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Local Structure of Alkaline-Earth Boroaluminate Crystals and Glasses: I, Crystal Chemical Concepts—Structural Predictions and Comparisons to Known Crystal Structures

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This paper presents a model which predicts glass structures based on local charge balance considerations. The model is shown to be consistent with known structures of borate, aluminate, and boroaluminate crystals and predicts that boroaluminate glasses should contain 3- and 4-coordinate boron, 4-, 5-, and 6-coordinate aluminum, and oxygens coordinated to one, two, three, and perhaps even four network-forming cations. The predicted glass structures are more complex than previous models for boroaluminate glasses, explaining the solid-state NMR data for the boroaluminate glasses discussed in Part II. [Key words: borates, aluminoborates, glass, models, structure.]

I. Introduction

Most glasses, including boroaluminates, are generally assumed to consist of random networks formed by oxygens bridging two network-forming cations such as B^{3+} or Al^{3+}. Most glass structural models[1-8] assume that in B_2O_3 glass, all boron is present in neutral sites in which B^{3+} is coordinated to three oxygens. As modifier cations such as alkali and alkaline-earth cations are added, it is assumed that all modifiers are charge compensated by the creation of anionic, tetrahedrally coordinated boron sites at low modifier contents and by the formation of nonbridging oxygens at high modifier contents. For Al-containing glasses, it is generally assumed that Al in neutral sites is 6-coordinate, whereas anionic Al sites (charge compensated by modifier cations) are all 4-coordinate.

Interestingly, structures of borate,[9-14] aluminate,[15-22] and boroaluminate[23-29] crystals exhibit a wider range of local coordination geometries than is commonly attributed to glasses containing B and Al. In these crystalline phases, oxygens are commonly bonded to three network-forming cations, and Al is coordinated to five as well as four and six oxygens. Four-coordinate aluminum cations are found in modifier-free materials such as $2B_2O_3 \cdot 9Al_2O_3$.[23] In addition, structural information obtained for boroaluminate glasses via techniques such as solid-state nuclear magnetic resonance (NMR) spectroscopy[30] are not consistent with classical glass structure models.

From a glass structure perspective, boroaluminate glasses provide an opportunity to investigate the principles which control atomic structural environments in materials in which there are several possible nearest-neighbor (NN) and next-nearest-neighbor (NNN) bonding environments for both cations and anions. In Part I of this paper, we describe a simple conceptual model for oxide structures based on local charge balance considerations which can be used to rationalize local bonding configurations in both crystalline and glassy boroaluminates. We show that this simple model is consistent with known boroaluminate crystal structures. In Part II[30] we present results obtained via ^{11}B and ^{27}Al NMR spectroscopy of boroaluminate glasses which indicate that our local charge model provides a self-consistent picture for the structure of these glasses. We will explain how the model can be used to help assign ^{27}Al NMR peaks and rationalize changes in relative peak intensities with changing glass composition.

II. Glass Structure Model

(1) Model Rationale—Relative Site Stabilities

The basis for our simple structural model is that the bonding requirements of oxygens in the structure must be satisfied. Chemical bonding in oxides is complex, involving both ionic and covalent interactions. For simplicity, we consider oxides to consist of metal cations bonded to oxygen anions. In this picture, oxygens come closest to having their bonding requirements satisfied if the sum of the positive charges donated to each oxygen by bonding to NN cations is $+2$, exactly neutralizing the formal charge on oxygen of -2. The charge donated by different cations is evaluated using Brown and Shannon bond strengths,[31] given in valence units (VU's), which have been proven useful in rationalizing proposed crystal structures and in investigating ^{29}Si NMR chemical shifts.[32,33] For many small cations, average VU's are simply the charge divided by the coordination number for the cation as in Pauling's second rule.[34] Typical VU's are 1.0 for B(3) and Si(4), 0.75 for B(4) and Al(4), 0.6 for Al(5), and 0.5 for Al(6). Larger cations such as alkalis and alkaline earths have much lower VU's (typically 0.1 to 0.4) due to their higher coordination and lower charge. We will use the typical values, ignoring second-order effects due to variations in interatomic distances.

Consider first the charge donated to the oxygens by just the network formers, here B and Al in any coordination (Table I). If the VU sum is $+2$, the bonding requirements of oxygen are exactly satisfied, resulting in a stable bonding configuration. If the VU sum is greater than $+2$, the oxygen is overbonded (positively charged) and relatively unstable. If the sum is less than $+2$, the oxygen is underbonded (negatively charged), but can be stabilized by coordination to one or more modifier (large) cations such as the alkaline earths.

The rules used to evaluate the stability of possible oxygen bonding configurations based on VU values are the following:

(1) The net charge on oxygen cannot be positive. We use Brown and Shannon's[31] criterion that the VU sum cannot exceed 2.2 (10% excess charge on oxygen). Charge imbalances of this magnitude can be accommodated by changing inter-

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Table I. Typical Brown and Shannon[31] Bond Strengths to Oxygens for the Possible Coordinations by Al and B in Boroaluminate Structures*

Cations coordinating oxygens	ΣVU‡	Charge on oxygen
Overbonded, disallowed		
B(3)–B(3)–B(3)*†	+3.0	+1.0
B(3)–B(3)–AlB(4)	+2.75	+0.75
B(3)–B(3)–Al(5)	+2.6	+0.6
B(3)–B(3)–Al(6)	+2.5	+0.5
B(3)–AlB(4)–AlB(4)	+2.5	+0.5
B(3)–AlB(4)–Al(5)	+2.35	+0.35
B(3)–AlB(4)–Al(6)	+2.25	+0.25
AlB(4)–AlB(4)–AlB(4)	+2.25	+0.25
Slightly overbonded, allowed, but less stable than neutral sites		
B(3)–Al(5)–Al(5)	+2.2	+0.2
Al(6)–Al(6)–Al(5)–Al(5)†	+2.2	+0.2
B(3)–Al(5)–Al(6)	+2.1	+0.1
AlB(4)–AlB(4)–Al(5)	+2.1	+0.1
Al(6)–Al(6)–Al(6)–Al(5)†	+2.1	+0.1
Al(6)–Al(6)–Al(6)–Al(6)†	+2.0	0
Neutral		
B(3)–B(3)	+2.0	0
B(3)–Al(6)–Al(6)	+2.0	0
AlB(4)–AlB(4)–Al(6)	+2.0	0
Near neutral, less stable		
AlB(4)–Al(5)–Al(5)	+1.95	−0.05
AlB(4)–Al(5)–Al(6)	+1.85	−0.15
Al(5)–Al(5)–Al(5)	+1.8	−0.2
Underbonded, can be compensated by modifiers, allowed		
AlB(4)–Al(6)–Al(6)	+1.75	−0.25
B(3)–AlB(4)	+1.75	−0.25
Al(5)–Al(5)–Al(6)	+1.7	−0.3
Al(5)–Al(6)–Al(6)	+1.6	−0.4
B(3)–Al(5)	+1.6	−0.4
Al(6)–Al(6)–Al(6)	+1.5	−0.5
B(3)–Al(6)	+1.5	−0.5
AlB(4)–AlB(4)	+1.5	−0.5
AlB(4)–Al(5)	+1.35	−0.65
AlB(4)–Al(6)	+1.25	−0.75
Al(5)–Al(5)	+1.2	−0.8
Al(5)–Al(6)	+1.1	−0.9
Al(6)–Al(6)	+1.0	−1.0
B(3)nbo	+1.0	−1.0
Underbonded, highly unlikely if B present		
AlB(4)nbo	+0.75	−1.25
Al(5)nbo	+0.6	−1.4
Al(6)nbo	+0.5	−1.5

*Assumed bond strengths (valence units, VU): B(3) = 1.0, B(4) = 0.75, Al(4) = 0.75, Al(5) = 0.6, Al(6) = 0.5. †Other O(4) units are not listed as they are seriously overbonded. ‡Valence units.

atomic distances and angles (changing *s* and *p* or σ and π character of the bonds.)

(2) The net charge on oxygen due to coordination to network-forming cations can be substantially negative, but only if the oxygen is also coordinated to modifier cations to neutralize its charge.

(3) The oxide will consist of a mixture of structural units which minimizes the anionic character (i.e., the excess negative charge when only the effects of network formers are considered) on the greatest number of oxygens. As the modifier content increases, the structure will contain oxygens having progressively higher anionic character.

(4) Modifier cations with higher ionic potential (proportional to formal ionic charge/ionic radius, *Z/r*) can help stabilize oxygens with greater anionic character.

(5) The maximum coordination number for oxygen, including modifier cations, is 4, which is the highest coordination commonly found in borate and boroaluminate crystals.

Possible oxygen sites and relative site stabilities under the assumptions listed above appear in Table I. In Table I, and in the rest of the discussion, oxygens are identified on the basis of coordination to network-forming cations. B(3) and B(4) refer to trigonally and tetrahedrally coordinated B^{3+}; Al(4), Al(5), and Al(6) refer to aluminum cations bonded to four, five, and six oxygens; AlB(4) refers to a tetrahedral cation which could be either Al or B; nbo stands for a nonbridging oxygen (also abbreviated O(1)). Oxygens bonded to two, three, and four cations are designated as O(2), O(3), and O(4), respectively (Fig. 1).

Additional constraints on any proposed glass structure are that the bonding requirements of Al and B must be satisfied simultaneously with those of O and that the net negative charge on all oxygens must balance the positive charge of the modifier cations. The Al and B bonding requirements are evaluated by examining the stoichiometric formula for a given composition. For example, for the formula $MAlBO_4$ (where M is a divalent modifier cation), if the structure contains only Al(6) and B(3), the four oxygens in the formula unit must be bonded to a total of 6 + 3 = 9 cations. Combinations of oxygen types producing a total of nine bonds for the four oxygens include 1 O(3) + 3 O(2) or 2 O(3) + O(2) + O(1). Within the allowed subset of oxygen combinations, the net number of bonds to Al and B must be correct. In the above example for the 2 O(3) + O(2) + O(1) combination, if both O(3) sites are bonded to 1 B(3) and 2 Al(6) (abbreviated B(3)–Al(6)–Al(6), see Fig. 1), and if the nonbridging oxygen O(1) is on B(3), the O(2) site must be an Al(6)–O–Al(6) (abbreviated Al(6)–Al(6)) site in order to have a total of six bonds to Al and three bonds to B for the four-oxygen set.

(2) Model Example—$MAlBO_4$

To illustrate the model, we now describe the complete local charge analysis of possible structures for the aluminoborate composition $MAlBO_4$. The analysis considers coordination geometries B(3), B(4), Al(4), Al(5), Al(6), O(4), O(3), O(2), and O(1) (nbo's). The analysis starts by considering oxygen site types which are possible assuming known coordination geometries for both B and Al. (In a glass, mixtures of the combinations listed below could coexist.) The six possible combinations of B and Al geometries are B(3) + Al(4), B(3) + Al(6), B(4) + Al(4), B(4) + Al(6), B(3) + Al(5), and B(4) + Al(5). Each of the possible combinations leads to a limited set of probable combinations for the four oxygens in the formula unit $MAlBO_4$ as described below.

(A) B(3) + Al(4): The $MAlBO_4$ formula contains four oxygens which must be associated with three O–B and four O–Al bonds for a total of seven bonds. The first step in the analysis is to determine how the seven bonds can be distributed among O(3), O(2), and O(1) sites by counting the total number of bonds associated with each possible oxygen

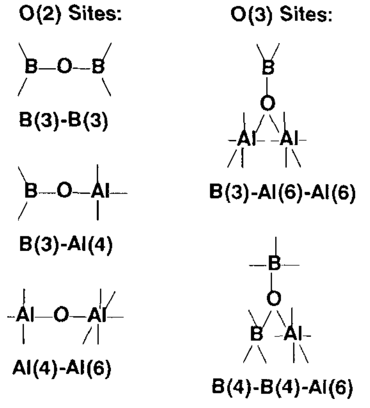

Fig. 1. Schematic representations of possible oxygen sites in boroaluminate structures using the nomenclature described in the text.

distribution. Four O(3) sites cannot be present, because this distribution requires 12 bonds (4 × 3) to network-forming cations, but only 7 can exist for the system. Combinations which are possible for oxygen (yielding seven bonds) are 1 O(4) + 3 O(1), 3 O(2) + O(1), and O(3) + O(2) + 2 O(1). However, Table I shows that there are no O(4) or O(3) units which can be constructed using B(3) and Al(4) which are not substantially overbonded and therefore unstable. Therefore, the only viable combination of oxygens is 3 O(2) + O(1).

The final step in the analysis is determining which cations are associated with each oxygen type. The minimum local charge (Table I) results if the O(1) is on B(3). The three O(2) oxygens which remain must have two bonds to B(3) and four bonds to Al(4) to satisfy the coordination requirements for each cation. For example, all three O(2)'s cannot be Al–O–Al groups, because this combination would contain six Al–O bonds, whereas only four are allowed. Using this analysis, two oxygen combinations are allowed: 2 B(3)–Al(4) + Al(4)–Al(4) + B(3)nbo or B(3)–B(3) + 2 Al(4)–Al(4) + B(3)nbo. In these combinations, the number of "satisfied" oxygens is estimated by counting the total number of oxygens having a net charge of less than −0.5. The B(3)–Al(4) sites are "satisfied" with a charge of −0.25, while the other oxygens are not. Therefore, of the combinations listed above, 2B(3)–Al(4) + Al(4)–Al(4) + B(3)nbo is preferred because it has two "satisfied" oxygens, whereas the other combination has only one.

(B) B(3) + Al(6): For this cation combination, there must be a total of nine bonds to oxygens. Oxygen combinations satisfying the net bonding requirement are 1 O(4) + 1 O(3) + 2 O(1), 2 O(3) + O(2) + O(1), and O(3) + 3 O(2). The only O(3) units which are either neutral or anionic, satisfying local charge requirements, are B(3)–Al(6)–Al(6) and Al(6)–Al(6)–Al(6). Similarly, the only allowed O(4) unit is Al(6)–Al(6)–Al(6)–Al(6). With these constraints, the most stable oxygen combinations (with two satisfied oxygens) meeting the bonding requirements of both B(3) and Al(6) are Al(6)–Al(6)–Al(6)–Al(6) + B(3)–Al(6)–Al(6) + 2 B(3)nbo, 2 B(3)–Al(6)–Al(6) + Al(6)–Al(6) + B(3)nbo, and B(3)–Al(6)–Al(6) + B(3)–B(3) + 2 Al(6)–Al(6). Allowed but less stable combinations (one or zero satisfied oxygens) include B(3)–B(3) + 2 Al(6)–Al(6)–Al(6) + B(3)nbo and 3 B(3)–Al(6) + Al(6)–Al(6)–Al(6).

(C) B(4) + Al(6): Here, the four oxygens must have ten bonds to cations, requiring 2 O(4) + 2 O(1), O(4) + O(3) + O(2) + O(1), O(4) + 3 O(2), 2 O(3) + 2 O(2), or 3 O(3) + O(1). However, since local charge arguments show that B(4) should convert to B(3) in favor of creating nbo's on either B(4) or Al(6), no combinations with O(1) are allowed. For the 2 O(3) + 2 O(2) configuration, the only combination of oxygens meeting cation bonding requirements and containing "satisfied" oxygens (two oxygens are satisfied) is 2 B(4)–B(4)–Al(6) + 2 Al(6)–Al(6). For the other combination, the only stable O(4) has 4 Al(6)'s, leading to two distributions with Al(6)–Al(6)–Al(6)–Al(6): one with 2 B(4)–B(4) + Al(6)–Al(6), and one with B(4)–B(4) + 2 B(4)–Al(6). Both O(4) combinations contain one stable oxygen.

(D) B(4) + Al(4): Oxygen combinations supplying the correct number (8) of bonds to cations are O(4) + O(2) + 2 O(1), 4 O(2), O(3) + 2 O(2) + O(1), and 2 O(3) + 2 O(1). However, for B(4) + Al(4) combinations, O(4)'s and O(3)'s are substantially overbonded (net charge = +1.0 and +0.25, respectively), O(1)'s are substantially underbonded (net charge = −1.25), and neither is allowed. The O(2) combinations 2 B(4)–B(4) + 2 Al(4)–Al(4), B(4)–B(4) + 2 B(4)–Al(4) + Al(4)–Al(4), and 4 B(4)–Al(4) are all allowed. However, all of the above oxygens have net charge of −0.5, so no oxygens are "satisfied" in any of the above combinations, making the B(4) + Al(4) combination less likely than combinations (1) to (3) above.

(E) B(3) or B(4) + Al(5): An analysis similar to those described above indicates that no O(4)'s are allowed for Al(5) with either B(3) or B(4). For B(3) + Al(5), the most probable combination (two oxygens "satisfied") is B(3)–Al(5)–Al(5) + Al(5)–Al(5)–Al(5) + 2 B(3)nbo, with other possible combinations including B(3)–Al(5)–Al(5) + B(3)–Al(5) + Al(5)–Al(5) + B(3)nbo, Al(5)–Al(5)–Al(5) + 2 B(3)–Al(5) + B(3)nbo, and (least likely, with no satisfied oxygens) 3 B(3)–Al(5) + Al(5)–Al(5). For B(4) + Al(5), both allowed combinations (Al(5)–Al(5)–Al(5) + B(4)–B(4) + 2 B(4)–Al(5) and B(4)–Al(5)–Al(5) + 3 B(4)–Al(5)) have one satisfied oxygen, making the combinations less likely than the most stable B(3), Al(5) combination.

The above analysis suggests that local bonding configurations of B(3) + Al(4), Al(5), and Al(6), and B(4) + Al(6) should be allowed for the composition MAlBO$_4$. A further refinement of the preferred oxygen site distribution can be made by considering the ionic potential (valence/ionic radius, Z/r) of the modifier cation. Low ionic potential cations (e.g., Sr^{2+}) should favor distributions in which most oxygens have about the same local charge, such as 2 B(3)–Al(4) + Al(4)–Al(4) + B(3)nbo, whereas high field strength cations such as Mg should favor a mixture of sites containing sites which are more highly anionic (compensating the Mg) plus sites which are near neutral, such as 2 B(4)–B(4)–Al(6) + 2 Al(6)–Al(6). (Note that both distributions yield a net charge on all oxygens of −2.) The predictions of the local charge model are consistent with the structures reported for MAlBO$_4$ crystals. Structures of both M = Ca and Sr crystals[25,26] contain 2 B(3)–Al(4) + Al(4)–Al(4) + B(3)nbo, and the structure of MgAlBO$_4$[27] contains 2 B(4)–B(4)–Al(6) + 2 Al(6)–Al(6).

The above constraints can be used to predict the most stable set of oxygen coordinations expected for any crystalline or glassy boroaluminate composition. For example, the model predicts that for crystalline CaAl$_2$B$_2$O$_7$, the seven oxygens in the formula unit should consist of 6 B(3)–O–Al(4) + 1 Al(4)–O–Al(4), and that no O(3) units or nonbridging oxygens should be present. This prediction corresponds exactly to the observed structure.[25] Predictions of preferred structures for different compositions are given in Table II along with listings of actual structures where known. However, before discussing boroaluminate structures, we describe some predictions for the simpler borate and aluminate systems.

(3) Borate Crystals and Glasses

Strict application of the VU model predicts that all oxygens in borate glasses should be either O(2) or O(1). No 3-coordinate oxygens are allowed, because oxygens bonded to any combinations of 3 B(3)'s or B(4)'s have charges ranging from +1.0 to +0.25 and are thus substantially overbonded (Table I). With increasing modifier content, the general predicted sequence of appearance of anionic (underbonded) oxygens is

$$\text{B(3)–B(4)} \rightarrow \text{B(4)–B(4)} \rightarrow \text{B(3)nbo} \rightarrow \text{B(4)nbo}$$

For many modifiers, the order is consistent with the observed trends in crystal structures[9] in going from B$_2$O$_3$ to pentaborates to triborates to diborates to metaborates to pyroborates and finally to orthoborates. This sequence is also consistent with current structural models for borate glasses based on ^{10}B NMR data.[10]

While our model generally predicts the most stable crystal structures for borates, deviations from the predictions are known for high-pressure phases or phases containing modifier cations with high ionic potentials. For example, while the most stable phase of CaB$_2$O$_4$ (phase I[11]) has the metaborate structure (2 B(3)–B(3) + 2 B(3)nbo) predicted to be optimal by our model, three other metastable structures have been observed, depending on the synthesis pressure. The highest pressure phase (phase IV[12]) contains only B(4)–B(4) oxygens, which are predicted to be relatively less stable in our model. CuB$_2$O$_4$, containing the high ionic potential cation Cu^{2+}, has the same structure[13] as phase IV. While most diborates (MB$_4$O$_7$) have the 6 B(3)–B(4) + B(4)–B(4) structure predicted to be most stable by our model, the Pb and Sr diborates have an unusual structure[14] in which all borons are tetrahedral and two oxygens are trigonally coordinated. In our model, the B(4)–B(4)–B(4) oxygens in this structure are slightly overbonded (net charge = +0.25) and are predicted to be relatively unstable. The above examples illustrate that while our local charge model is useful for predicting structures, it is not infallible.

(4) *Aluminate Crystals and Glasses*

In contrast to borates, aluminates with low modifier content should contain many O(3) units, with the most stable being the neutral site Al(4)–Al(4)–Al(6) (Table I). The O(4) site Al(6)–Al(6)–Al(6)–Al(6) could be present. Sites involving Al(5) should also be common, with other stable units being Al(4)–Al(5)–Al(5), Al(4)–Al(4)–Al(5), and Al(5)–Al(5)–Al(5). The coexistence of Al(4), Al(5), and Al(6) in aluminates with low modifier content is born out in crystalline $CaO \cdot 6Al_2O_3$, which is reported to contain all three coordinations.[18] Al(5) is also present in crystalline aluminosilicates (Al_3SiO_5, andalusite[35]) and boroaluminates ($2B_2O_3 \cdot 9Al_2O_3$[23]). We believe that Al(5) does not occur more often in crystals because it is difficult to create ordered arrays of oxygens to accommodate it. This restriction is lifted in amorphous materials, in which Al(5) should be common. Al(5) has been reported to be present in amorphous alumina films,[36] aluminosilicate glasses,[37] and aluminophosphate glasses.[38]

As the modifier content in aluminates increases, O(3) and O(4) units are predicted to be replaced by O(2)'s, and Al(6) and Al(5) should be replaced by Al(4)'s until the major structural units are interconnected Al(4)–O–Al(4) sites as in crystalline $CaAl_2O_4$.[21] At even higher modifier contents, a complete structural analysis indicates that networks containing Al(4)–O–Al(4) units and nbo's on Al(4) units should be preferred, as in crystalline $Ca_3Al_2O_6$.[22] Raman spectra of calcium aluminate glasses[16] show that nbo's appear around Ca/Al of 0.5, consistent with our analysis.

The crystal structures of MAl_2O_4 (M = Mg or Ca) illustrate the effects of the modifier cation on local structure. When every aluminum is octahedral, the local charge analysis yields the spinel structure (seen in the $MgAl_2O_4$ crystal) in which all oxygens are Al(6)–Al(6)–Al(6). When all the aluminums are tetrahedral, the local charge analysis yields a structure in which only Al(4)–Al(4) oxygens are present, corresponding to the $CaAl_2O_4$ crystal structure.[21] The local charge model predicts that both structures should have equal stability, since all oxygens in both structures have a charge of −0.5. The observed crystal structures indicate that, as in the borate case, modifier cations with greater Z/r tend to favor structures with higher cation and oxygen coordination numbers, even for structures predicted to have equivalent stability.

(5) *Boroaluminate Crystals and Glasses*

Boroaluminates can potentially contain all the oxygen sites of both borate and aluminate structures, and in addition oxygens bonded to both B and Al (Table I). O(4), O(3), and O(2) sites are allowed for the boroaluminates as for the aluminates. Two additional neutral sites predicted to be stable in boroaluminates are B(3)–Al(6)–Al(6) and B(4)–B(4)–Al(6). Both sites occur in crystalline boroaluminates, the first in $AlBO_3$[24] and the second in $MgAlBO_4$.[27] The B(3)–Al(5)–Al(6) site is also predicted to be very stable. Thus, as in aluminate compositions with low modifier contents, Al(4), Al(5), and Al(6) should be stable in boroaluminates of low modifier content. All three coordinations occur in crystalline $2B_2O_3 \cdot 9Al_2O_3$.[23] Al(4), Al(5), and Al(6) are also predicted to be stable in anionic boroaluminate sites such as B(3)–Al(4), B(3)–Al(5), and B(3)–Al(6) with net charges of −0.25, −0.4, and −0.5, respectively. All three anionic sites are easily charge compensated by modifier cations.

Charge balance considerations indicate that the ionic potential of the modifier cation should also affect the distribution of anionic oxygen sites in the boroaluminates. Ca (typical VU = 0.25) exactly neutralizes the B(3)–Al(4) site, but not the B(3)–Al(5) site, which is thus predicted to be less stable in calcium boroaluminate glasses. Mg (typical VU = 0.33) causes slight overbonding when charge compensating the B(3)–Al(4) oxygen and slight underbonding for the B(3)–Al(5) oxygen. Thus, the two sites are predicted to have similar stabilities in magnesium boroaluminate glasses, leading to higher relative concentrations of Al(5) in Mg compositions than Ca compositions as observed.[30] This example illustrates the point (see Model Rationale) that increasing the ionic potential on the modifier cation tends to concentrate negative charge on more local sites, which in boroaluminate glasses increases the concentration of Al(5) and Al(6) relative to Al(4).

Application of charge balance models to the boroaluminates can be illustrated by relisting the local oxygen site distributions predicted to be stable for the composition $MAlBO_4$: (a) 2 B(3)–Al(4) + Al(4)–Al(4) + B(3)nbo and (b) 2 B(4)–Al(6)–Al(6) + 2 Al(6)–Al(6), (c) Al(6)–Al(6)–Al(6)–Al(6) + B(3)–Al(6)–Al(6) + 2 B(3)nbo, (d) 2 B(3)–Al(6)–Al(6) + Al(6)–Al(6) + B(3)nbo, (e) B(3)–B(3) + B(3)–Al(6)–Al(6) + 2 Al(6)–Al(6), and (f) B(3)–Al(5)–Al(5) + Al(5)–Al(5)–Al(5) + 2 B(3)nbo.

Six points of interest emerge from this analysis:

(1) The analysis correctly predicts observed crystal structures. Combination (a) corresponds to the structures of $CaAlBO_4$ and $SrAlBO_4$,[28] and combination (b) corresponds to the structure of $MgAlBO_4$.[27] In an amorphous phase, these two structures and those containing Al(5) should coexist, helping explain why the Bishop and Bray[3] prediction that Al should only be in 4-coordination at high modifier contents is not realized (see Part II[30]).

(2) Combination (b) contains two oxygens with a charge of −1, whereas combination (a) has only one highly anionic oxygen. The greater charge localization in combination (b) is predicted to be more stable for modifier cations with greater ionic potentials. Because combination (b) contains Al(6) rather than Al(4), the model predicts that Al(6) should gain stability relative to Al(4) in Mg-containing glasses relative to Ca-containing glasses. This prediction is in agreement with the above crystal structures and with the higher Al(6) concentrations observed in magnesium boroaluminate glasses.[30]

(3) Favored oxygen units in boroaluminate glasses tend to contain bonds to both Al and B, indicating that the glasses should not phase separate into aluminate- and borate-rich volumes. We see no evidence of phase contrast indicative of phase separation in transmission electron micrographs of our boroaluminate glasses, in agreement with the observations of other workers.[6]

(4) A wide range of anionic sites can be present in boroaluminates. Such sites are not limited to nbo's and oxygens bonded to B(4) and Al(4) as usually assumed, but can also contain Al(5) and Al(6) (Table I). Conversely, the presence of B(4) or Al(4) in a site does not necessarily guarantee that the site will be anionic (e.g., the site B(4)–B(4)–Al(6)).

(5) Proposed structures containing Al(4) sites with either 4 Al(4) or 4 B(4) NNN are expected to be unstable relative to combinations (a) and (b) above because all of the oxygens are substantially underbonded in such structures and generate net site charges of −2. Known crystalline boroaluminates do not contain such units. Calcium aluminates can contain such structures, but only because no boron is present to produce more stable, less underbonded structures. Elimination of unlikely structures is an important feature of our local charge model, as will become apparent in Part II,[30] where we analyze ^{27}Al and ^{11}B NMR results.

(6) As shown in Part II, this analysis provides guidelines for predicting how crystal and glass structures should depend on composition which are consistent with all known NMR results.

III. Summary

A local charge model has been developed to provide qualitative predictions concerning borate, aluminate, and boroaluminate glass structures. For crystalline compounds, the model successfully predicts structures out to the next-nearest-neighbor level for most compounds examined. For boroaluminate glasses, the model indicates local bonding configurations expected to stabilize boron cations coordinated to three or four oxygens, aluminum cations coordinated to four, five, or six oxygens, and oxygens coordinated to one, two, three, or possibly four network-forming cations. The model differs from previous models of glass structure in that it allows for significant Al(5) concentrations, large concentrations of 3-coordinate oxygens in neutral sites such as B(3)–Al(6)–Al(6) and B(4)–B(4)–Al(6), and anionic sites such as B(3)–Al(6) which are not associated with B(4), Al(4), or nonbridging oxygens. The model also predicts that changing the ionic potential of modifier cations should change the site distribution in both crystals and glasses, with high ionic potential cations promoting the stability of higher coordination numbers around both network-forming cations and oxygen anions. We believe that the general approach used to evaluate the relative probabilities of different local bonding configurations should be applicable to many composition families, explaining phenomena such as the aluminum-avoidance rule in aluminosilicates.[39] In Part II,[30] we use our model to provide qualitative predictions concerning the composition dependence of site populations in boroaluminate glasses which are in agreement with both NMR peak intensities and chemical shifts.

References

[1] A. E. Owen, "Properties of Glasses in the System $CaO–B_2O_3–Al_2O_3$," *Phys. Chem. Glasses,* **2**, 87–98 (1961).

[2] A. Naruse, Y. Abe, and A. Takami, "Role of Aluminum Ion in the Structure of Alkaline Earth Aluminoborate Glasses," *Yogyo Kyokaishi,* **79**, 11–22 (1971).

[3] S. G. Bishop and P. J. Bray, "Nuclear Magnetic Resonance Studies of Calcium Boroaluminate Glasses," *Phys. Chem. Glasses,* **7**, 73–81 (1966).

[4] S. Sakka, "Study on Coordination of Aluminum Ions in Germanate, Borate, and Phosphate Glasses on the Basis of Al*Kα* X-ray Fluorescence Spectra," *Yogyo Kyokaishi,* **85**, 299–305 (1977).

[5] A. Osaka, H. Oda, and K. Takahashi, "Constitution of Alkaline Earth Aluminoborate Glasses," *Yogyo Kyokaishi,* **94**, 849–55 (1986).

[6] R. Dupree, D. Holland, and D. S. Williams, "An Examination by Magic Angle Spinning NMR of the Changes in the Environment of ^{27}Al during the Devitrification of an Aluminoborate Glass," *Phys. Chem. Glasses,* **26**, 50–52 (1985).

[7] M. Hahnert and E. Hallas, "Aluminum Coordination in Aluminoborate Glasses" (in Ger.), *Z. Chem.,* **26**, 144–45 (1986).

[8] M. Hahnert and E. Hallas, "NMR Investigation of Aluminoborate Glasses" (in Ger.), *Rev. Chim. Miner.,* **24**, 221–33 (1987).

[9] J. Krogh-Moe, "Interpretation of the Infra-red Spectra of Boron Oxide and Alkali Borate Glasses," *Phys. Chem. Glasses,* **6**, 46 (1965).

[10] S. A. Feller, W. J. Dell, and P. J. Bray, "^{10}B NMR Studies of Lithium Borate Glasses," *J. Non-Cryst. Solids,* **51**, 21 (1982).

[11] M. Marezio, H. A. Plettinger, and W. H. Zachariasen, "Refinement of the Calcium Metaborate Structure," *Acta Crystallogr.,* **16**, 390 (1963).

[12] M. Marezio, J. P. Remeika, and P. D. Dernier, "The Crystal Structure of the High Pressure Phase, CaB_2O_4(IV), and Polymorphism in CaB_2O_4," *Acta Crystallogr.,* **B25**, 965 (1969).

[13] M. Martinez-Ripoll, S. Martinez-Carrera, and S. Garcia-Blanco, *Acta Crystallogr.,* **B27**, 677 (1971).

[14] A. Perloff and S. Block, "The Crystal Structure of the Strontium and Lead Tetraborates, $SrO \cdot 2B_2O_3$ and $PbO \cdot 2B_2O_3$," *Acta Crystallogr.,* **20**, 274 (1966).

[15] D. Müller, W. Gessner, A. Samoson, E. Lippmaa, and G. Scheler, "Solid-State ^{27}Al NMR Studies on Polycrystalline Aluminates of the System $CaO–Al_2O_3$," *Polyhedron,* **5** 779 (1986).

[16] P. McMillan and B. Piriou, "Raman Spectroscopy of Calcium Aluminate Glasses and Crystals," *J. Non-Cryst. Solids,* **55**, 221 (1983).

[17] C. R. Peters, M. Bettman, J. W. Moore, and M. D. Glick, "Refinement of the Structure of Sodium *β*-Alumina," *Acta Crystallogr.,* **B27**, 1826 (1971).

[18] K. Kato and H. Saalfeld, "Refinement of the Crystal Structure of $CaO \cdot 6Al_2O_3$" (in Ger.), *Neues Jahrb. Mineral.,* **109**, 192 (1968).

[19] D. Muller, W. Gessner, and G. Scheler, "Chemical Shift and Quadrupole Coupling of the ^{27}Al NMR Spectra of $LiAlO_2$ Polymorphs," *Polyhedron,* **2**, 1195 (1983).

[20] V. I. Ponomarev, D. M. Kheiker, and N. V. Belov, "Crystal Structure of Calcium Dialuminate, CA_2," *Sov. Phys.— Crystallogr. (Engl. Transl.),* **15**, 995 (1971).

[21] W. Horkner and H. K. Muller-Buschbaum, "The Crystal Structure of $CaAl_2O_4$" (in Ger.), *J. Inorg. Nucl. Chem.,* **38**, 983 (1976).

[22] P. Mondal and J. W. Jeffery, "The Crystal Structure of Tricalcium Aluminate, $Ca_3Al_2O_6$," *Acta Crystallogr.,* **B31**, 689 (1975).

[23] M. Ihara, K. Imai, and J. Fukunaga, and N. Yoshida, "Crystal Structure of Boroaluminate, $9Al_2O_3 \cdot 2B_2O_3$," *Yogo Kyokaishi,* **88** [2] 77–84 (1980).

[24] A. Vegas, F. H. Cano, and S. Garcia-Blanco, "Refinement of Aluminum Orthoborate," *Acta Crystallogr.,* **B33**, 3607–609 (1977).

[25] W. Von Schuckmann, "The Structure of Calcium Aluminoborates, $CaAl[O/BO_3]$" (in Ger.), *Neues Jahrb. Mineral., Monatsh.,* 80–86 (1968).

[26] P. B. Moore and T. Araki, "Johachidolite, $CaAl[B_3O_7]$, a Borate with Very Dense Atomic Structure," *Nature (London) (Phys. Sci.),* **240**, 63–65 (1972).

[27] J. H. Fang and R. E. Newnham, "The Crystal Structure of Sinhalite," *Miner. Mag.,* **35**, 196–97 (1965).

[28] T. Nagai and M. Ihara, "Crystal Structure of Distrontium Boroaluminate, $2SrO \cdot Al_2O_3 \cdot B_2O_3$," *Yogyo Kyokaishi,* **80**, 432–37 (1972).

[29] G. K. Abdullaev and K. S. Mamedov, "Crystal Structure of Lithium Aluminoborate—$Li_6[Al_2(BO_3)_4]$," *Kristallografiya,* **19**, 165–67 (1974).

[30] B. C. Bunker, R. J. Kirkpatrick, R. K. Brow, C. Nelson, and G. L. Turner, "Local Structure of Alkaline-Earth Boroaluminate Crystals and Glasses: II, ^{11}B and ^{27}Al MAS NMR Spectroscopy of Alkaline-Earth Boroaluminate Glasses," *J. Am. Ceram. Soc.,* **74** [6] 1430–38 (1991).

[31] I. D. Brown and R. D. Shannon, "Empirical Bond Strength–Bond Length Curves for Oxides," *Acta Crystallogr.,* **A29**, 266–82 (1973).

[32] K. A. Smith, R. J. Kirkpatrick, E. Oldfield, and D. M. Henderson, "High-Resolution Solid-State Sodium-23, Aluminum-27, and Silicon-29 Nuclear Magnetic Resonance Spectroscopic Study of Rock Forming Silicates," *Am. Mineral.,* **68**, 1206–15 (1983).

[33] B. L. Sheriff and H. D. Grundy, "Calculation of ^{29}Si MAS NMR Chemical Shifts from Silicate Mineral Structures," *Nature (London),* **332**, 819–27 (1988).

[34] L. Pauling, *The Nature of the Chemical Bond,* 3d ed. Cornell University Press, Ithaca, NY, 1960.

[35] J. K. Winter and S. Ghose, "Thermal Expansion and High-Temperature Crystal Chemistry of the Al_2SiO_5 Polymorphs," *Am. Mineral.,* **64**, 573–86 (1979).

[36] R. Dupree, I. Farnan, A. J. Forty, S. El-Mashri, and L. Bottyan, "A MAS NMR Study of the Structure of Amorphous Alumina Films," *J. Phys.,* **46** [12] C8-113–C8-117 (1985).

[37] S. H. Risbud, R. J. Kirkpatrick, A. P. Taglialavore, and B. Montez, "Solid-State NMR Evidence of 4-, 5-, and 6-Fold Aluminum Sites in Roller-Quenched $SiO_2–Al_2O_3$ Glasses," *J. Am. Ceram. Soc.,* **70** [1] C-10–C-12 (1987).

[38] R. K. Brow, R. J. Kirkpatrick, and G. L. Turner, "Local Structure of $xAl_2O_3 \cdot (1 - x)NaPO_3$ Glasses: An NMR and XPS Study," *J. Am. Ceram. Soc.,* **73** [8] 2293–300 (1990).

[39] W. Loewenstein, "The Distribution of Aluminum in the Tetrahedra of Silicate and Aluminates," *Am. Mineral.,* **39**, 92–96 (1954). □