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Title: Synthetic Routes, Ceramic Densification, and Properties of Potassium Beta"-Alumina

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The preparation of dense potassium β "-alumina solid electrolyte (K-BASE) ceramic is of interest because of its possible use in thermal to electric conversion using potassium-based AMTEC cells. K-BASE is one of the best ionic conductors in single crystal form as well as one of the few β "-aluminas which can be prepared directly. K-BASE was prepared by Crosbie and Tennenhouse's ion exchange method as well as by modification of two reported synthetic routes from precursor microhomogeneous metal alkoxides via hydrolysis and from metal oxalates via thermal decomposition. Inclusion of stabilizing ions in the precursors allow preparation of nearly phase-pure K-BASE. We have reported that the conductivity of the ion exchanged K-BASE above 700K is close to that of Na-BASE, and now report successful direct synthesis of K-BASE, results of conventional sintering studies as well as rapid sintering including laser annealing and flame spraying. New results include the modified synthetic routes and the stability of the K-BASE composition to very rapid melting or sintering.

Synthetic Routes, Ceramic Densification, and Properties of Potassium β'' -Alumina

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The preparation of potassium β'' -alumina solid electrolyte (K-BASE) ceramic is of interest because of its possible use in potassium AMTEC cells, AMTEC, the alkali metal thermal-to-electric converter is a power source which can utilize heat input at 900 to 1300K. It is modular, has no moving parts, and has potential efficiencies of $> 20\%$. It is of interest for space power as well as terrestrial applications.

K-BASE is an excellent room temperature solid ionic conductors in single crystal form, with conductivity above that of its sodium analog, [1] It is one of the few β'' -aluminas which can be prepared directly, but its thermal decomposition via loss of K_2O occurs more readily and at lower temperatures than for sodium β'' -alumina (Na-BASE). This hinders direct single crystals or high density ceramic preparation.

Fairly dense K-BASE ceramics were prepared by Crosbie and Tennenhouse via ion exchange with KCl vapor at 1300-1400K. [2] We have reported the high temperature conductivity of K-BASE prepared by their method; the conductivity above 700K was close to that of Na-BASE, but it dropped much more rapidly below 700K than in the case of the sodium analog or single crystal. [3] Molybdenum electrodes on K-BASE electrolyte samples in potassium vapor at $900K < T < 1250K$ showed good mass transport and electrode kinetics.

We have attempted to prepare dense K-BASE ceramics by the KCl ion exchange technique as well as by modification of two reported synthetic routes from precursor microhomogeneous metal alkoxides via hydrolysis and from metal oxalates via thermal decomposition. [4,5] Inclusion of stabilizing ions such as Mg^{2+} in the precursors allow preparation of nearly phase-pure K-BASE, although small amounts of amorphous material or a potassium rich β -alumina phase with a lengthened c axis cannot be ruled out. Several weak to moderate intensity peaks have been shown to be specific to each of the β and β'' phases, and only those unique peaks characteristic of the β'' -alumina phase were observed, when stoichiometry was controlled. [6] In addition, formation of the β -phase could be detected by scanning electron microscopy since the characteristic crystallite habit changed significantly. Energy dispersive analysis and x-ray fluorescence were used for elemental analysis of the samples.

Fine free-flowing, somewhat hygroscopic powders were obtained via the direct synthesis routes, but traditional tape-casting and pressed pellet sintering did not provide dense ceramics, due to the crystallite growth mode; the ceramics did sinter and became stronger but porosity remained high or increased. Tests with a variety of sintering agents did not increase density, although the sintering rate increased.

The stability limits for annealing K-BASE in air were roughly determined with respect to time and temperature. While samples began losing K_2O at temperatures as low as 1400K in vacuum or 1600K in air over a period of several hours, the β'' -alumina phase could be retained for several minutes at temperatures as high as 1950K. These observations suggested rapid liquid phase sintering or melting might be possible without unacceptable changes in composition. Several methods of rapid sintering including laser annealing and flame spraying have been attempted, with somewhat successful results in both cases. Laser annealing or surface melting has been used to produce dense homogeneous layers of probably amorphous material on the surface of sintered discs. Composition was not changed significantly by this process. Flame spraying has also been used to produce coatings of a nearly dense precursor phase which is also probably amorphous or glassy, but is rather hygroscopic. Work at this time is oriented toward fabrication of larger samples, and resintering to crystallize the dense phase. Conductivity results for the near 100 % dense ion exchanged ceramic, as well as any results on macroscopic samples of rapidly sintered material will be presented. The research described in this paper was performed by the Jet Propulsion Laboratory, California Institute of Technology, and was supported by the National Aeronautics and Space Administration, the Department of Energy, and the Air Force Phillips Laboratory. We acknowledge helpful discussions with Drs. J. Kummer, N. Weber, J. Rasmussen and B. Dunn.

References

1. J. Briant and G. Barrington, *J. Solid State Chem.* 33, 385 (1980)
2. G. Crosbie and G. Tennenhouse, *J. Amer. Ceram. Soc.* 65, 187 (1982)
3. R. Williams, B. Jeffries-Nakamura, M. Underwood, M. Ryan, D. O'Connor, and S. Kikkert, *Solid State Ionics*, 53-56, 806 (1992)
4. D. Pearlman, U.S. Patent No. 4083919, (1978)
5. T. Takahashi, K. Kuwabara, and H. Ohyanagi, *J. Appl. Electrochem.*, 11, 77 (1981)
6. C. Schmid, *J. Mater. Sci. Lett.*, 5, 263 (1986)