

Minimizing the Water Leaching of Zincborate Glass by La_2O_3 Addition for LTCC Applications

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ABSTRACT

A series of La_2O_3 -added zincborosilicate glasses was fabricated by systematically varying La_2O_3 addition up to 15 mol% under the constraint of a $\text{ZnO}:\text{B}_2\text{O}_3$ ratio of 1:2. The degree of water leaching after ball milling of the prepared glasses in water medium was relatively quantified by the change in zinc peak intensity in energy dispersive spectroscopy. 8 mol% of La_2O_3 was the most efficient addition in inhibiting the glass leaching by water. The role of La_2O_3 in inhibiting the leaching was explained in terms of change of structural units in the glass network. When the optimum 8 mol% La_2O_3 -added $\text{ZnO}:\text{B}_2\text{O}_3$ glass was used as sintering aid for Al_2O_3 , the fabricated alumina-glass composite at 875°C demonstrated dielectric constant of 6.11 and quality factor of 15470 GHz, indicating the potential of leaching-minimized La_2O_3 - $\text{ZnO}:\text{B}_2\text{O}_3$ glass for application to low temperature co-firing ceramic technology.

Key words: Water leaching, Glass, La_2O_3 , Zincborate, LTCC

1. Introduction

Technologies for low temperature co-firing of metallic electrodes with refractory ceramic materials enable the realization of passive components such as resistors, coils, and capacitors in a laminated ceramic stack for mobile telecommunication systems. One of the key issues in the low temperature co-firing ceramics (LTCC) technology is to lower the sintering temperature of refractory ceramics less than about 900°C where printed electrodes of metallic particles from pastes are well sintered. To date, use of the low-melting glass together with the refractory ceramics has been the most predominantly adopted way to reduce the sintering temperature of ceramics. In this regard, considerable effort has been devoted to the development of appropriate glass compositions¹⁻⁵; borate-based glasses have been successful in reducing the sintering temperature of refractory ceramics.⁶⁻⁸

Currently, the green sheets used for the fabrication of laminated ceramic stack are fabricated by tape casting from slurries with glass and ceramic particles. A problem exists in that borate glasses are fairly dissolved in water during ball milling process for the slurry preparation. As time lapses, the dissolved components work to agglomerate the particles and increase the viscosity of the slurry, inhibiting the slip casting.⁹ As a way to overcome such problems, control of the organic additives has been considered as a rec-

ipe.¹⁰⁻¹¹ However, a fundamental solution to the problem would involve minimizing the glass dissolution itself.⁹

Therefore, the current work focuses on the development of a water-leaching-resistant borate glass. In this regard, La_2O_3 addition to a glass has long been known to be efficient, while, in some composition regimes, La_2O_3 addition was shown to be harmful.⁸⁻⁹ Here, in order to find the optimal La_2O_3 addition to minimize the degree of water leaching, we systematically investigate a series of La_2O_3 -added zincborosilicate glasses by varying La_2O_3 addition up to 15 mol% under the constraint of a $\text{ZnO}:\text{B}_2\text{O}_3$ ratio of 1:2. To date, the quantification of the degree of leaching by measuring weight loss of the ball milled powder in water medium has been a challenging task due to the handling loss of the ball milled powder. In the current work, a simple and efficient method which precisely determines the relative degree of water leaching has been adopted based on energy dispersive spectroscopy.

2. Experimental procedure

Varying amounts of La_2O_3 powder (up to 15 mol%) were mixed with ZnO (99.9% purity, Aldrich, Milwaukee, WI) and B_2O_3 (99.9% purity, Kojundo Chemical Laboratory Co., Ltd. Tokyo, Japan) powders under the constraint of a $\text{ZnO}:\text{B}_2\text{O}_3$ mole ratio of 1:2 in a rotating Y-shaped glass tube for 24 h. The investigated compositions are shown in Table 1 and in ternary diagram (Fig. 1). The mixed powder was shifted to platinum crucible and melted at 1200°C for 30 min, followed by a quenching to a metallic mold. The quenched glass was ground by mortar and pestle to pass a

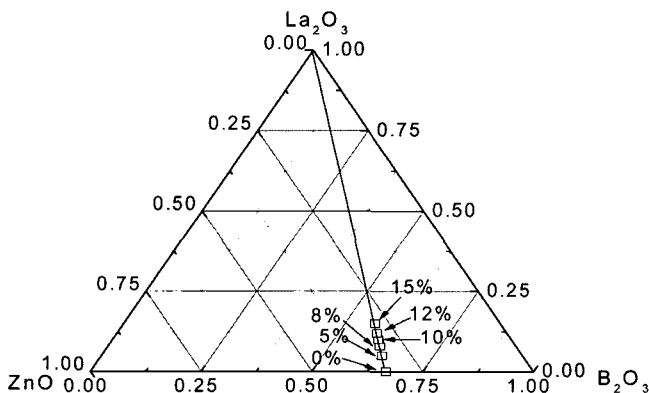
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Table 1. Composition of the Prepared Glasses (mol%)

La ₂ O ₃	ZnO	B ₂ O ₃
0	66.7	33.3
5	63.3	31.7
8	61.3	30.7
10	60.0	30.0
12	58.7	29.3
15	56.7	28.3

**Fig. 1.** Investigated compositions (mol%) with varying La₂O₃ under the constraint of ZnO:B₂O₃=1:2 ($x\text{La}_2\text{O}_3\text{-(1-x)}/3\text{ZnO-2(1-x)}/3\text{B}_2\text{O}_3$).

75 μm sieve.

Prepared glasses were ball milled in water medium using zirconia balls for 24 h, followed by drying in an oven. Ball milled powder and as-sieved powder (without ball milling) with the same initial composition were uniaxially pressed into disc shapes ($\phi 5\text{ mm} \times 5\text{ mm}$) at 100 MPa, and shifted to aluminum jigs. The two powder compacts on jigs were juxtaposed at the center of a vacuum chamber for physical vapor deposition of platinum on top of the powder compacts. The platinum coated specimens were shifted to vacuum chamber at the same time for the characterization by energy dispersive spectroscopy.

8 mol% La₂O₃-added glass frit after the ball milling in water medium for 24 h was mixed with alumina powder (average diameter of about 5 μm) and further ball milled for 2 h for mixing purpose. The alumina-glass mixture was dried, uniaxially pressed at 100 MPa to form an $\phi 10\text{ mm} \times 6\text{ mm}$ disk, followed by sintering at 875°C for 1h. The dielectric constant and quality factor of the sintered body were measured by using a network analyzer (Model HP8720C, Hewlett Packard, Palo Alto, CA) based on the transmission cavity method using a Cu cavity and Teflon supporter.

3. Results and Discussion

Energy dispersive spectra of the glasses before and after the ball milling (in water medium for 24 h) are compared in Fig. 2 for each La₂O₃ addition. In Fig. 2, platinum peak originates from the physical vapor deposition during sample prep-

aration stage. It can be assumed that the same amount of platinum was deposited to both of the specimens because the specimens were simultaneously juxtaposed at the center of the chamber during deposition. Thus, the maximum peak intensity (height) of platinum at 2.07 keV was normalized at each composition; the normalized results are shown in Fig. 2.

When no La₂O₃ is added (Fig. 2(a)), the peak intensity (height) of zinc at 8.64 keV (the maximum zinc peak, which is not superimposed to other peaks) decreases significantly after the ball milling. This finding indicates that zincborate glass is significantly leached out during the ball milling process in water medium.

Since the degree of change in zinc peak intensity can be regarded as the degree of leaching of the glass by water, the change in peak intensity of zinc before and after the ball milling shown in Fig. 2 was quantified by the term $(I_0 - I)/I_0 \times 100$, where I_0 and I are the intensities (heights) of zinc peaks (8.64 keV) before and after the ball milling, respectively. The result is summarized in Fig. 3. The degree of leaching by water decreases up to the addition of 8 mol% La₂O₃, and increases back thereafter. At the optimum condition of 8 mol% La₂O₃, the magnitude of the reduction of zinc peak intensity is only 5.5% after ball milling for 24 h. This result clearly explains some contradicting results in existing works which reported that the lanthanoborate glasses showed poor resistance to attack by aqueous solutions depending on composition.¹²⁻¹³⁾

The inhibition of the leaching of the glass by water has been clearly demonstrated, but only up to a certain addition of La₂O₃; therefore, it is necessary to consider: (1) the reason why La₂O₃ addition improves the leaching resistance; (2) if an optimum dose of La₂O₃ exists. It is well known that vitreous B₂O₃ consists of planar BO₃ triangles. In borate glasses, addition of alkali oxide to B₂O₃ network creates BO₄ tetragonal units up to 33.3 mol% of modifying oxides; further addition leads to reconversion of BO₄ to BO₃ units, weakening the glass network.

ZnO serves as either a network modifier or a network former. In zincborate glasses, ZnO works as network former,¹⁴⁻¹⁶⁾ thereby $[\text{ZnO}_{4/2}]^{2-}$ structural unit and Zn^{2+} exist via the scheme of the reaction, $2\text{ZnO} = [\text{ZnO}_{4/2}]^{2-} + \text{Zn}^{2+}$.^{15,16)} In existing works,^{15,16)} the oxygens supplied by modifiers were interpreted to be utilized by Zn^{2+} , which is incorporated to the glass to strengthen the network. Similarly, the addition of La₂O₃ modifier in the current work is believed to take Zn^{2+} in the zincborate glass to form ZnO₄ tetrahedral units; thereby, the glass network is strengthened to inhibit the leaching by water. After all the Zn^{2+} is used up, additional La₂O₃ will only work as a network modifier, which explains the weakening back of the glass network to increase the leaching after 8 mol% La₂O₃. As the lanthanum borate binary glass is based on the mixed trigonal and tetragonal metaborate rings,¹⁷⁾ an overly high dose of La₂O₃ up to 15 mol% in the current work will increase the number of trigonal unit to weaken the network with decreased La-O bond length.¹⁸⁾

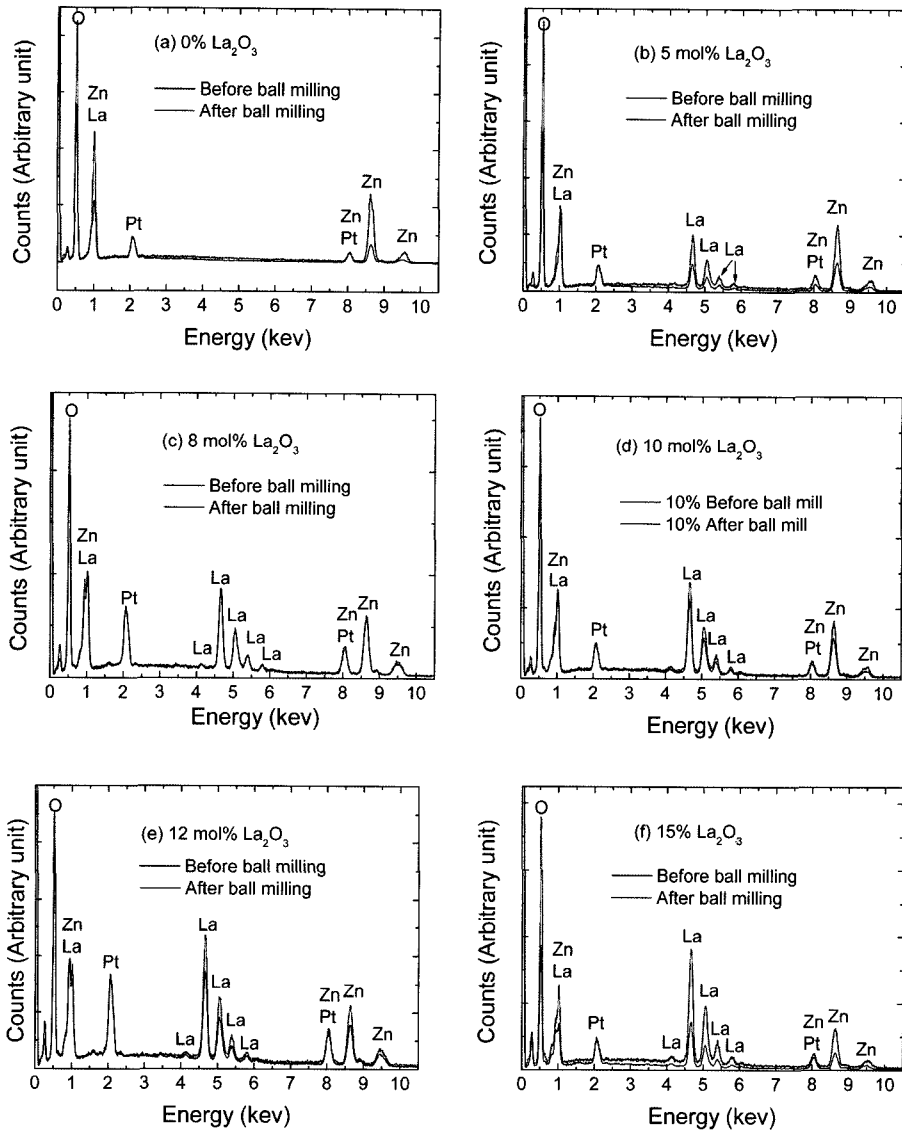


Fig. 2. Comparison of the energy dispersive spectra for the specimen before and after the ball milling in water medium for 24 h. (a) no La₂O₃ addition, (b) 5% La₂O₃, (c) 8 mol% La₂O₃, (d) 10 mol% La₂O₃, and (e) 15 mol% La₂O₃.

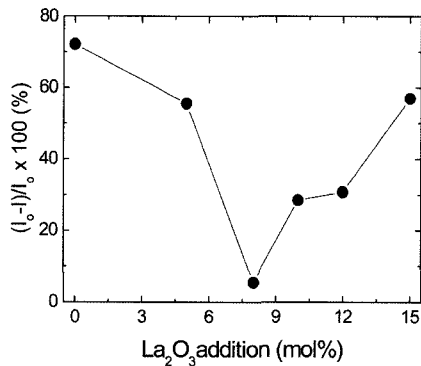


Fig. 3. Change in the reduction percentage of the zinc peak intensity, $(I_0 - I)/I_0 \times 100$, as a function of La₂O₃ addition. I_0 and I are the peak intensities of zinc before and after the ball milling of the powder in water medium, respectively.

Having observed the role of La₂O₃ in suppressing the leaching of the zincborate glass by water, the potential of the optimum 8.0La₂O₃-30.7ZnO-61.3B₂O₃ as a glass composition for LTCC technology needs to be checked. When the glass with optimum composition was mixed with Al₂O₃ powder (50 wt%) by ball milling for 2 hr in water medium and fired at 875°C for 1h, the glass-Al₂O₃ composite demonstrated 6.11 in dielectric constant and 16470 GHz in quality factor. These properties indicate that the developed lanthanum zincborate glass has the potential to be used as a water-leaching-resistant glass composition for LTCC technology.

4. Conclusion

A series of La₂O₃-added zincborosilicate glasses was fabri-

cated by systematically varying La_2O_3 addition up to 15 mol% under the constraint of the $\text{ZnO}:\text{B}_2\text{O}_3$ ratio of 1:2. The degree of glass leaching after ball milling of the prepared glasses in water medium was relatively quantified by the change in zinc peak intensity in energy dispersive spectroscopy. La_2O_3 addition up to 8 mol% decreased the degree of leaching by water, while an overly high dose of La_2O_3 increased back the leaching thereafter. The oxygens supplied by the La_2O_3 modifier were interpreted to be utilized by Zn^{2+} existing in a zincborate glass, thereby strengthening the glass network. After all the Zn^{2+} is used up, additional La_2O_3 after 8 mol% La_2O_3 will only work as network modifier, which explains the weakening back of the glass network to increase the leaching by water. When the optimum 8 mol% La_2O_3 -added $\text{ZnO}-\text{B}_2\text{O}_3$ glass was used as sintering aid for Al_2O_3 , the fabricated alumina-glass composite at 875°C demonstrated a dielectric constant of 6.11 and a quality factor of 15470 GHz, indicating the potential of the water-leaching-minimized La_2O_3 - $\text{ZnO}-\text{B}_2\text{O}_3$ glass for application to low temperature co-firing ceramic technology.

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