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AN APPRAISAL OF THE TERNARY SYSTEM BAO-CAO-AL<sub>2</sub>O<sub>3</sub>. (U)

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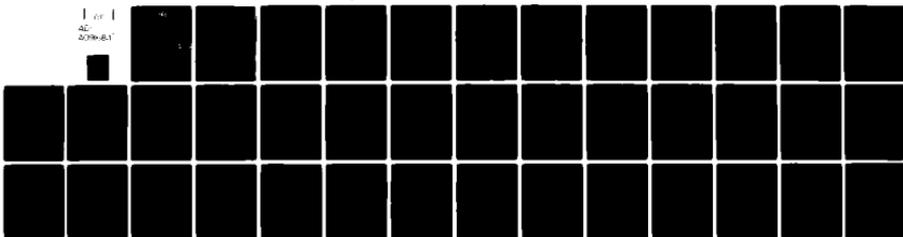
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**An Appraisal of the  
Ternary System BaO-CaO-Al<sub>2</sub>O<sub>3</sub>**

**G. M. WOLTEN  
Chemistry and Physics Laboratory  
Laboratory Operations  
The Aerospace Corporation  
El Segundo, Calif. 90245**

**1 October 1980**

**Interim Report**

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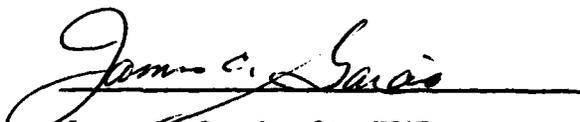
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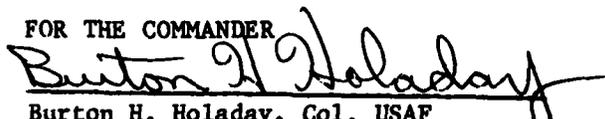
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This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

  
James C. Garcia, Lt, USAF  
Project Officer

  
Joseph J. Cox, Jr., LtCol, USAF  
Chief, Advanced Technology Division

FOR THE COMMANDER  
  
Burton H. Holaday, Col, USAF  
Directorate of Space Systems Planning  
Deputy for Technology



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## INTRODUCTION

A barium-oxygen monolayer or partial monolayer on a metal substrate lowers the work function for electron emission of the metal surface. A long-lasting source of barium for the cathodes of travelling wave tubes is provided by making the cathodes of a porous tungsten matrix that is impregnated with a ceramic material composed of barium oxide (BaO), calcium oxide (CaO), and aluminum oxide ( $\text{Al}_2\text{O}_3$ , alumina).

A number of different ratios of the three oxides have been used. Current interest centers on two of these, the S-cathode in which the BaO:CaO: $\text{Al}_2\text{O}_3$  mol ratio is 4:1:1, and the B- and M-cathodes in which it is 5:3:2.

This report was written in response to a request to analyse and interpret the ternary phase diagram for the mixture of the three oxides in order to better understand the nature of the impregnant, how it might change in time, and whether there are opportunities for optimizing the composition and the processing parameters.

Readily available information on the ternary phase diagram was incomplete, especially in the composition range of greatest interest. A determined literature search uncovered substantial additional information (much of it in journals that do not have a wide circulation in this country), which took considerable time to acquire. When this was accomplished, it appeared that sufficient information was on hand to assemble a complete isothermal cut through the ternary diagram at  $1250^\circ\text{C}$ . This is sufficiently close to the typical  $1050^\circ\text{C}$  operating temperature of a cathode to be useful. Additional information suggests little change from 1250 to  $1400^\circ\text{C}$ . Outside this temperature range, information is available only for the BaO- $\text{Al}_2\text{O}_3$  binary system, at both higher and lower temperatures, which allows some speculation as to how the ternary system might change with a change in temperature, but such extrapolations should be made cautiously because of the complexity of the ternary system.

The desirability of selected additional experimentation for a complete understanding is thus apparent. However, the purpose of this report is to summarize and interpret the presently available but distributed information in a single-source document.

## THE SYSTEM CaO-BaO

CaO melts above 2600°C, and BaO melts above 1900°C. We are not aware of any study in which mixtures of the two compounds were melted in order to establish the course of the liquidus in the binary system. The liquidus is a plot of the temperature of complete melting versus composition.

A number of ternary phase diagrams in which CaO and BaO are two of the three components are in the literature, e.g., the CaO-BaO-TiO<sub>2</sub> system.<sup>1</sup> All of these diagrams indicate an absence of any solid solution between CaO and BaO in the ternary field adjacent to the CaO-BaO side, but the authors do not comment on that. Only one publication has come to our attention in which the possibility of solid solution between CaO and BaO is addressed specifically.<sup>2</sup> The authors found no evidence for solid solution in mixtures sintered at 1100°C. We estimate their detection limit to have been better than 2%, perhaps of the order of 1%. The possibility of some degree of solid solution at substantially higher temperatures is not excluded, but there is none at the temperatures of interest in the present context. Any sintered material containing CaO and BaO would therefore be a mechanical mixture of the components. Somewhere in the range of mixtures there must be a eutectic, but neither its composition nor its melting point is known. Schematically, the phase diagram would look like either Figure 1(a) or Figure 1(b).

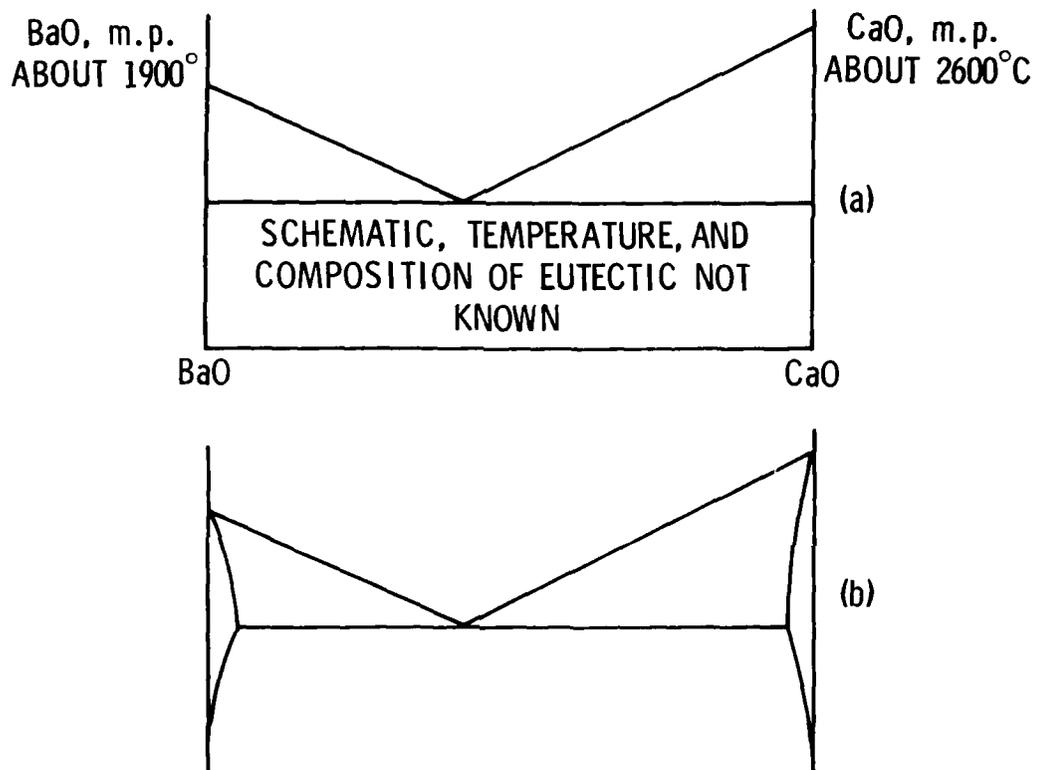


Figure 1. The CaO-BaO System. (a) No detectable solid solubility at room temperature after sintering for 2 hr at 1100°C. High-temperature solubility unknown. (b) Alternative form of diagram. Some limited solid solution assumed at higher temperatures.

## THE SYSTEM CaO-Al<sub>2</sub>O<sub>3</sub>

The CaO-Al<sub>2</sub>O<sub>3</sub> system is of major importance to the Portland cement industry, and BaO-Al<sub>2</sub>O<sub>3</sub> plays a role in high-density cements. Much of the phase equilibrium work has been conducted by or on behalf of the cement industry. In the industry, a simplified nomenclature is often used, which will be convenient to introduce here. Whenever we use this nomenclature, the letters B, C, and A stand for 1 mol or one formula unit of BaO, CaO, and Al<sub>2</sub>O<sub>3</sub>, respectively. A compound with the formula 3CaO-Al<sub>2</sub>O<sub>3</sub> (or Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>) will thus be designated C<sub>3</sub>A.

The CaO-Al<sub>2</sub>O<sub>3</sub> system has been the subject of a number of investigations. Figure 2 has been constructed from the interpretation of R. W. Nurse et al.<sup>3</sup> These authors show that this diagram applies only under strictly anhydrous conditions.<sup>4</sup> If the furnace atmosphere has a normal moisture content, the eutectic between C<sub>3</sub>A and CA gives way to a new compound with the approximate composition C<sub>12</sub>A<sub>7</sub>. This compound is not just hygroscopic but binds water in the form of hydroxyl groups and can be represented approximately as Ca<sub>12</sub>Al<sub>14</sub>O<sub>32</sub>(OH)<sub>2</sub>. This modification of the phase diagram, because of moisture, is fully described in the quoted paper, but Figure 3, which shows these results, is taken from a monograph on the chemistry of cements.<sup>5</sup>

Most compositions in both the CaO-Al<sub>2</sub>O<sub>3</sub> and the BaO-Al<sub>2</sub>O<sub>3</sub> systems are prone to absorb both H<sub>2</sub>O and CO<sub>2</sub>, forming hydrates, hydroxy-compounds, carbonates, and oxy-carbonates. C<sub>12</sub>A<sub>7</sub> must be an extreme case; it contains 1.3% bound water at about 950°C, a temperature at which most other materials would be presumed to be anhydrous.

The initial impregnant compositions are in equilibrium only with CaO but not any of the calcium aluminates. This will not be true in the later stages of cathode operation when there has been some depletion in BaO as a result of evaporation. This will be discussed in the final paragraphs of this report.

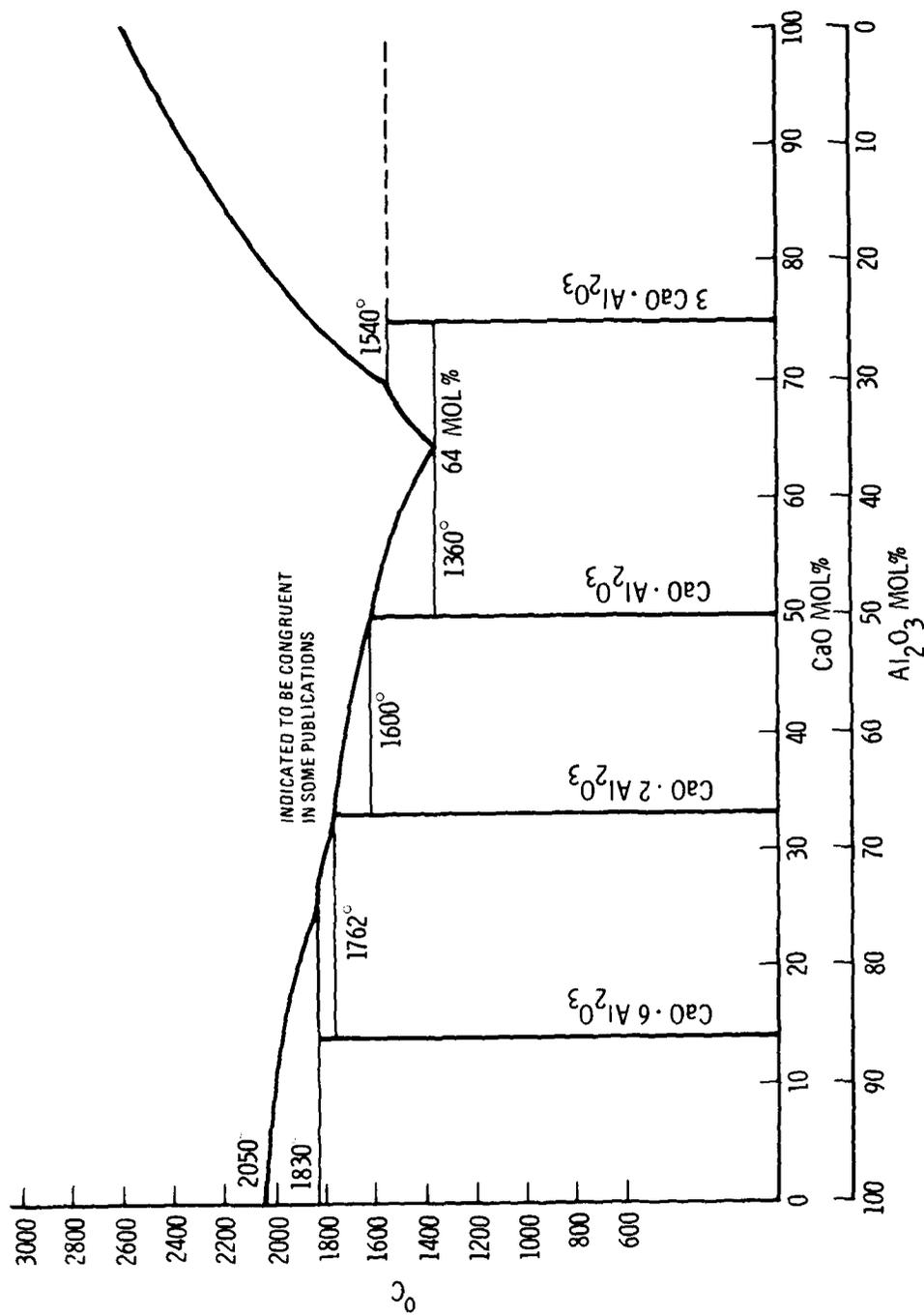


Figure 2. The CaO-Al<sub>2</sub>O<sub>3</sub> System Under Anhydrous Conditions

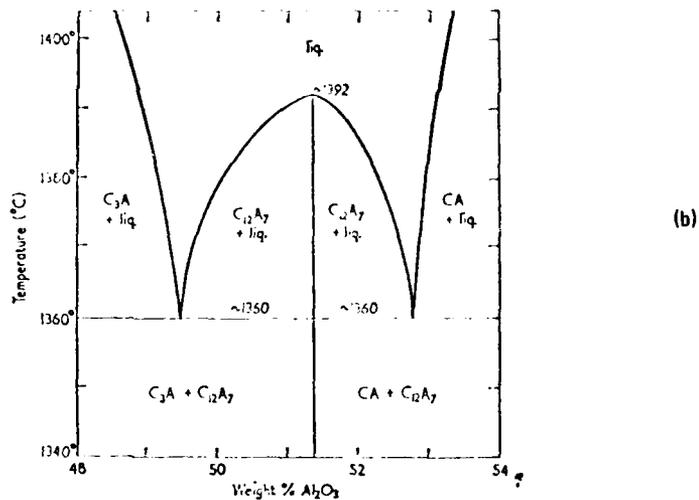
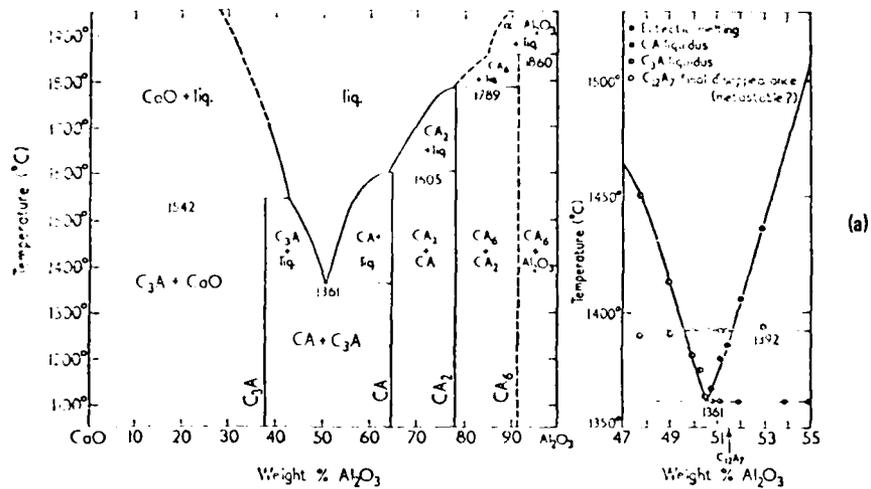


Figure 3. The  $\text{CaO-Al}_2\text{O}_3$  System as Modified by Presence of Moisture. (a) The system  $\text{CaO-Al}_2\text{O}_3$ : (left) probable diagram for strictly anhydrous conditions; (right) detail for compositions around  $\text{C}_{12}\text{A}_7$ . (b) Part of the system  $\text{CaO-Al}_2\text{O}_3$  considerably modified from the diagram of Rankin and Wright.<sup>1</sup>  $\text{C}_{12}\text{A}_7$  is shown as melting congruently; this diagram represents approximately the behavior of this part of the system in atmosphere of ordinary humidity.

## THE SYSTEM BaO-Al<sub>2</sub>O<sub>3</sub>

The BaO-Al<sub>2</sub>O<sub>3</sub> system has also been investigated more than once. Figure 4 has been prepared from a rendering of the system in the 1964 Supplement to Phase Diagrams for Ceramists, but the dual values of various temperatures given in the drawing represent the data of the different investigators. The region between 50 and 100 mol% BaO is important to an understanding of impregnant phases. Subsequent to the publication of the data on which Figure 4 is based, Appendino<sup>7</sup> conducted a thorough investigation of phase relationships below the melting curve in the barium-rich portion of the system. His results are summarized in Figure 5.

B and B<sub>3</sub>A have a eutectic at 17 mol% Al<sub>2</sub>O<sub>3</sub>, at a temperature near or slightly above 1500°C. The horizontal line at this temperature, touching the liquidus at the eutectic, is called the solidus for the B-B<sub>3</sub>A equilibrium. We are thus talking about "subsolidus" phase relationships. These are very important to the present subject because, as will be shown, impregnant equilibria involve phases along the B-A side of the ternary diagram.

When a BaO-Al<sub>2</sub>O<sub>3</sub> composition in this range first solidifies from the melt, it consists of B and B<sub>3</sub>A. At some undetermined temperature below the solidus, solid-state reactions occur and new compounds appear. Above 1130°C, in the region from 0 to 11 mol% A, the equilibrium phases are B and B<sub>8</sub>A; from 11 to 20 mol% A, the phases are B<sub>8</sub>A and B<sub>4</sub>A, and from 20 to 25 mol% A, they are B<sub>4</sub>A and B<sub>3</sub>A.

B<sub>8</sub>A decomposes again at 1050°C, and B<sub>4</sub>A at 940°C. However, a new phase, B<sub>10</sub>A, makes its appearance below 1130°C. B<sub>7</sub>A appears below 1050°C, and B<sub>5</sub>A below 940°C. At temperatures below 940°C, there are thus four fields in which, with increasing alumina content, the respective equilibria are between (1) B and B<sub>10</sub>A, (2) B<sub>10</sub>A and B<sub>7</sub>A, (3) B<sub>7</sub>A and B<sub>5</sub>A, and (4) B<sub>5</sub>A and B<sub>3</sub>A.

The intermediate temperature range, 1130 to 940°C, is one in which the system changes from the first to the second set of intermediate phases, and slight changes in temperature will change the nature of the phases that are

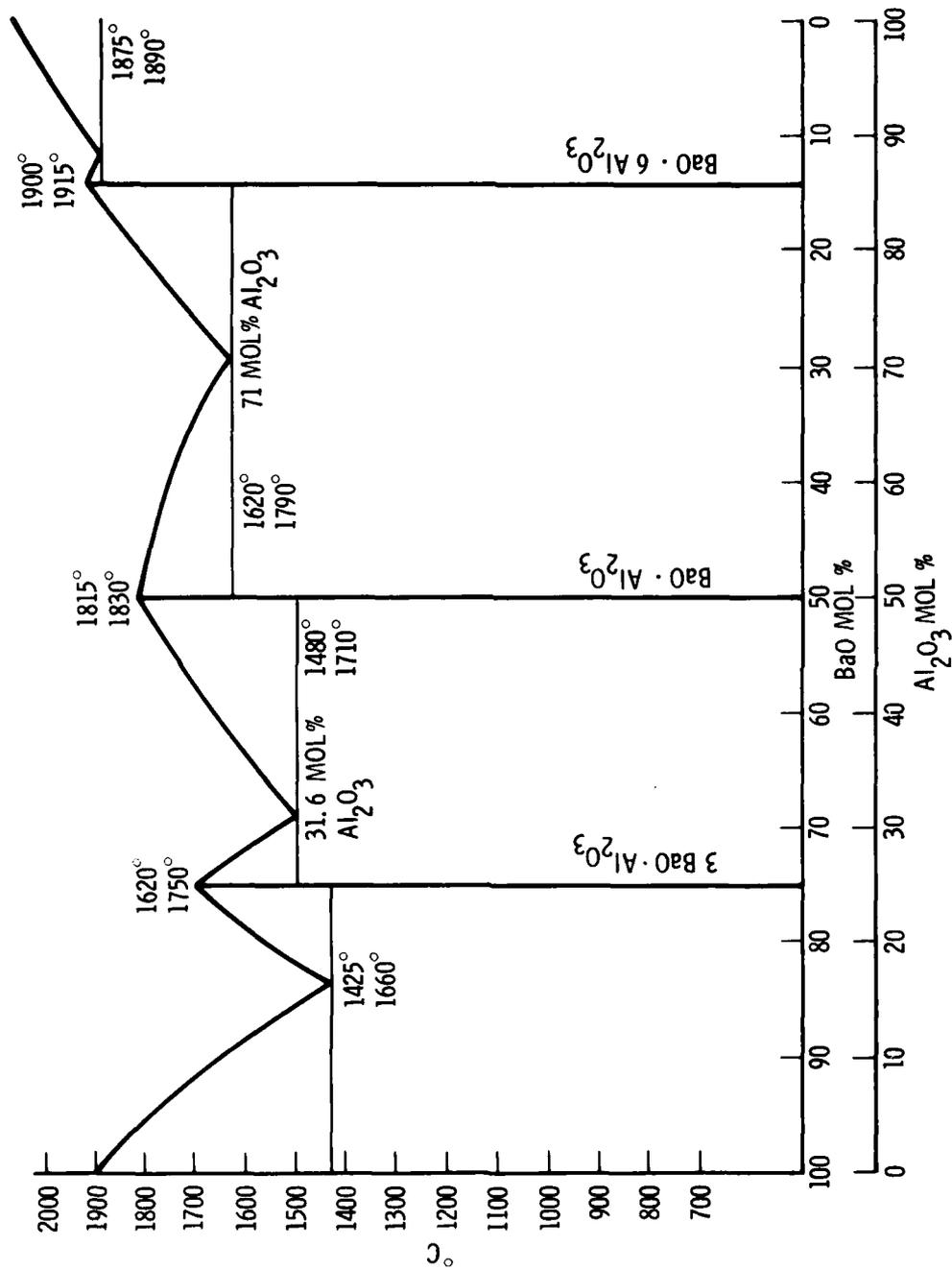


Figure 4. The BaO-Al<sub>2</sub>O<sub>3</sub> System as Shown in Phase Diagram for Ceramists

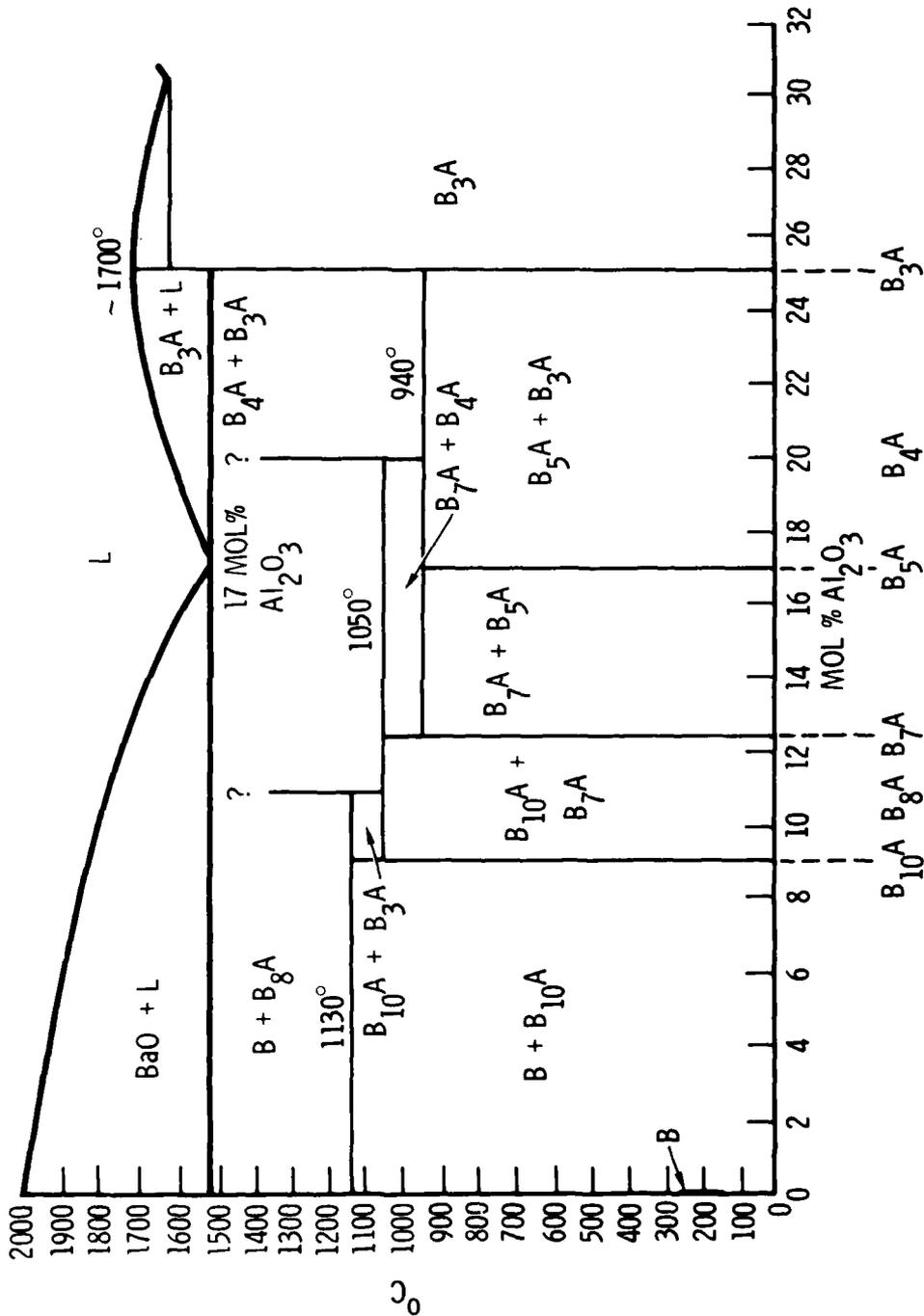


Figure 5. Barium-Rich Portion of BaO-Al<sub>2</sub>O<sub>3</sub> System According to Appendino

present. This is highly significant because typical cathode operating temperatures are centered on this range, namely 1000 to 1100°C.

An important question to ask is: How fast are these reactions? In order to ensure the attainment of equilibrium, Appendino heated the specimens for periods of time that varied from 100 hours at 1400°C to "a good many hundreds" (parecchie centinaia) of hours at 900°C. There is no indication of how much these times could have been shortened and still result in recognizable amounts of the new phases. Solid-state reactions that require diffusion (as all of these do) are much slower than similar reactions in the liquid or vapor state, but they can vary for different cases from seconds to years. The rates of diffusion of mobile entities (ions, atoms, and molecules) in a solid decrease with decreasing temperature. Tammann's rule of thumb, often used by metallurgists, is that the mobility becomes negligible below about one-half the absolute melting temperature. This would be about 600°C at the B-B<sub>3</sub>A eutectic composition and about 850°C for BaO.

The ternary B-C-A diagram has been explored in the temperature range from 1250 to 1400°C, in which B<sub>4</sub>A and B<sub>8</sub>A are stable, in addition to B<sub>3</sub>A and BA which are stable at all temperatures. B<sub>8</sub>A does not exist far enough into the ternary to be significant for the 4:1:1 and 5:3:2 compositions. B<sub>4</sub>A and B<sub>3</sub>A are important phases, and so is a ternary compound, B<sub>3</sub>CA, discovered by Appendino.<sup>8</sup> There is no information on the range of temperatures through which B<sub>3</sub>CA is stable other than that it exists at 1250°C. There is no ternary diagram for temperatures lower than 1250°C and, hence, no information whether the stability fields of B<sub>10</sub>A, B<sub>7</sub>A, and B<sub>5</sub>A extend far enough into the ternary to affect the impregnant compositions at lower temperatures. Nor do we know how readily equilibrium would be attained at these lower temperatures.

The reason for referring to the ternary diagram here prior to its more complete discussion later in this report is to show that any limitations to its usefulness are connected mainly with the complexity of the binary BaO-Al<sub>2</sub>O<sub>3</sub> diagram that is under discussion in this section, specifically with its changing nature as a function of temperature.

Assuming that the formation and decomposition of the relevant intermediate phases is not extremely sluggish, temperature fluctuations in an operating cathode would cause these reactions to go back and forth and thereby agitate the impregnant. This could cause the liberation of BaO to be more rapid than it would be in the absence of such reactions and could be an essential feature of the chosen compositions. Even in the absence of temperature fluctuations, the mere fact that some phases are close (in temperature) to a stability limit could have the same effect, especially in the presence of electric fields. It has been shown that electric fields can enhance solid-state diffusion.<sup>9</sup>

TERNARY COMPOUNDS

A.  $5\text{BaO}\cdot\text{CaO}\cdot 2\text{Al}_2\text{O}_3$

In the Powder Diffraction File (PDF),<sup>10</sup> under pattern No. 15-74, is listed, without indexing a 15-line diffraction pattern for a material identified as  $\text{Ba}_5\text{CaAl}_4\text{O}_{12}$  (alternative formula as above), implying that this is a unique compound. Also listed in the PDF, as pattern No. 15-331, is the 21-line diffraction pattern for  $\text{Ba}_3\text{Al}_2\text{O}_6$  ( $\text{B}_3\text{A}$ ) published by Brisi and Montorsi<sup>11</sup> and assigned to a cubic unit cell with  $a_0 = 16.51 \text{ \AA}$ .

The first of these patterns is referenced to a publication by Maklatov and Ostanchenko,<sup>12</sup> in which the authors investigated cathode coatings or impregnants (they do not say which) with the overall compositions  $2.5\text{BaO}$ ,  $0.5\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ , and  $2.5\text{BaO}$ ,  $0.5\text{CaO}$ ,  $\text{WO}_3$ . After appropriate sintering, the specimens were found to consist of single phases. The authors never state that they considered these compositions to be unique compounds, but they do leave the reader with that impression. In fact, Brisi and Montorsi, as well as Massazza,<sup>13</sup> found that up to 24% of the barium atoms in  $\text{B}_3\text{A}$  can be continuously replaced by calcium atoms to give mixed crystals (solid solutions)  $\text{B}_{3-x}\text{C}_x\text{A}$ , where  $x$  can range from 0 to 0.72. The alleged compound  $\text{B}_{2.5}\text{C}_{0.5}\text{A}$  is thus only an intermediate composition in a solid solution series. All three of the Italian teams quoted in this report support this conclusion, which had already been reached by us independently.

$\text{B}_3\text{A}$  is isostructural with  $\text{C}_3\text{A}$ ; therefore the solid solution series  $\text{B}_{3-x}\text{C}_x\text{A}$  in the absence of a unique intermediate compound would also be isostructural with both  $\text{B}_3\text{A}$  and  $\text{C}_3\text{A}$ . The latter is cubic, space group  $\text{Pa}\bar{3}$ , with  $a_0 = 15.262 \text{ \AA}$ . Very complete diffraction patterns for  $\text{C}_3\text{A}$  have been listed in a Bureau of Standards publication.<sup>14</sup> Ninety lines are given in the "front reflection" region alone, i.e.,  $d$ -spacings larger than  $1.2 \text{ \AA}$ . Thus, Brisi's 21-line pattern for  $\text{B}_3\text{A}$  is clearly very incomplete. With  $a_0 = 16.508 \text{ \AA}$  for  $\text{B}_3\text{A}$  known, the complete pattern can easily be calculated. There are 38 possible lines with spacings larger than  $2.4 \text{ \AA}$  alone, and these are listed in Appendix A. When calcium is substituted for barium, the unit cell shrinks by  $0.015 \text{ \AA}$  for each 1 mol% of substitution. At the composition  $\text{B}_{2.5}\text{C}_{0.5}\text{A}$ , the

unit cell is 16.293 Å in size, and corresponding d-spacings are 1.3% smaller than for  $B_3A$ . The differences between the two patterns in the PDF not accounted for by this shrinkage occur because both patterns are very incomplete and represent slightly different selections from the much larger number of lines that would be seen in more complete patterns, such as those available for  $C_3A$ .

B.  $Ba_3CaAl_2O_7$  ( $B_3CA$ )

Appendino reports finding this compound in the ternary system at 1250°C. Its composition is slightly variable. The C content can range from 0.8 to 1.1, with B varying in a complementary manner such that the sum of B and C is 4.0. One is immediately struck with the fact that in a purely formal sense,  $B_3CA$  is  $B_4A$  with one-quarter of the barium atoms replaced by calcium atoms. In Appendix B, tentative unit cells that we have derived for all of Appendino's new compounds are listed. The cells for  $B_4A$  and  $B_3CA$  are very similar, the latter being slightly smaller but having very similar axial ratios. The diffraction patterns of the two compounds are also quite similar. One must ask whether this suggests an analogy to the case previously discussed. It may be that  $B_3CA$  is just one composition along a solid solution series in which calcium is progressively substituted for barium in the basic  $B_4A$  structure.

Appendino's principal evidence that  $B_3CA$  constitutes a separate phase rests on his finding of a miscibility gap between  $B_4A$  and  $B_3CA$  along the line joining them in the phase diagram. Appendino clearly did some very good work and was aware of pitfalls. Nevertheless, one should not assume without further confirmation that all of his results must be entirely correct or that all of his specimens were representative of complete equilibrium. It is at least possible that the miscibility gap is spurious and  $B_3CA$  not a true compound. If this were true, it would somewhat simplify the rather complex phase diagram, although not enough so as to make this a forceful argument.

C.  $BaCa_2Al_8O_{15}$  ( $BC_2A_4$ )

This compound has been reported in the alumina-rich portion of the ternary system. It appears to be adequately established. Since it is in a portion of the diagram that has no bearing on our current interest, no further analysis will be attempted here.

## THE TERNARY SYSTEM BaO-CaO-Al<sub>2</sub>O<sub>3</sub>

A ternary system ABC results from the joining of three binary systems, AB, BC, and AC. One arranges the three binary systems such that their base lines form an equilateral triangle, the corners of which are labelled with the three components. The principle is shown in Figure 6A. The binaries are then folded up along their base lines to form the triangular prism of Figure 6B. The temperature coordinate now runs parallel to the height of the prism, and a triangular grid on the floor of the prism contains the composition coordinates, as shown in Figure 6c.

In lieu of constructing a three-dimensional space model, one can investigate and look at a variety of projections of the prism, or at planes (two-dimensional cuts) through the prism. What is available for the BaO-CaO-Al<sub>2</sub>O<sub>3</sub> system is primarily a horizontal (isothermal) cut through the prism at 1250°C. From a partial cut at 1400°C it is evident that there is little change between 1250°C and 1400°C. We can also speculate as to what the cut might look like in the relevant portion of the diagram just below the solidification temperature, say, around 1500°C, give or take a little.

When there are binary compounds along the edges of the ternary system that do not decompose upon addition of the third component, or when there are ternary compounds within the system, then the ternary system subdivides into smaller triangles, each of which is a ternary system in itself, although it cannot always be considered in isolation from neighboring triangles. A simple case is illustrated in Figure 6d. When the number of compounds exceeds two, there are several ways of subdividing the system. In general, the correct way must be determined by experiment.

The B-C-A system subdivided by its numerous compounds is shown in Figure 7. The diagram on the left is from Brisi and Montorsi<sup>11</sup> and was determined at 1250°C. The diagram on the right is from Massazza<sup>13</sup> and was determined at 1400°C. Its distorted appearance, compared to the former, is only the result of the fact that it is plotted in weight percent instead of mol percent; actually, the two diagrams match rather closely. The only substantial

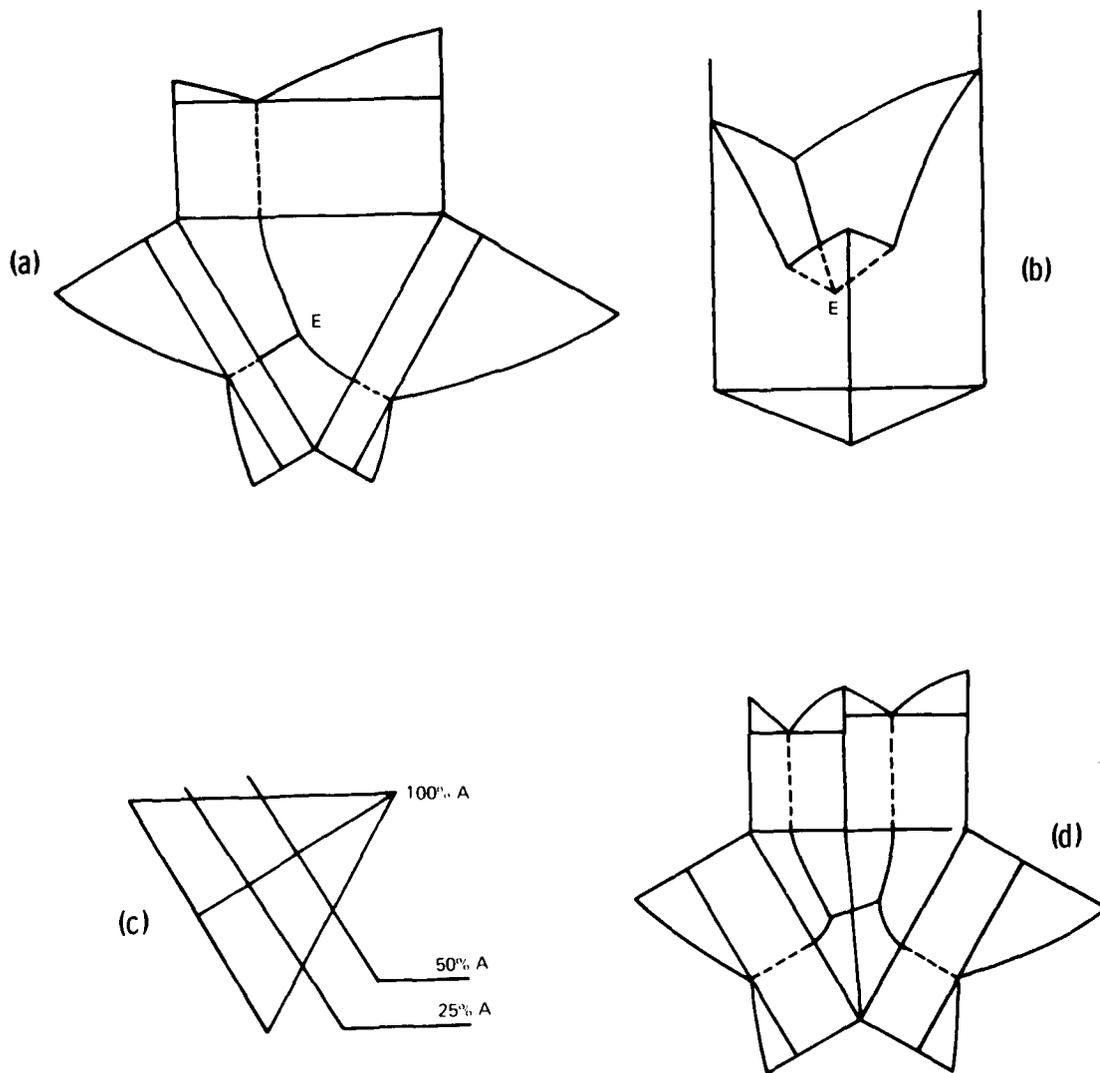


Figure 6. Some Principles of Construction for Ternary Phase Diagrams.  
 (a) Three binary systems combine to form a ternary. E is the ternary eutectic. (b) The space figure. (c) The concentration triangle. (d) A compound divides a ternary into two ternaries.

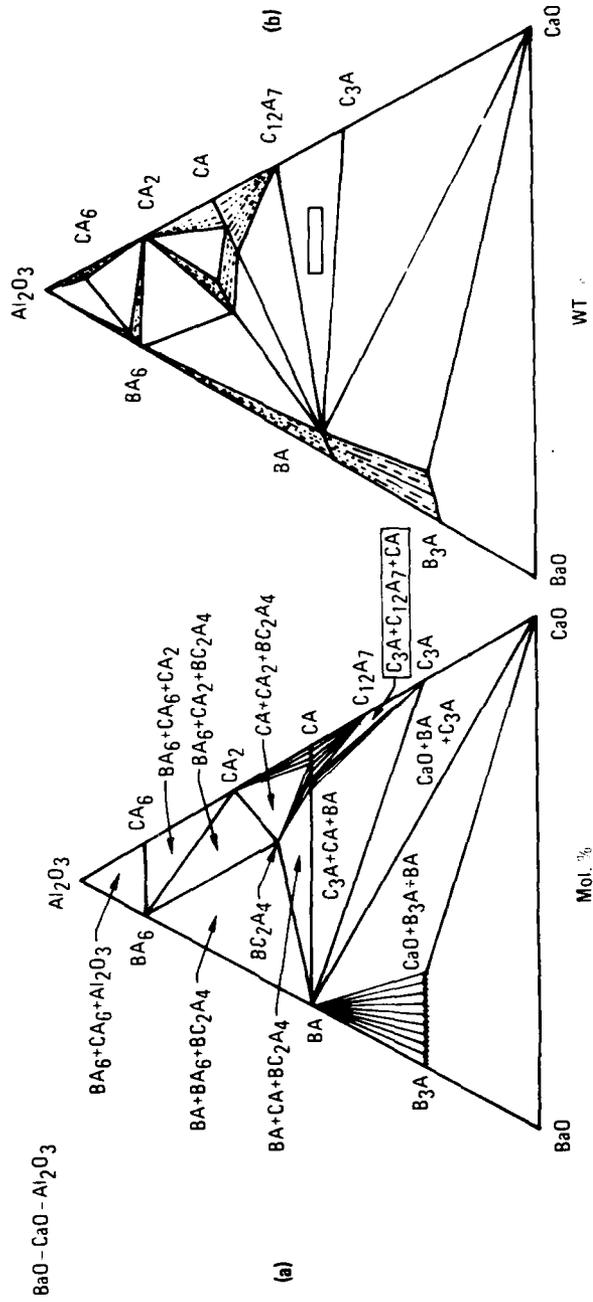


Figure 7. Isothermal Cuts Through BaO-CaO-Al<sub>2</sub>O<sub>3</sub> System. (a) According to Brisi and Montorsi at 1200°C. (b) According to Nassazza at 1400°C. Information for the lowest area is missing; the area cannot have four corners.

disagreement lies in the treatment of a single subtriangle, indicated by a box, below  $C_{12}A_7$ . One cannot know whether this represents conflicting interpretations or an actual change from one temperature to the other. Minor differences are new or somewhat enlarged areas of solid solution (hatched) at the higher temperature, as one might expect.

The clear areas are three-phase regions. Any composition falling into one of these areas will, upon solidification, consist of three phases whose compositions are given by the corners of the triangle. For example, the composition of a 211 impregnant lies about where, in the figure on the left, the legend CaO is located in the second clear area from the bottom. Therefore, the phases should be BA, C, and a solid solution based on  $B_3A$ .

The hatched areas are two-phase regions. They are filled with straight lines which are called "tie-lines" or "conodes." These connect two phases in equilibrium. Any specimen whose overall composition falls, for example, into the hatched triangle between BA and  $B_3A$  would consist of two phases given by the ends of the conode upon which the composition of this specimen falls. One would be BA and the other a solid solution based on  $B_3A$ .

Two-phase regions need not be triangular. If both phases at the ends of the tie-line are solid solutions, then the area is a quadrangle. The dividing lines through the diagram also represent two-phase equilibria. For example, along the line connecting BA with  $C_3A$ , only these two phases can be present, and the line is a "quasi-binary cut" through the ternary system.

On the other hand, all ternary phase fields (clear areas) must be triangular. The lowest field in the diagrams violates this rule only because some information is still missing. Neither Brisi and Montorsi nor Massazza investigated this part of the diagram. The missing information was supplied by Appendino.<sup>8</sup> We combined Appendino's data with Brisi's and produced the composite diagram of Figure 8. Obviously, it is quite complicated. It includes the compounds  $B_8A$  and  $B_4A$ , which are stable at 1250°C but not at the melting point, and it also includes the previously discussed  $B_3CA$ . Figure 9, taken directly from Appendino's paper, is an enlargement of the region investigated by him. This also happens to be the region containing the

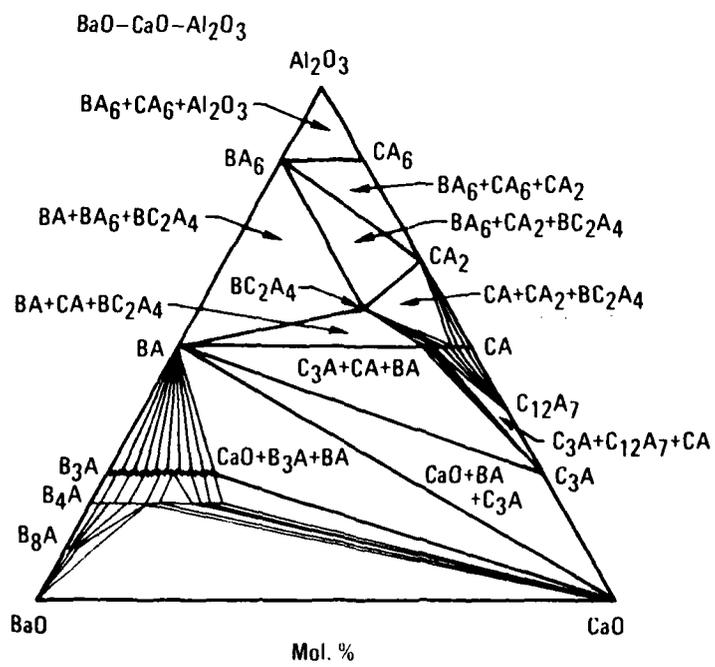
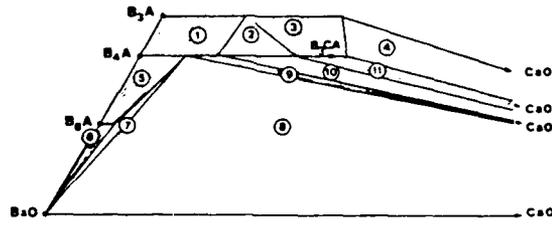


Figure 8. Composite BaO-CaO-Al<sub>2</sub>O<sub>3</sub> Diagram



- ① TWO-PHASE REGION. SS OF C IN  $B_4A$  IN EQUILIBRIUM WITH SS OF C IN  $B_3A$
- ② THREE-PHASE REGION. LOW-C END OF  $B_3CA$  COMPOSITION RANGE IN EQUILIBRIUM WITH HIGH-C END OF SS OF C IN  $B_4A$  AND WITH A FIXED COMPOSITION AT ONE HALF THE MAXIMUM C-CONTENT OF A SS OF C IN  $B_3A$ .
- ③ TWO-PHASE REGION. RANGE OF  $B_3CA$  COMPOSITIONS IN EQUILIBRIUM WITH SS OF C IN  $B_3A$ .
- ④ THREE-PHASE REGION. C IN EQUILIBRIUM WITH HIGH-C ENDS OF  $B_3CA$  AND SS OF C IN  $B_3A$ .
- ⑤ TWO-PHASE REGION. SS OF C IN  $B_8A$  AND IN  $B_4A$  IN EQUILIBRIUM.
- ⑥ TWO-PHASE REGION. B IN EQUILIBRIUM WITH SS OF C IN  $B_8A$ .
- ⑦ THREE-PHASE REGION. B IN EQUILIBRIUM WITH HIGH-C END OF SS OF C IN  $B_8A$  AND A FIXED COMPOSITION OF INTERMEDIATE C-CONTENT OF THE SS OF C IN  $B_4A$ .
- ⑧ THREE-PHASE REGION. SS NAMED LAST IN ⑦ IN EQUILIBRIUM WITH B AND C.
- ⑨ NARROW TWO-PHASE REGION, ALMOST A QUASI-BINARY. HIGH-C RANGE OF SS OF C IN  $B_4A$  IN EQUILIBRIUM WITH C.
- ⑩ THREE-PHASE REGION. TWO FIRST-NAMED SS IN ② IN EQUILIBRIUM WITH C.
- ⑪ NARROW TWO-PHASE REGION, ALMOST A QUASI-BINARY. RANGE OF  $B_3CA$  COMPOSITIONS IN EQUILIBRIUM WITH C.

LEGEND: SS = SOLID SOLUTION(S). C = CaO. B = BaO. A =  $Al_2O_3$ .

$B_3CA = 3BaO.CaO.Al_2O_3$        $B_4A = 4BaO.Al_2O_3$ , ETC.

Figure 9. Enlarged Detail in Portion of Ternary Phase Diagram

impregnant compositions of interest. The text under Figure 9 explains all the fields shown. The location of impregnant 532 coincides with the circled digit 4 in area 4, and impregnant 411 falls into area 8, fairly close to the area 9 boundary and nearly vertically below the clear triangular area 2.

This 1250°C phase diagram should be applicable also at somewhat lower temperatures, down to  $1000 \pm 50^\circ\text{C}$ . It predicts the following phases, in order of decreasing concentration:

1. 532 composition:  $B_3CA$  solid solution,  $B_3A$  solid solution, C.
2. 411 composition:  $B_4A$  solid solution, B, C.

Solid solution, in this context, refers to substitution of some barium by calcium.

We have a few x-ray diffraction results, so far limited both in number and in precision, for raw impregnant material of both types. A  $B_3A$  solid solution and C have been identified, and, in some cases, the presence of B is likely.  $B_4A$ ,  $B_3CA$ , and BA have not been seen. At this point, it must be emphasized strongly that all of the possible phases except CaO and BaO have diffraction patterns in which the potentially observable reflections are very numerous and hence closely spaced. The best chance for distinguishing one phase from another lies in observing the largest possible spacings (up to 22 Å) with the best attainable precision and in obtaining high intensities so that as many lines as possible will be seen. Spacings smaller than about 2 Å will not be very useful for making the necessary distinctions.

It is conceivable that a freshly impregnated cathode reflects the equilibrium characteristic of a temperature just below the melting point, rather than the one described by Figures 8 and 9 for 1250°C. At this higher temperature, say at or above 1500°C,  $B_4A$ , and  $B_8A$ , and most likely also  $B_3CA$ , do not exist. A reasonable guess about the phase diagram at this temperature is given in Figure 10. The 532 impregnant is predicted to consist only of a  $B_3A$  solid solution and C, and the 411 impregnant, to consist of a  $B_3A$  solid solution, B, and C. It is not clear why this matches our preliminary x-ray results, because the latter were obtained on calcined material that has never been at the high temperature considered here.

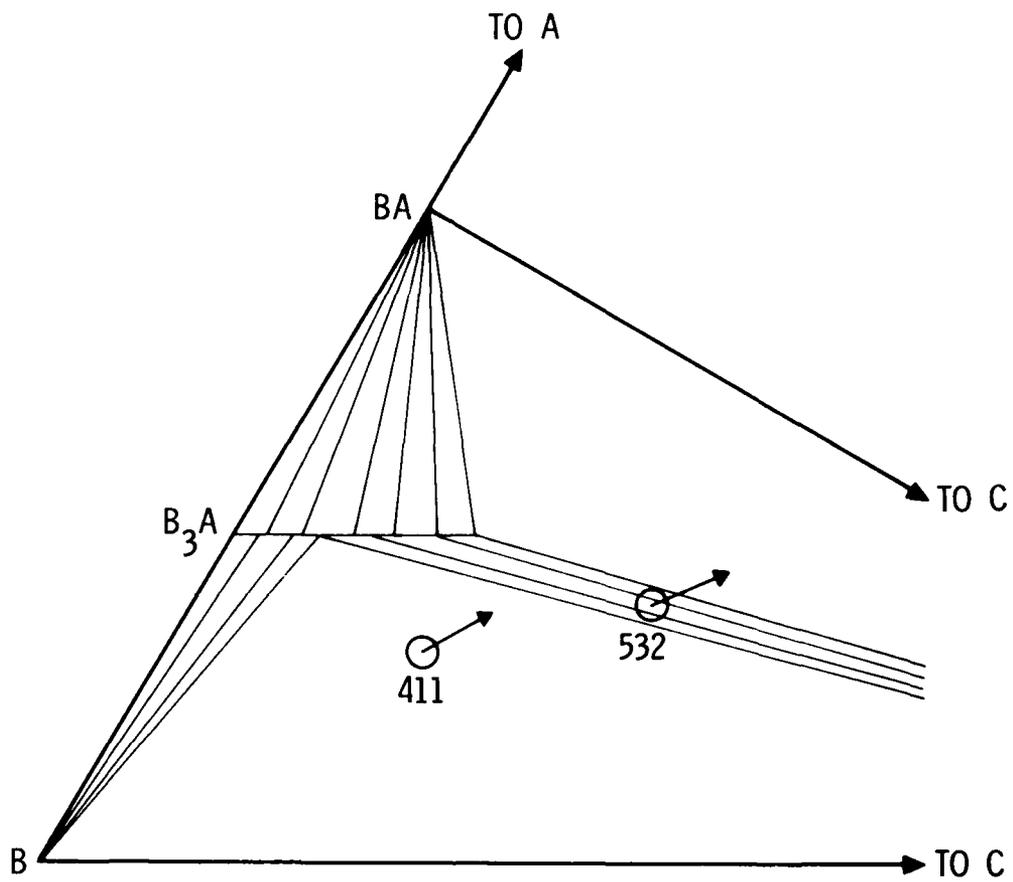


Figure 10. Hypothetical Phase Diagram Just below Melting Point. The arrows on the impregnant compositions indicate the direction of change when BaO evaporates.

It may be that the high-temperature equilibrium phases form more easily than the low-temperature equilibrium ones. A typical calcining schedule for producing the impregnant is 70 hours at 1150°C, whereas Appendino heated his ternary specimens for 500 hours at 1250°C. It is not unusual for a slow equilibrium process to go through several intermediate metastable phases that first appear and then disappear before the final equilibrium phases are produced. The highest temperature phases would be produced rapidly only when the impregnant is melted during the impregnation process. Prolonged operation of the cathode at 1000°C would ultimately cause the establishment of phases that should be much closer to the phase diagram for 1250°C, because at 1000°C  $B_4A$  is still stable, and  $B_8A$ , which is not, is not relevant to the impregnant.

So far, all of the discussions have been in terms of the initial impregnant composition. If one draws a straight line from the BaO corner of the ternary diagram through the point that represents one of the initial compositions, one obtains the direction in which this composition will change as BaO evaporates, as indicated in Figure 10. From Figure 9, it is evident that upon continued BaO evaporation, the impregnant composition will in time leave and enter successive triangles above and to the right of the initial one, eventually reaching the CaO- $Al_2O_3$  side of the diagram near  $C_{12}A_7$ . Since, however, CaO evaporates as well, although at a slower rate than BaO, the line of composition motion will not remain straight but curve upward, with the final composition being closer to CA than to  $C_{12}A_7$ .

Finally, the loss of BaO will not be uniform but will be greater near the surface of the cathode and less in the interior. Therefore, after many hours of operation, the composition will no longer be uniform. There will be a gradient as a function of depth, and different phases may exist at different distances from the surface.

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APPENDIX A

CALCULATED DIFFRACTION PATTERNS FOR TRIBARIUM ALUMINATE  
AND ITS SOLID SOLUTIONS WITH CALCIUM.

| $\sqrt{\frac{h^2 + k^2 + l^2}{a^2}}$ * | hkl     | Ba <sub>3</sub> Al <sub>2</sub> O <sub>6</sub> | Ba <sub>2.5</sub> Ca <sub>0.5</sub> Al <sub>2</sub> O <sub>6</sub> | Ba <sub>2.28</sub> Ca <sub>0.72</sub> Al <sub>2</sub> O <sub>6</sub> |
|--|---------|--|--|--|
| 1                                      | 100     | 16.51  | 16.27  | 16.15  |
| 3                                      | 111     | 9.53   | 9.39   | 9.32   |
| 4                                      | 200     | 8.25   | 8.13   | 8.07   |
| 5                                      | 210     | 7.38   | 7.27   | 7.22   |
| 6                                      | 211     | 6.74   | 6.64   | 6.59   |
| 8                                      | 220     | 5.84   | 5.75   | 5.71   |
| 9                                      | 300,221 | 5.50   | 5.42   | 5.38   |
| 11                                     | 311     | 4.98   | 4.90   | 4.87   |
| 12                                     | 222     | 4.77   | 4.70   | 4.66   |
| 13                                     | 320     | 4.58   | 4.51   | 4.48   |
| 14                                     | 321     | 4.41   | 4.35   | 4.32   |
| 16                                     | 400     | 4.13   | 4.07   | 4.04   |
| 17                                     | 410,322 | 4.00   | 3.95   | 3.92   |
| 18                                     | 411,330 | 3.89   | 3.84   | 3.81   |
| 19                                     | 331     | 3.79   | 3.73   | 3.70   |
| 20                                     | 420     | 3.69   | 3.64   | 3.61   |
| 21                                     | 421     | 3.60   | 3.55   | 3.52   |
| 22                                     | 332     | 3.52   | 3.47   | 3.44   |
| 24                                     | 422     | 3.37   | 3.32   | 3.30   |
| 25                                     | 500,430 | 3.30   | 3.25   | 3.23   |
| 26                                     | 510,431 | 3.24   | 3.19   | 3.17   |
| 27                                     | 511,333 | 3.18   | 3.13   | 3.11   |
| 29                                     | 520,432 | 3.065  | 3.021  | 2.999  |
| 30                                     | 521     | 3.014  | 2.970  | 2.946  |
| 32                                     | 440     | 2.918  | 2.876  | 2.855  |
| 33                                     | 522,441 | 2.874  | 2.832  | 2.811  |
| 34                                     | 530,433 | 2.831  | 2.790  | 2.770  |

\* THERE ARE NO COMBINATIONS OF hkl FOR WHICH THE SQUARE ROOT OF THE SUM OF THE SQUARES IS 7, 15, 23, 29, 31, 39. FOR 7 AND 15, THE DIFFRACTIONS ARE EXTINCT IN SPACE GROUP Pa3.

|    |             |       |       |       |
|----|-------------|-------|-------|-------|
| 35 | 531         | 2.790 | 2.750 | 2.730 |
| 36 | 600,442     | 2.751 | 2.711 | 2.692 |
| 37 | 610         | 2.714 | 2.674 | 2.655 |
| 38 | 611,532     | 2.678 | 2.639 | 2.620 |
| 40 | 620         | 2.610 | 2.572 | 2.553 |
| 41 | 621,540,443 | 2.578 | 2.540 | 2.522 |
| 42 | 541         | 2.547 | 2.510 | 2.492 |
| 43 | 533         | 2.517 | 2.481 | 2.463 |
| 44 | 622         | 2.489 | 2.452 | 2.435 |

COMPOSITION

A<sub>0</sub>

Ba<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>  
16.508 Å

Ba<sub>2.5</sub>Ca<sub>0.5</sub>Al<sub>2</sub>O<sub>6</sub>  
16.293 Å

Ba<sub>2.28</sub>Ca<sub>0.72</sub>Al<sub>2</sub>O<sub>6</sub>  
16.148 Å

## APPENDIX B

### UNIT CELLS FOR B<sub>4</sub>A, B<sub>5</sub>A, B<sub>7</sub>A, B<sub>8</sub>A, B<sub>10</sub>A, AND B<sub>3</sub>CA

Appendino gives x-ray diffraction powder patterns for these compounds but nothing more, that is, he gives only the d-spacings and relative intensities. There are two reasons why it would be useful to know the unit cells of the compounds. First, the patterns are likely to be incomplete. Additional lines might be observed if these compounds were to be encountered. A knowledge of the unit cells would permit calculation of the complete pattern, so that one could decide whether additional lines belong to the compound in question or another one. Second, knowing the unit cell is synonymous with knowing the crystal system, i.e., at least the gross symmetry. This would help identify crystals that may be observed under the microscope in an experimental preparation.

For these reasons, the derivation of unit cells from the powder patterns was undertaken, and it was found that all patterns could be indexed on the basis of orthorhombic cells that were fairly similar to one another. The reader should be cautioned that unit cells derived from powder patterns are correct, on the average, no more than 70% of the time, and that therefore all cells so derived must be considered tentative. In the present cases, it is not likely that the true symmetry is higher than orthorhombic, but it is quite possible that it is lower. The cells may only be pseudo-orthorhombic, with the true symmetry being monoclinic.

The cell parameters are given in Table B-1. The indexing (Table B-2) is somewhat tentative. With the unit cells assumed to be valid, an unambiguous match can be made for the larger spacings, say, the top halves of the listed patterns. For the smaller spacings, the list of possible matches becomes large and closely spaced. One then chooses the best match, but the measured spacings are of finite precision and are generally inaccurate by one or two units in the last decimal. This, combined with slight inaccuracies in the lattice parameters, can change the indexing for the smaller spacings.

Table B-1. The Unit Cells

|   |   |   |   |  |  |
|---|---|---|---|--|--|
| $4\text{BaO} \cdot \text{Al}_3\text{O}_3$ | $5\text{BaO} \cdot \text{Al}_2\text{O}_3$ | $7\text{BaO} \cdot \text{Al}_2\text{O}_3$ | $8\text{BaO} \cdot \text{Al}_2\text{O}_3$ | $10\text{BaO} \cdot \text{Al}_2\text{O}_3$ | $3\text{BaO} \cdot \text{CaO} \cdot \text{Al}_2\text{O}_3$ |
| a = 17.949                                | a = 16.597                                | a = 16.848                                | a = 17.096                                | a = 10.309                                 | a = 17.024   |
| b = 21.393                                | b = 20.020                                | b = 20.052                                | b = 20.298                                | b = 11.185                                 | b = 20.340   |
| c = 16.209                                | c = 14.007                                | c = 12.852                                | c = 15.690                                | c = 7.626                                  | c = 16.112   |

Table B-2. Calculated Diffraction Patterns

| B <sub>3</sub> CA |     |                                 |       |   |     |
|-------------------|-----|---------------------------------|-------|---|-----|
| d                 | l   | hkl                             | d     | l | hkl |
| 5.081             | 5   | 040                             | 1.423 | 8 |     |
| 4.881             | 20  | 140                             |       |   |     |
| 4.255             | 40  | 400                             |       |   |     |
| 4.029             | 50  | 004                             |       |   |     |
| 3.512             | 5   | 431                             |       |   |     |
| 3.442             | 10  | 224,342                         |       |   |     |
| 3.297             | 10  | 413,350                         |       |   |     |
| 3.206             | 8   | 234                             |       |   |     |
| 3.104             | 30  | 144                             |       |   |     |
| 2.945             | 60  | 450                             |       |   |     |
| 2.921             | 100 | 404                             |       |   |     |
| 2.897             | 70  | 414                             |       |   |     |
| 2.622             | 4   | 630                             |       |   |     |
| 2.443             | 5   | 273                             |       |   |     |
| 2.378             | 30  | 463                             |       |   |     |
| 2.350             | 35  | 146                             |       |   |     |
| 2.261             | 7   | 090,624                         |       |   |     |
| 2.198             | 15  | 732,634                         |       |   |     |
| 2.138             | 8   | 175                             |       |   |     |
| 2.128             | 30  | 800                             |       |   |     |
| 2.014             | 20  | 008                             |       |   |     |
| 2.010             | 25  | 384                             |       |   |     |
| 1.900             | 7   | 734                             |       |   |     |
| 1.881             | 10  | 447                             |       |   |     |
| 1.827             | 3   | 338,1.11.1                      |       |   |     |
| 1.819             | 3   | 408                             |       |   |     |
| 1.797             | 10  | 10 POSSIBLE LINES               |       |   |     |
| 1.727             | 2   | 513                             |       |   |     |
| 1.715             | 15  | 950                             |       |   |     |
| 1.695             | 15  | 0.12.0                          |       |   |     |
| 1.669             | 7   | 4.10.4,10.2.1                   |       |   |     |
| 1.661             | 10  | 477                             |       |   |     |
| 1.483             | 5   | 11.1.3,11.3.2,<br>3.4.10.3,13.2 |       |   |     |

| B <sub>4</sub> A |     |         |       |    |                   |
|------------------|-----|---------|-------|----|-------------------|
| d                | l   | hkl     | d     | l  | hkl               |
| 5.342            | 6   | 040,003 | 1.873 | 4  | 485               |
| 5.193            | 11  | 103     | 1.847 | 10 | 367               |
| 4.498            | 10  | 400     | 1.832 | 5  | 726               |
| 4.048            | 15  | 004     | 1.812 | 2  | 386               |
| 3.550            | 3   | 510,060 | 1.800 | 5  | 009,736           |
| 3.493            | 3   | 224,333 | 1.783 | 18 | 914,0.12.0        |
| 3.458            | 7   | 403     | 1.761 | 15 | 068               |
| 3.391            | 2   | 502     | 1.741 | 4  | 0.12.2,528        |
| 3.321            | 8   | 260     | 1.701 | 25 | 6.10.2,5.11.1     |
| 3.243            | 5   | 005     | 1.662 | 20 | 2.12.3,971        |
| 3.227            | 3   | 044     | 1.636 | 2  | 10.1.4,747        |
| 3.121            | 3   | 433     | 1.508 | 12 | 639               |
| 3.015            | 100 | 215,404 | 1.454 | 4  | 947,11.1.5,2.0.11 |
| 2.913            | 35  | 611     | 1.410 | 10 | 10.9.2,778        |
| 2.818            | 40  | 315     |       |    |                   |
| 2.685            | 2   | 433     |       |    |                   |
| 2.647            | 7   | 245     |       |    |                   |
| 2.584            | 2   | 055,206 |       |    |                   |
| 2.564            | 3   | 700     |       |    |                   |
| 2.543            | 4   | 623     |       |    |                   |
| 2.490            | 5   | 720,642 |       |    |                   |
| 2.447            | 10  | 316     |       |    |                   |
| 2.416            | 4   | 562     |       |    |                   |
| 2.391            | 15  | 515     |       |    |                   |
| 2.327            | 5   | 570     |       |    |                   |
| 2.259            | 25  | 374     |       |    |                   |
| 2.208            | 3   | 390     |       |    |                   |
| 2.159            | 4   | 307,506 |       |    |                   |
| 2.104            | 4   | 1.10.1  |       |    |                   |
| 2.026            | 30  | 008,366 |       |    |                   |
| 1.972            | 3   | 851     |       |    |                   |
| 1.922            | 3   | 930,447 |       |    |                   |

| B <sub>5</sub> A |     |                 |       |   |                      |
|------------------|-----|-----------------|-------|---|----------------------|
| d                | l   | hkl             | d     | l | hkl                  |
| 5.007            | 10  | 040             | 1.373 | 3 | 12.1.1,10.4.5,11.2.4 |
| 4.152            | 50  | 400             | 1.349 | 3 | 2.14.3,11.6.2        |
| 3.847            | 8   | 051             | 1.336 | 5 | 6.11.5               |
| 3.501            | 30  | 004             | 1.302 | 7 |                      |
| 3.391            | 40  | 152             |       |   |                      |
| 3.373            | 35  | 114             |       |   |                      |
| 3.144            | 15  | 333             |       |   |                      |
| 2.995            | 100 | 502             |       |   |                      |
| 2.900            | 80  | 234             |       |   |                      |
| 2.754            | 5   | 105             |       |   |                      |
| 2.712            | 7   | 244,601         |       |   |                      |
| 2.666            | 10  | 620             |       |   |                      |
| 2.487            | 10  | 434,622         |       |   |                      |
| 2.463            | 12  | 081             |       |   |                      |
| 2.424            | 15  | 325             |       |   |                      |
| 2.284            | 30  | 380,642         |       |   |                      |
| 2.236            | 10  | 345             |       |   |                      |
| 2.188            | 10  | 183             |       |   |                      |
| 2.088            | 15  | 464.            |       |   |                      |
| 2.083            | 20  | 265             |       |   |                      |
| 2.002            | 10  | 0.10.0,156      |       |   |                      |
| 1.935            | 10  | 217             |       |   |                      |
| 1.915            | 3   | 761             |       |   |                      |
| 1.785            | 8   | 763,804,545,606 |       |   |                      |
| 1.757            | 10  | 705             |       |   |                      |
| 1.751            | 8   | 824             |       |   |                      |
| 1.697            | 10  | 186             |       |   |                      |
| 1.668            | 10  | 0.12.0          |       |   |                      |
| 1.522            | 3   | 925             |       |   |                      |
| 1.501            | 2   | 496,2.11.5      |       |   |                      |
| 1.452            | 15  | 468,982,5.11.4  |       |   |                      |
| 1.435            | 5   | 0.11.6,349,088  |       |   |                      |

| B <sub>8</sub> A |     |             |       |    |                                 |
|------------------|-----|-------------|-------|----|---------------------------------|
| d                | l   | hkl         | d     | l  | hkl                             |
| 5.075            | 4   | 040         | 1.718 | 2  | 029                             |
| 4.263            | 5   | 042,400     | 1.698 | 20 | 196,594                         |
| 3.914            | 4   | 004         | 1.664 | 5  | 3.11.3,268,647                  |
| 3.556            | 40  | 143,204     | 1.641 | 10 | 149,864                         |
| 3.509            | 8   | 214         | 1.570 | 6  | 747,439                         |
| 3.383            | 15  | 060         | 1.319 | 4  | 9.11.1                          |
| 3.336            | 10  | 501         | 1.289 | 3  | 10.0.8                          |
| 3.264            | 20  | 413,440     | 1.252 | 2  | 2.4.12,3.3.12,<br>0.16.2,5.5.11 |
| 3.195            | 6   | 314,441     | 1.207 | 3  | 10.10.5                         |
| 3.138            | 50  | 005         | 1.154 | 2  |                                 |
| 3.108            | 100 | 062,044     |       |    |                                 |
| 2.992            | 20  | 522         |       |    |                                 |
| 2.964            | 50  | 433         |       |    |                                 |
| 2.889            | 15  | 404         |       |    |                                 |
| 2.615            | 30  | 461,550,006 |       |    |                                 |
| 2.580            | 25  | 551         |       |    |                                 |
| 2.561            | 7   | 064         |       |    |                                 |
| 2.479            | 5   | 181,552     |       |    |                                 |
| 2.450            | 4   | 641,264     |       |    |                                 |
| 2.363            | 4   | 463,316     |       |    |                                 |
| 2.240            | 5   | 007         |       |    |                                 |
| 2.218            | 10  | 416         |       |    |                                 |
| 2.155            | 30  | 217         |       |    |                                 |
| 2.079            | 3   | 391         |       |    |                                 |
| 1.962            | 15  | 057         |       |    |                                 |
| 1.946            | 10  | 393         |       |    |                                 |
| 1.904            | 5   | 437         |       |    |                                 |
| 1.884            | 3   | 038         |       |    |                                 |
| 1.850            | 8   | 703,394,556 |       |    |                                 |
| 1.807            | 5   | 860         |       |    |                                 |
| 1.777            | 7   | 494         |       |    |                                 |
| 1.738            | 8   | 077         |       |    |                                 |

| B <sub>7</sub> A |     |            | B <sub>10</sub> A |     |         |
|------------------|-----|------------|-------------------|-----|---------|
| d                | l   | hkl        | d                 | l   | hkl     |
| 5.012            | 10  | 040        | 5.618             | 10  | 020     |
| 4.211            | 40  | 400        | 5.157             | 26  | 200     |
| 3.409            | 50  | 303        | 3.808             | 30  | 002,220 |
| 3.213            | 15  | 004        | 3.162             | 100 | 022     |
| 3.157            | 4   | 104        | 3.064             | 80  | 202     |
| 3.066            | 100 | 024        | 2.811             | 15  | 231     |
| 2.904            | 80  | 450        | 2.583             | 100 | 132     |
| 2.889            | 60  | 153,034    | 2.466             | 50  | 103,240 |
| 2.535            | 10  | 414,631    | 2.310             | 80  | 023     |
| 2.497            | 15  | 272        | 1.994             | 8   | 422     |
| 2.399            | 10  | 035        | 1.904             | 10  | 004     |
| 2.383            | 20  | 363,073    | 1.857             | 8   | 432     |
| 2.298            | 3   | 650,164    | 1.787             | 10  | 413     |
| 2.164            | 10  | 055        | 1.751             | 30  | 260     |
| 2.106            | 25  | 800        | 1.740             | 5   | 261     |
| 2.045            | 5   | 391        | 1.722             | 10  | 423     |
| 1.953            | 10  | 760        | 1.673             | 8   | 062     |
| 1.905            | 8   | 474        | 1.647             | 15  | 451     |
| 1.888            | 10  | 3.10.0,615 | 1.634             | 10  | 360,532 |
| 1.846            | 8   | 851        | 1.603             | 10  | 503     |
| 1.805            | 10  | 0.11.1,574 | 1.412             | 3   | 613     |
| 1.748            | 2   | 715        | 1.393             | 3   | 305     |
| 1.721            | 15  | 781        | 1.389             | 5   | 514     |
| 1.699            | 4   | 735        | 1.347             | 3   | 731     |
| 1.671            | 5   | 0.12.0     | 1.291             | 2   | 264     |
| 1.618            | 5   | 904        | 1.254             | 10  | 116     |
| 1.580            | 3   | 726        | 1.219             | 5   | 191     |
| 1.479            | 2   | 4.10.5     | 1.193             | 3   | 822     |

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