TiO<sub>2</sub> was found to be slightly above 1400°C,

which is nearly the same as that reported by O'Bryan and Thomson (12) but much higher than that reported by Negas *et al.* (10). The compound  $\text{BaTi}_2\text{O}_5$  could not be prepared, even in small quantities, in the solid state and the equilibrium phase assemblages observed on firing a stoichiometric mixture of  $\text{BaO}:\text{2TiO}_2$  at temperatures up to  $1300^\circ\text{C}$  were  $\text{BaTiO}_3$  and  $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ . The compound was readily obtained when the same mixture was melted at  $1325^\circ\text{C}$  and quenched from liquid. This result supports the observation previously made by Jonker and Kwestroo (7) and Negas *et al.* (10) and confirms that  $\text{BaTi}_2\text{O}_5$  forms only in the presence of liquid at temperatures above  $1300^\circ\text{C}$ .

In the system  $\text{BaO}-\text{Al}_2\text{O}_3$ , the compounds  $\text{Ba}_3\text{Al}_2\text{O}_6$ ,  $\text{BaAl}_2\text{O}_4$ , and  $\text{BaAl}_{13.2}\text{O}_{20.8}$  ( $\text{BaO}\cdot 6\cdot 6\text{Al}_2\text{O}_3$ ) were prepared by solid state reaction of  $\text{BaCO}_3$  and  $\alpha\text{-Al}_2\text{O}_3$  at temperatures above  $1400^\circ\text{C}$ . However, the X-ray powder diffraction pattern of the compound  $\text{BaO}\cdot 4\cdot 6\text{Al}_2\text{O}_3$  reported by Haberey *et al.* (23) could not be distinguished from that of the  $\text{BaO}\cdot 6\cdot 6\text{Al}_2\text{O}_3$  because of the identical  $d$ -values for the compounds. Further, none of the barium aluminates reported by Appendino (22) in the BaO-rich region of the system could be detected because of the severe reaction of BaO with Pt metal at temperatures above  $1000^\circ\text{C}$  which gave rise to complicated X-ray diffraction patterns.

Subsolidus compatibility relations existing in the  $\text{BaO}-\text{TiO}_2-\text{Al}_2\text{O}_3$  system were established by equilibrating 140 ternary compositions at different temperatures. The phase diagram of the ternary system together with the compositions studied to establish the various tie-lines at  $1200^\circ\text{C}$  is shown in Fig. 1. Additional compositions studied but not shown merely corroborate those given in the diagram. The BaO-rich portion of the system could not be investigated because of the reaction of Pt metal with free BaO and the phase relations in this area remain

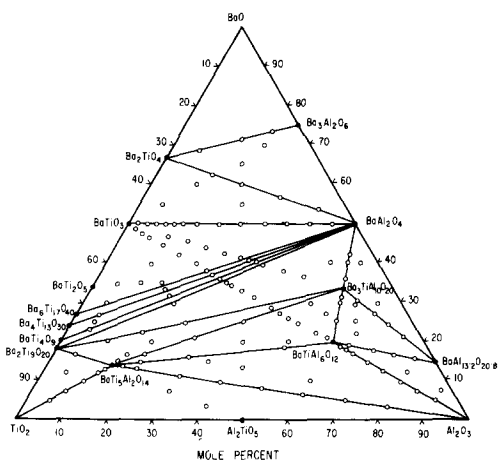


FIG. 1. Subsolidus phase equilibria in the system  $\text{BaO}-\text{TiO}_2-\text{Al}_2\text{O}_3$  at  $1200^\circ\text{C}$ .

uncertain. The X-ray diffraction analysis revealed that in the range of compositions studied, three ternary compounds exist in the system and their compositions were established as  $\text{BaO}\cdot 5\text{TiO}_2\cdot \text{Al}_2\text{O}_3$ ,  $\text{BaO}\cdot \text{TiO}_2\cdot 3\text{Al}_2\text{O}_3$ , and  $3\text{BaO}\cdot \text{TiO}_2\cdot 5\text{Al}_2\text{O}_3$ . The X-ray crystallographic data for the compounds are summarized in Table I.

The tie-lines between the various phases as shown in Fig. 1 constitute a total of 16 compatibility triangles at  $1200^\circ\text{C}$ . This temperature was chosen as being just below the lowest temperature at which the first sign of liquid formation was observed in the system. As might be expected, the lowest solidus temperature occurred in phase assemblages that contained a higher barium titanate. The existence of several ternary phases and the disposition of the subsolidus compatibility triangles produce several regions of comparatively high solidus temperatures in the system. However, at higher temperatures the compatibility relations in the system become more complex because of the instability of several binary as well as ternary compounds. The compound  $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$  has a temperature stability maximum at  $1440^\circ\text{C}$  above which it dissociates in the solid state to  $\text{BaAl}_2\text{O}_4$  and

TABLE I  
X-RAY CRYSTALLOGRAPHIC DATA FOR BARIUM TITANIUM ALUMINATES

	BaTi <sub>5</sub> Al <sub>2</sub> O <sub>14</sub>	BaTiAl <sub>6</sub> O <sub>12</sub>	Ba <sub>3</sub> TiAl <sub>10</sub> O <sub>20</sub>
Symmetry	Tetragonal	Tetragonal	Orthorhombic
Unit cell (Å)	$a = 7.025$ $c = 10.156$	$a = 10.070$ $c = 9.107$	$a = 14.854$ $b = 11.365$ $c = 4.986$
Cell content (z)	2	4	2
Density (g/cm <sup>3</sup> ) Expt.	4.32	3.84	4.13
Calc.	4.34	3.87	4.14

BaTiAl<sub>6</sub>O<sub>12</sub>. Thus the two tie-lines BaAl<sub>2</sub>O<sub>4</sub>-Ba<sub>3</sub>TiAl<sub>10</sub>O<sub>20</sub> and Ba<sub>3</sub>TiAl<sub>10</sub>O<sub>20</sub>-BaTiAl<sub>6</sub>O<sub>12</sub> merge into a single thermodynamically stable join, BaAl<sub>2</sub>O<sub>4</sub>-BaTiAl<sub>6</sub>O<sub>12</sub>, above 1440°C. The disappearance of the compound Ba<sub>3</sub>TiAl<sub>10</sub>O<sub>20</sub> also, in effect, merges the two three-phase triangles BaAl<sub>2</sub>O<sub>4</sub>-Ba<sub>3</sub>TiAl<sub>10</sub>O<sub>20</sub>-BaAl<sub>13.2</sub>O<sub>20.8</sub> and BaTiAl<sub>6</sub>O<sub>12</sub>-Ba<sub>3</sub>TiAl<sub>10</sub>O<sub>20</sub>-BaAl<sub>13.2</sub>O<sub>20.8</sub> into a large three-phase triangle, BaAl<sub>2</sub>O<sub>4</sub>-BaTiAl<sub>6</sub>O<sub>12</sub>-BaAl<sub>13.2</sub>O<sub>20.8</sub>. The compound Al<sub>2</sub>TiO<sub>5</sub> has a temperature stability minimum at 1300°C above which a tie-line appears between Al<sub>2</sub>TiO<sub>5</sub> and BaTi<sub>5</sub>Al<sub>2</sub>O<sub>14</sub>. As a result, the three-phase triangle TiO<sub>2</sub>-BaTi<sub>5</sub>Al<sub>2</sub>O<sub>14</sub>-Al<sub>2</sub>O<sub>3</sub> changes into two separate entities, TiO<sub>2</sub>-BaTi<sub>5</sub>Al<sub>2</sub>O<sub>14</sub>-Al<sub>2</sub>TiO<sub>5</sub> and Al<sub>2</sub>O<sub>3</sub>-BaTi<sub>5</sub>Al<sub>2</sub>O<sub>14</sub>-Al<sub>2</sub>TiO<sub>5</sub>. The compound BaTi<sub>2</sub>O<sub>5</sub> does not have a stability field in the ternary system at the subsolidus temperatures. In the present investigation, the compound was detected only in the samples which were quenched from the melt.

The compounds Ba<sub>2</sub>TiO<sub>4</sub>, BaTiO<sub>3</sub>, Ba<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>, and BaAl<sub>2</sub>O<sub>4</sub> melt congruently. Therefore, the subsolidus joins Ba<sub>2</sub>TiO<sub>4</sub>-Ba<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>, Ba<sub>2</sub>TiO<sub>4</sub>-BaAl<sub>2</sub>O<sub>4</sub>, and BaTiO<sub>3</sub>-BaAl<sub>2</sub>O<sub>4</sub> form true pseudobinary subsystems at liquidus temperatures. No appreciable solid solubility was detected in

these pseudobinary joins at the subsolidus temperatures.

### Acknowledgments

This work was supported by the Boris Kidrič Foundation for Scientific Research. The author is grateful to Professor D. Kolar for his interest and encouragement during the course of the investigation.

### References

1. W. W. COFFEN, *Trans. Amer. Inst. Elec. Eng. Part 1* **72**, 704 (1953).
2. E. G. GRAF, *Ceram. Age* **58**, 16 (1951).
3. K. E. NELSON AND R. L. COOK, *Bull. Amer. Ceram. Soc.* **38**, 499 (1959).
4. P. BAXTER, N. J. HELLICAR, AND B. LEWIS, *J. Amer. Ceram. Soc.* **42**, 465 (1959).
5. E. SCHMIDT, *Ber. Deut. Keram. Ges. H-9* **43**, 554 (1966).
6. D. E. RASE AND R. ROY, *J. Amer. Ceram. Soc.* **38**, 102 (1955).
7. G. H. JONKER AND W. KWESTROO, *J. Amer. Ceram. Soc.* **41**, 390 (1958).
8. E. TILLMANNS AND W. H. BAUR, *Acta Crystallogr. Sect. B* **26**, 1645 (1970).
9. E. TILLMANNS, *Inorg. Nucl. Chem. Lett.* **7**, 1169 (1971).
10. T. NEGAS, R. S. ROTH, H. S. PARKER, AND D. MINOR, *J. Solid State Chem.* **9**, 297 (1974).
11. H. M. O'BRYAN, JR., J. THOMSON, JR., AND J. K. PLOURDE, *J. Amer. Ceram. Soc.* **57**, 450 (1974).
12. H. M. O'BRYAN, JR., AND J. THOMSON, JR., *J. Amer. Ceram. Soc.* **57**, 522 (1974).

13. E. TILLMANN, *Acta Crystallogr. Sect. B* **25**, 1444 (1969).
14. E. TILLMANN, *Cryst. Struct. Commun.* **1**, 1 (1972).
15. H. M. O'BRYAN, JR., AND J. THOMSON, JR., *J. Amer. Ceram. Soc.* **58**, 454 (1975).
16. H. WARTENBERG AND H. J. REUSCH, *Z. Anorg. Allg. Chem.* **207**, 1 (1932).
17. S. WALLMARK AND A. WESTGREN, *Ark. Kem. Mineral. Geol.* **B-12**, 1 (1937).
18. E. T. CARLSON, T. J. CHACONAS, AND L. S. WELLS, *J. Res. Nat. Bur. Stand.* **45**, 381 (1950).
19. N. A. TOROPOV AND E. J. GALACHOV, *Berl. Akad. Wiss. SSSR* **82**, 69 (1952).
20. G. PURT, *Radex Rundsch.* **4**, 198 (1960).
21. J. E. PLANZ AND H. MÜLLER-HESSE, *Ber. Deut. Keram. Ges.* **38**, 440 (1961).
22. P. APPENDINO, *Ann. Chim. (Rome)* **61**, 822 (1971).
23. F. HABEREY, G. OEHLSCHEGEL, AND K. SAHL, *Ber. Deut. Keram. Ges.* **54**, 373 (1977).
24. S. M. LANG, C. L. FILLMORE, AND L. H. MAXWELL, *J. Res. Nat. Bur. Stand.* **48**, 298 (1952).
25. J. P. GUHA, D. KOLAR, AND B. VOLAVSEK, *J. Solid State Chem.* **16**, 49 (1976).