PREPARATION AND CHARACTERIZATION OF BaO-ZnO-SiO$_2$ GLASS-CERAMICS FOR POSSIBLE USE IN SOFC

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Abstract

Development of suitable sealant materials is one of the major requirements for implementation of planar solid oxide fuel cells. Among several approaches, rigid glass or glass-ceramic seals have been found to be useful. Glasses having composition 51.0BaO-9.0ZnO-(40-y)SiO$_2$-yNd$_2$O$_3$ (y = 1, 2 wt. %) were prepared by melt-quench technique and converted to glass-ceramics by controlled crystallization. Thermal Expansion Coefficient (TEC) and electrical insulating properties for glass with y = 1 wt. % were found closer to the required values for a suitable sealant. However, flow properties are to be modified in view of making a seal, which is a major task.

Introduction

One of the major challenges for implementation of planar Solid Oxide Fuel Cells (SOFCs), is the development of suitable sealant materials, to separate the air and fuel. Several approaches have been used to achieve the necessary adherence, mechanical integrity and stability, including both rigid seals (no applied load during operation) and compressive seals (load applied to seal during operation) [1, 2]. The most common approach is to use rigid glass [3] or glass–ceramic seals [4, 5], the properties of which can be tailored specifically, for use in SOFCs, through variation of the glass composition [6, 7]. The key requirements for sealing materials include thermo-mechanical and chemical stability along with Thermal Expansion Coefficients (TECs) similar to those of other cell components, (9 – 13) × $10^{-6}$/°C [1, 5, 7]. The seal should also behave as an electrical insulator,
with total conductivity ($\sigma'$) lower than $10^{-4}$ S/cm, in order to avoid parasitic currents decreasing the system efficiency. Here, we report the preparation of BaO-ZnO-SiO$_2$ based glass and glass-ceramics samples and some initial studies on their thermo-mechanical and electrical properties, with a view to develop materials for high temperature sealants. The most important point is that, all these properties should hold good at high operating temperature (800 – 900 °C). This is possibly the first attempt on the national scene, to initiate glass-ceramic sealant work for SOFC.

**Experimental**

The glass samples having composition 51.0BaO-9.0ZnO-(40-y)SiO$_2$-yNd$_2$O$_3$ with y = 1.2 wt % were prepared by melt-quench technique. Analytical grade compounds of ZnO, BaCO$_3$, SiO$_2$ and Nd$_2$O$_3$ were used as starting materials, for the preparation of base glass. Starting charge for making glass was prepared, by double calcination. Calcination was carried out at maximum 950°C for 24 h after thorough mixing and grinding. The melting of doubled calcined material was carried out in a covered Pt-10% Rh crucible at a temperature of 1550°C for 1 to 2 h duration for proper mixing and then poured in to a pre-heated graphite mould. The annealing was carried out at 725°C for 4 h in inert atmosphere and then cooled down to room temperature at a rate of 20°C/h.

To convert these glass samples into glass-ceramics, crystallization temperature was measured using a TG-DTA system (Model: DTA-92-15, M/s. SETARAM, France). Measurements were done in the temperature range of 30–1000 °C employing a heating rate of 10 °C/min. Based on the results of DTA, conversion of glass into glass-ceramics was carried out, at 1050 °C in a programmable resistance furnace, using a controlled heating schedule. Initially for nucleation, the temperature of the sample was kept at around 750°C for 2 h and raised to 1050 °C to facilitate the crystallization.

Both the glass and glass-ceramics samples were characterized for their density, thermal expansion coefficient and microhardness measurements. Density (p) was measured at room temperature by Archimedes principle using water as an immersion liquid with an accuracy of ± 0.03 g/cm$^3$. Thermal expansion coefficients, glass-transition temperature ($T_g$) and glass softening temperature ($T_{ss}$) were measured using a Dilatometer (Model: TMA - 92, M/s. SETARAM, France) in the temperature range of 30-800°C, using a silica probe. The samples about 3 mm thick, with both ends flat, were kept in quartz sample holder with a constant load of 5gm for all measurements. Before starting the experiment, the chamber was evacuated up to $10^2$ mbar pressure and then the chamber was flushed with high purity Argon gas. All the measurements were carried out in flowing Argon atmosphere with a constant flow rate of 40-50 l/h. The temperature was raised up to maximum 1000°C at a rate of 10 °C/min. Thermal expansion coefficient being reported, is the average in the temperature range of 30-500 °C.

Micro hardness measurements were carried out, under a constant load of 100g for 5 s duration using Vicker’s microhardness tester (Model: VMHT-30M). Before measurements, the samples were polished with 0.3mm alumina powder to get good reflective surface. From the measurements of the diagonals of Vickers impressions on the sample surface, microhardness was found out by using standard formula. An average of at least 10 indentations was taken as the value of microhardness.

Identification of various crystalline phases in glass-ceramics samples was carried out, using powder X-ray diffractometer (Philips, model PW 1710) with CuK$\alpha$ as X-ray radiation source. The crystalline phases were identified by matching the peak positions of the intense peaks with PCPDF standard cards.
The electrical measurements were carried out, in the frequency range of 10Hz to 10MHz and over the temperature range of 323- 673K using an impedance analyzer (Alpha-A high performance frequency analyzer, M/s. Novocontrol technologies, Germany). Electrical connections were provided on both sides of the glass sample using conducting gold coating.

Results and discussion

Clear bubble-free transparent glasses were prepared for all compositions. For glass having composition 51.0BaO-9.0ZnO-39.0SiO2-1.0Nd2O3, DTA plot is shown in Fig. 1. It is found that crystallization temperature is 907°C for this glass. Nominal composition, density, Tg, Tds, TEC and MH of glasses and glass-ceramics are given in Table1.

The density values for the glass and glass ceramics samples are found to be 3.91 and 3.86 gm/ cc, respectively for 51.0BaO-9.0ZnO-39.0SiO2-1.0Nd2O3 (y = 1 wt %) composition. Thermal expansion increases from 10.39 to 15.06 x 10^-6/°C, after conversion of base glass to glass-ceramics. The glass transition and dilatometric softening temperature obtained from the dilatometer measurements are 693 °C and 720 °C, respectively. For the glass-ceramics, softening point was not observed up to 1000 °C. The microhardness was found to increase from 4.25 to 4.70 GPa after conversion into glass-ceramics.

Table 1: Nominal composition, density, Tg, Tds, TEC and MH of glasses and glass-ceramics
XRD plot for the glass-ceramic having composition 51.0BaO-9.0ZnO-39.0SiO$_2$-1.0Nd$_2$O$_3$ is shown in Fig. 2. It is found that major crystalline phase is Barium orthosilicate (BaSi$_2$O$_5$). Thermal expansion of this phase is $140 \times 10^{-7}/^\circ\text{C}$, therefore, this phase is responsible for observed high thermal expansion coefficient.

The dc conductivity ($\sigma_{dc}$) was extracted from Jonscher Universal Power (JUP) law fit as shown in Fig. 3. The $\sigma_{dc}$ was found to increase from $2.66 \times 10^{-9}$ to $2.90 \times 10^{-9}$ S/cm with increase in temperature up to 673K. The higher resistivity value even at higher temperature, with the thermal expansion value $10.39 \times 10^{-6}/^\circ\text{C}$ (30-500 $^\circ\text{C}$) for the glass sample, is an advantage in using this material as a possible sealant in SOFC.

**Conclusion**

Glass and glass-ceramic having composition 51.0BaO-9.0ZnO-39.0SiO$_2$-1.0Nd$_2$O$_3$ were prepared which showed good insulating properties even at high temperature (673K). Thermal expansion coefficient was found to be matching with the other components of the SOFC cell. These glass ceramics also show high glass transition and softening temperature as required for SOFC sealants. However, the glass did not show good flow properties so further work is needed to improve the flow properties by changing the composition of glass and processing.

Along with this, studies will also be carried out to check the suitability of sealant material with interconnect, electrode and electrolyte materials, chemical and thermal stability at high operating temperature and harsh fuel cell environment.

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References


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Dr G. P. Kothiyal joined Bhabha Atomic Research Centre in 1970 as a Scientific Officer after completion of Post Graduate Training in Physics from 13th batch of BARC Training School. Currently serving as Head, Glass and Ceramics Technology Section of TPPED, BARC, he is spearheading the programme on special glasses and glass-ceramics and produced them with designed/tailored properties for applications in high voltage and Ultra High Vacuum (UHV) related devices/systems. Such materials/devices have also been delivered for use in nuclear, laser, defence and space applications as level sensors, multi-pin feedthroughs, spacers/isolators, sealant/electronic microcircuit packing, etc. He is a PhD guide in Physics at University of Mumbai and Homi Bhabha National Institute (HBNI) Mumbai. He is a referee for various journals like Pramana, J Non Crystalline Solids, J. Material Science, Materials Science and Engineering, Materials Science Forum, Bulletin of Materials Science, J Thermal Analysis and Calorimetry, etc. He has published more than 180 papers in International/National journals/proceedings and delivered a number of invited talks/lectures. He is a recipient of Materials Research Society of India (MRSI) Medal (Lecture award) for the year 2003.