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Study of new proton conducting glasses for fuel cells

S.R. Tiple, V.K. Deshpande*

Department of Applied Physics, Visvesvaraya National Institute of Technology, Nagpur 440010, India

HIGHLIGHTS

- The proton conducting glasses containing Ammonium Sulphates are synthesized using conventional quenching technique.
- The T_g, CTE, density and electrical conductivity results are discussed.
- The glass giving optimum conductivity is used as an electrolyte for fuel cell.
- The power density obtained from the fuel cell is encouraging.

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ABSTRACT

The glasses in the series (35−x) BaO:65 P_2O_5:x $(NH_4)_2SO_4$ are synthesized and characterized by T_g, CTE, density and electrical conductivity measurements. The decrease in density and T_g is observed with addition of $(NH_4)_2SO_4$. The increase in CTE compliments the observed variation in T_g. The protonic conductivity increases with addition of $(NH_4)_2SO_4$ up to 7.5 mol% and decreases beyond this composition. The increase in the ratio of O/P, which in turn, creates more non-bridging oxygens, enhances the conductivity. Further, sulfur is mainly incorporated in sulfophosphate glasses as isolated SO_4^{2-} group which also results in increase in conductivity. The glass with maximum conductivity [7.5$(NH_4)_2SO_4$:27.5BaO:65 P_2O_5] is used to fabricate a fuel cell. It gives the power density of 12.43 μW/cm^2. The power density of the fuel cell in the present work at room temperature is higher than that reported in literature at 473 K. The fuel cell has a potential of giving higher power density at higher temperature of 423 K.

1. Introduction

The new and clean power sources are being sought all over the world. One of such power sources is fuel cell. In addition, the fuel cells possess high efficiency of energy conversion, low noise, low maintenance cost as compared to other energy conversion systems. There are several electrolytes, including NAFION, which have been studied for fuel cell applications [1–4]. Most of the work reported on fuel cells (based on solid electrolyte) is either in high temperature range i.e. above 873 K (SOFC) [5,6] or in low temperature range i.e. below 373 K (PEMFC) [7–10]. On the other hand, there are unique benefits if the fuel cell is operated at intermediate temperature range from 373 to 573 K, viz., increase in efficiency, water produced as gas, possible use of cheaper catalyst [11–13]. The proton conducting glasses are potential electrolytes for the intermediate temperature range fuel cells. There are two ways by which the proton conducting glasses can be synthesized, i.e. by Sol–Gel method and conventional quenching technique. The Sol–Gel derived phosphate based glasses containing molecular water are studied [14,15]. However, the main problems with these glasses are (i) the time consuming process and (ii) shrinkage, which restricts the preparation of a large area membrane [16]. The proton mobility is found to be much higher in phosphate glasses as compared to that in the silicate glasses [17]. Also the ammonium sulfate being a hygroscopic material is considered to retain some water in its glassy form. In the present work synthesis and characterization of Barium Phosphate glasses with $(NH_4)_2SO_4$ addition for fuel cell is carried out.

2. Experimental

A series of Barium phosphate glasses containing $(NH_4)_2SO_4$ with general formula (35−x) BaO:65 P_2O_5:x $(NH_4)_2SO_4$ (x = 0, 2.5, 5, 7.5, 10 mol%) is prepared by conventional quenching technique. The starting materials viz. barium carbonate, ammonium dihydrogen phosphate, ammonium sulfate used for the synthesis of glass

* Corresponding author.
E-mail address: vkdeshpande@phy.vnit.ac.in (V.K. Deshpande).

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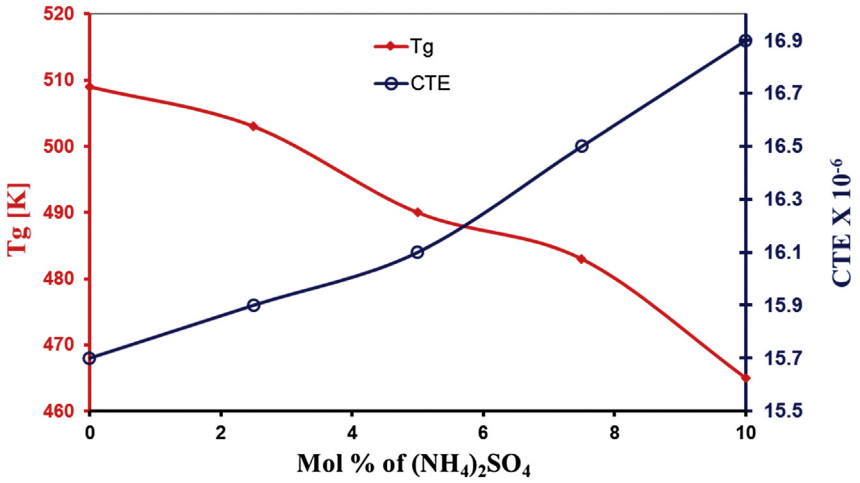

Fig. 1. Variation of T_g and CTE with mol % $(NH_4)_2SO_4$.

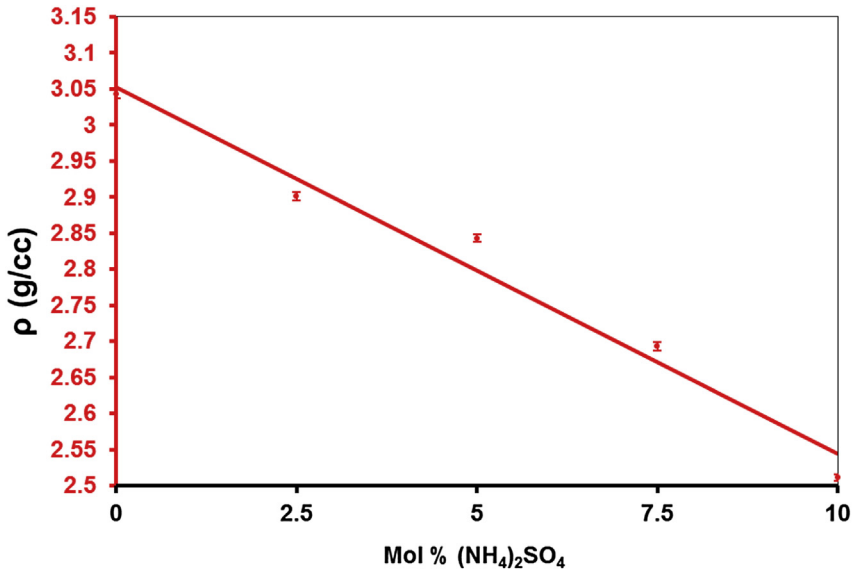

Fig. 2. Variation of Density for glass samples with mol % $(NH_4)_2SO_4$.

samples are of high purity (>99.5%). The Platinum crucible is used to melt the thoroughly mixed raw materials. The melt is soaked at 40 K above the melting point for an hour for homogenization and then quenched in an aluminum mould. The quenched samples are then annealed at 473 K for two hours. The glass transition temperature (T_g) and coefficient of thermal expansion (CTE) are measured using ORTON Dilatometer, version 5.1.2. The densities of glass samples are measured using Archimedes principle with toluene as an immersion liquid. The impedance measurements are carried out for all the glass samples as a function of temperature (335 K–485 K) using High Resolution Dielectric Analyzer (Alpha Analyzer, NOVOCONTROL) in the frequency range from 10 MHz to 1 Hz. A thin disc of glass sample (55 mm diameter and 1.2 mm thickness) is used as electrolyte for fuel cell. The variation of voltage and power density as a function of current density is studied to characterize the fuel cell.

3. Result and discussion

Fig. 1 shows the variation of glass transition temperature (T_g) and Coefficient of Thermal Expansion (CTE) with mol% of $(NH_4)_2SO_4$. It can be seen from this figure that with addition of ammonium sulfate the T_g decreases significantly. This may be attributed to the fact that sulfur is incorporated in sulfophosphate glasses as isolated SO_4^{2-} group [18], wherein the P_2O_5 is replaced by

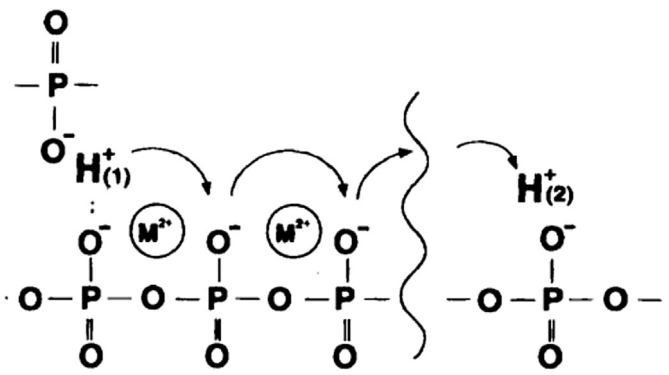

Fig. 3. Schematic representation for proton conduction mechanism in Phosphate Glasses, without molecular water.