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Rare Earth Phosphate Glass and Glass-Ceramic Proton Conductors

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The structure and conductivity of cerium and lanthanum phosphate glasses and glass-ceramics were investigated. The effects of varying the metal to phosphate ratio in the glasses, doping LaP_3O_9 glasses with Ce, and recrystallization of CeP_3O_9 glasses, on the glasses' microstructure and total conductivity were investigated using XRD, SEM, and AC impedance techniques. Strong increases in conductivity occurred when the glasses were recrystallized: the conductivity of a cerium metaphosphate glass increased conductivity after recrystallization from $10^{-7.5}$ S/cm to 10^{-6} S/cm at 400°C.

Introduction

The proton conductivity of alkaline-earth doped rare earth phosphate ceramics, glasses, and glass-ceramics have recently been investigated by several groups (1-6). Applications for these materials would be in midrange temperature fuel cells, which would have advantages over low temperature range PEMs and high temperature range SOFCs because of lowered sensitivity to CO poisoning, simpler thermal management, and low-cost electrocatalysis (1), provided proton conductivities can be in excess of 10^{-3} S/cm at these temperatures. The present work reports progress toward that goal.

The proton conductivity of rare earth phosphates can be improved by doping them with different cations, and synthesizing them with the ideal microstructure. The theory behind doping the trivalent rare earth phosphates with divalent cations is that protons should be introduced as charge-compensating defects, increasing the carrier concentration of the compounds and thus increasing the conductivity (6). Doping with multivalent cations such as Ce would have a similar effect, with the added benefit of adding a small amount of electrical conductivity to aid proton mobility. As for the microstructural considerations, a study done by our group shows that the amorphous, phosphorous-rich grain boundaries in crystalline phosphates may be the primary pathway for proton conduction. Increasing the volume ration of grain boundary to bulk grain by making a material with crystalline-amorphous nanocomposite microstructure could enhance the conductivity by several orders of magnitude (1).

In this study, the total conductivity of lanthanum and cerium phosphate glasses and glass-ceramics has been measured in samples with different metal to phosphate ratios, different degrees of Sr and Ce doping, and for amorphous and recrystallized samples.

Experimental

Sample Preparation

Glasses were prepared by melting the appropriate amounts of reagent-grade cerium or lanthanum oxide, strontium hydroxide hydrate, and 85% phosphoric acid in a platinum crucible at 1300°C for 30 min, and then pouring the melt onto a steel plate preheated to about 350°C. Lanthanum phosphate glasses were clear and transparent; cerium phosphate glasses were light orange and transparent. The glasses were annealed at 450°C for 2 hours, and then cut into wafers 1 cm in diameter x 0.5 mm in thickness using a slow speed diamond saw. To crystallize the glasses, the wafers were slowly heated in argon over a period of 3 hours to 700°C and held at that temperature for up to 2 hours.

Conductivity Measurement

Platinum mesh electrodes were attached to the polished glass and glass-ceramic wafers using platinum paste. A Solartron 1260 impedance analyzer was used to measure the total conductivity of the samples, with the frequency ranging from 10 MHz to 1 Hz, with alternating voltage amplitude 800 mV. The temperature ranged from 300-400°C. The measurements were taken in air.

Structural characterization

Bulk and powder XRD was performed on a Philips PW3040 X'Pert Pro Diffractometer using Cu Kα source operated with a 45 keV X-ray tube voltage. The microstructure and chemical content of the samples were probed using an analytical scanning electron microscope (SEM, Zeiss Gemini Ultra-55) equipped with an energy dispersive X-ray spectroscope (EDS).

Results and Discussion

Glass Conductivity

Varying the Metal to Phosphate ratio. Figure 1(a) shows the conductivity results for the lanthanum strontium phosphate $La_{0.4}Sr_{0.6}P_3O_9$ glass samples where the metal to phosphate (M:P) ratio was varied from 1:3 to 1:4. The conductivity of the glass with higher phosphate content was higher by about a factor of 5. Attempts to synthesize glass compositions with both lower and higher phosphate contents were unsuccessful. Adding less phosphate made the melting temperature of the starting materials too high. Adding more phosphate than M:P=1:4 was not successful because the excess phosphates volatilized during the synthesis.

Doping with Cerium. Figure 1(b) shows that the conductivity of the lanthanum strontium phosphate glass $La_{0.4}Sr_{0.6}P_3O_9$ increased by about a factor of 3 on doping with 2% cerium to $La_{0.4}Sr_{0.52}Ce_{0.08}P_3O_9$.

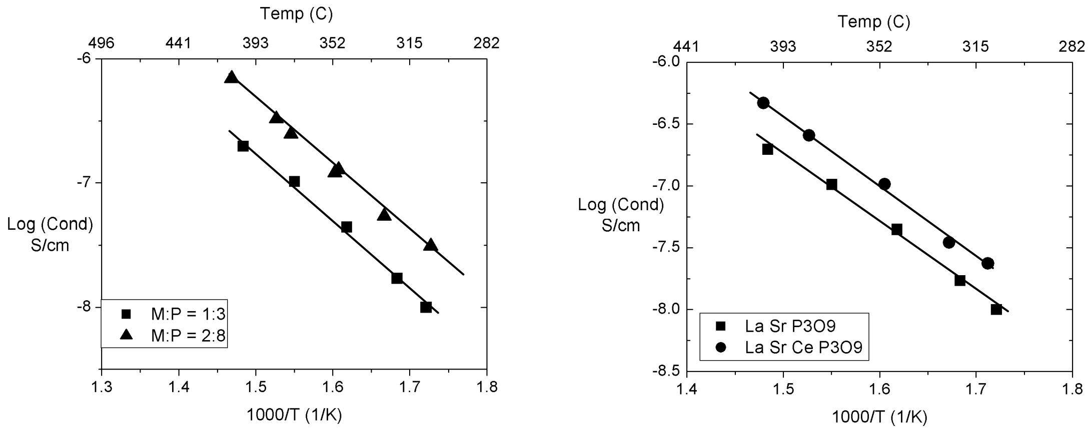

Figure 1 (a) Conductivity of lanthanum strontium phosphate glasses where the metal to phosphate ratio was varied. (b) Conductivity of lanthanum strontium phosphate glasses with 0% and 2% Ce doping.

<u>Recrystallization.</u>

Cerium phosphate glasses were slowly heated to 700°C and held for varying amounts of time. The wafers were broken in half, coated with gold, and examined using an SEM. Figure 2 is an image of a cross section of cerium phosphate (CeP_3O_9) glass that has been only partially recrystallized. The wafer was fairly thick (about a millimeter) and after an hour of heat treatment the recrystallization was not complete. The image shows that the crystals nucleated at the surfaces of the wafer and grew into the glass toward the center. Figure 3 shows a cross section of a thinner CeP_3O_9 wafer heat treated for 2 hours. The crystallization fronts met in the center of the wafer and occasionally left a gap. This is thought to de due to the sweeping of residual pores in the glass melt by the advancing crystallization front. The crystallites are about 200 nm long.

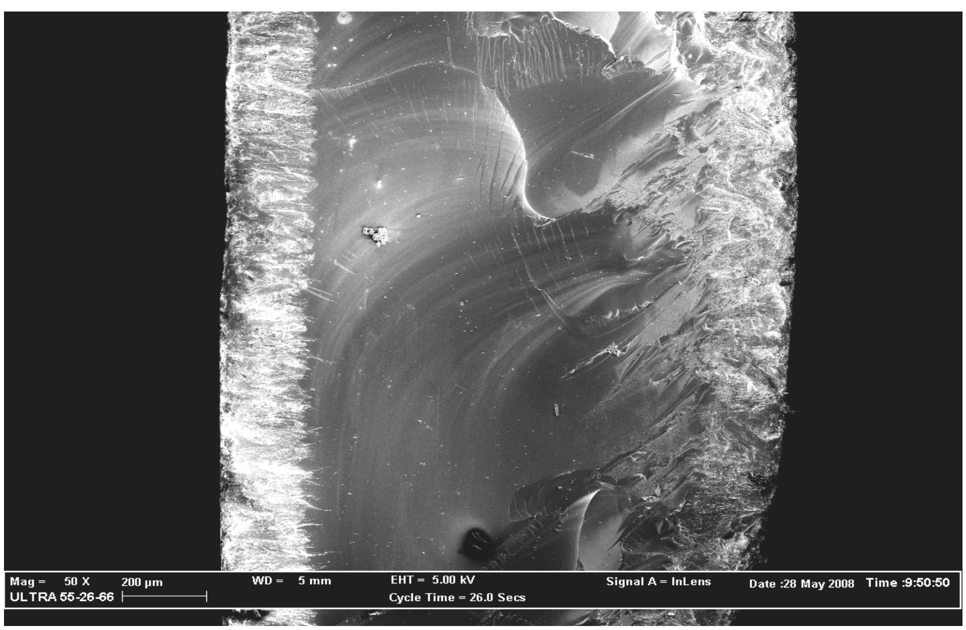

Figure 2. SEM image of a cross section of a partially crystallized CeP_3O_9 wafer. Crystals nucleate at the surface of the wafer and grow inward.

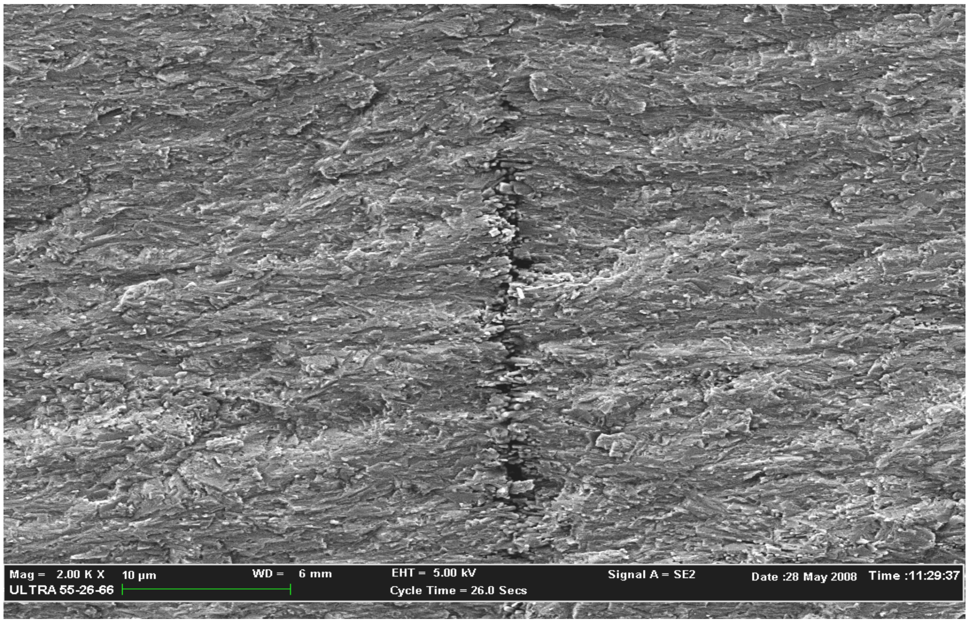

Figure 3. Completed crystallization of CeP_3O_9. Crystals grew inward from the wafer edges occasionally leaving an empty pocket at the interface where they met.

<u>Glass-ceramic conductivity</u>

Figure 4 shows that the conductivity of the CeP_3O_9 glass improved two orders of magnitude on recrystallization from $10^{-7.5}$ S/cm to 10^{-6} S/cm at 400°C. The activation energy decreased from 1.1 eV to 0.7 eV.

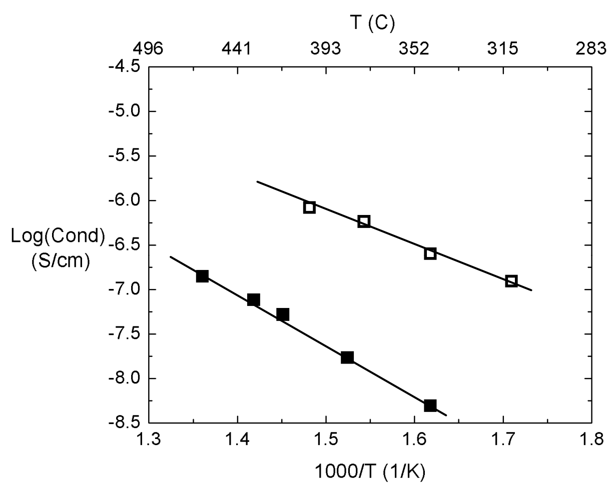

Figure 4. Conductivity of glass and recrystallized samples of CeP_3O_9.

Conclusions

Rare earth phosphates are potential candidates for proton conductors in the temperature range 300-500°C. Doping rare earth phosphate glasses with Ce, and increasing the amount of phosphorus in the glass increases the conductivity by a small amount (factor of 3-5). Recrystallizing the glasses improves the conductivity by an order of magnitude.

Acknowledgments

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