

Medium-range order in cesium borate glasses probed by double-resonance NMR

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Dedicated to Prof. Müller-Warmuth's in celebration of his 75th birthday

Abstract

Rotational-echo double-resonance NMR is used to probe the proximity of Cs^+ network modifiers to network-forming boron in binary cesium borate glasses. Low- and high-alkali glasses show distinctly different dephasing curves, which indicate preferential association of Cs^+ with four-co-ordinate boron (^4B) at low-alkali contents only. Different ^4B sites within a given glass appear to be subject to the same ^{133}Cs dipolar field, thus placing constraints on the possible assignments of multiple tetrahedral boron peaks to different types of medium-range order and guiding future structural modeling studies.

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1. Introduction

Borate glasses have been studied extensively by ^{11}B NMR for decades, with significant early contributions coming from the work of Bray [1,2] whose use of low-field non-spinning experiments led to important structural insights. Distinction between three- and four-co-ordinate boron in such experiments was based on differences in the quadrupolar interaction. With the development of magic-angle spinning technology and the availability of higher applied magnetic fields, resolution between three- and four-co-ordinate boron emerged due to different chemical shifts, simplifying quantification of short-range order [3–5]. Still, chemical shift differences between distinct types of three-co-ordinate borons (^3B) or four-co-ordinate borons (^4B) are generally too small to permit convenient identification and quantification.

In this context, we were surprised to find two distinct ^{11}B NMR peaks from four-co-ordinate borons in cesium borate glasses over a wide compositional range [6]. Their intensity variations were smooth from 3 to 35 mol% Cs_2O , and the two peak positions varied only a fraction of a ppm. Analogous studies of rubidium and potassium borate glasses revealed remarkably similar data, with nearly identical chemical shifts and intensity variations, marking out three rough compositional regimes which are related to structural organization beyond the first-co-ordination sphere [7]. Even more surprising is the correlation between the populations of different ^4B species and material properties measured in the bulk, suggesting that medium-range order has an influence on bulk behaviour [8,9].

One explanation for the observations is that in potassium, rubidium and cesium borate glasses, medium-range order involving reasonably stable polyanionic clusters (sometimes called “superstructural units”) dominates the network speciation. Using arguments based on the ^4B chemical shifts and quadrupole coupling constants of anhydrous crystalline alkali

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borates and on ab initio calculations of shieldings and electric-field gradients, we have hypothesized that both *triborate* and *diborate* units (Fig. 1a and c) are formed upon initial alkali-oxide addition to B_2O_3 glass (manuscript in progress) [6,7]. At approximately 20 mol% alkali oxide, the diborate population stops increasing in favour of the formation of *di-triborates* (Fig. 1b). Above about 28 mol% alkali oxide, the concentration of three-membered ring species (i.e., triborate and di-triborate) apparently declines, and diborate content increases. While this scheme is consistent with some previous work on borate and borosilicate glasses [10], it postulates the formation of relatively energetically unfavourable $[^4B-O-^4B]$ linkages at low alkali loadings, where such species are not observed in crystalline phases [11,12]. Indeed, recent ^{17}O NMR studies of related systems indicate some degree of “boron avoidance”, by analogy with “aluminium avoidance” in zeolites, and question the validity of the Dell and Bray model [13].

One way to test for putative diborate units is to probe the proximity of alkali cations relative to the different $[^4B]$ sites. Based on local charge balance, a negatively charged $[^4B]$ linked to another anionic tetrahedral boron should require more cesium cations to offset the buildup of negative charge on the bridging oxygen ($[^4B-O-^4B]$) than would a tetrahedral boron bonded only to trigonal borons ($[^4B-O-^3B]$). Alternately, the charge-modifying cation(s) would have to be closer to the highly charged bridging oxygen to satisfy the local charge-balance requirements. Whether by shorter distance or by cationic clustering about the bridging oxygen, the neighbouring $[^4B]$ will be subject to a greater dipolar field when adjacent to another $[^4B]$ than when sur-

rounded by only $[^3B]$ due to the localization of negative charge. Since the direct dipolar coupling interaction is simply related to internuclear distance, a measurement of the net cationic dipolar field from the network modifier at a given $[^4B]$ should aid in distinguishing between these two cases. This can be conveniently done for ^{11}B and ^{133}Cs using rotational-echo double-resonance (REDOR) NMR methodology, which provides a measure of the dipolar interaction between spin-coupled nuclei [14]. ^{133}Cs ($S = \frac{7}{2}$) is 100% naturally abundant, possesses a small electric quadrupole moment, and a moderate magnetogyric ratio. Although typical internuclear distances are long for this large cation ($r_{CsO} = 2.9\text{--}3.6 \text{ \AA}$, $r_{CsB} = 3.4\text{--}3.7 \text{ \AA}$) [15–17], the dipolar coupling constants are large enough to permit sufficient structural sensitivity. Originally developed for measurements of internuclear distances between spin-1/2 nuclei in crystalline compounds [14], recent work has expanded the applicability of REDOR to quadrupolar nuclei in amorphous materials [18–21]. While precise bond lengths are generally not accessible in the latter case, qualitative information concerning ^{11}B peak assignments should be readily available. Here, we use $^{11}B\{^{133}Cs\}$ REDOR experiments to test whether Cs–B interactions can assist in identifying the nature of medium-range order giving rise to distinct $[^4B]$ NMR signals in cesium borate glasses.

2. Materials and methods

Two binary cesium-borate glasses were made by the conventional melt-quench approach to contain 9 and 35 mol% Cs_2O . Cesium carbonate and amorphous B_2O_3 were ground together, heated in a platinum/gold-alloy crucible to $400^\circ C$ for decarbonation, and melted at $950^\circ C$ for 20 min before quenching in air. The glasses were clear, and no evidence of crystallization or phase separation was observed by optical microscopy. Polycrystalline cesium triborate (CsB_3O_5) was prepared by annealing the glass of appropriate composition at $800^\circ C$ [16,22]. The identity and purity of this material were confirmed by X-ray diffraction.

NMR experiments were conducted on a Varian Inova 600 spectrometer with a 3.2-mm triple-resonance MAS probe doubly tuned to 192.4 MHz (^{11}B) and 78.7 MHz (^{133}Cs). Single-resonance MAS experiments were run with spinning speeds of 16–22 kHz, and lineshape simulations performed using STARS (Varian, Inc.). ^{11}B triple-quantum MAS data were acquired using a B_1 field of 105 kHz for the excitation (5.5 μs) and conversion (1.4 μs) pulses, and a low-power (5 kHz) z -filter pulse (23 μs); [23,24] 100 t_1 increments were collected with an increment time of 22.725 μs at a spinning rate of 22002 Hz. REDOR experiments utilized the pulse sequence depicted in Fig. 2 under xy -8 phase cycling

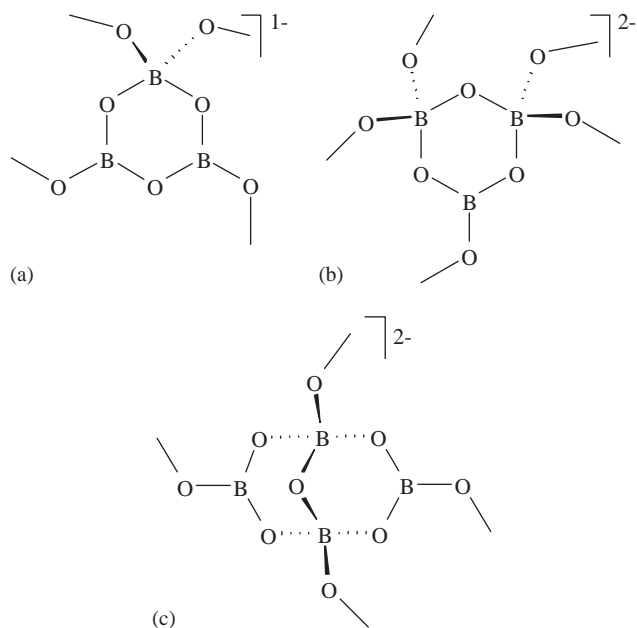


Fig. 1. Schematic diagram of polyanionic species discussed in the text: (a) triborate, (b) di-triborate, and (c) diborate.

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