EXECUTIVE SUMMARY OF UGC MINOR RESEARCH PROJECT

Project Title: - Synthesis and Characterization of Li ion conducting glasses and glass ceramics

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Objective:

1. Material Preparation:

a) Preparation of $L_{i2}O$ based Li ion conducting glasses using the concept of mixed former effect.
b) Preparation of glass- ceramics by controlled crystallization.
c) Preparation of electrode materials based mixed conductors.

2. Structural Characterization

- X-ray power diffraction (XRD): To determine the amorphous nature of glass
- Differential thermal analysis (DTA): To determine the glass transition temperature (Tg).
- Scanning electron microscope (SEM): to determine the morphology glass before and after heat treatment.

3. Electrical Characterization:

The magnitude of conductivity is determined by analyzing impedance data over the frequency at various temperatures with the help of LCR Meter Bridge. The ionic transport number is estimated by Wagner dc polarization method.

Material Preparation:

Material scientists & chemists have made a great deal of intensive effort to establish general criteria for the synthesis of amorphous materials. The established method for the production of glassy materials requires rapid cooling of the melt (melt quenching technique).

1) Preparation of Glasses (Electrolyte/ Electrode)

From the point of view of optimization of glass composition (following mixed former approach), and interest to study the competitive role of the second former and conditional former in network formation, a number of samples were required to prepare by fixed modifier fraction n for different former ratio y respect to host. The glasses were prepared during the entire work into two different series.

Series A: 30 Li_2O: (70-x) B_2O_3: (x) SiO2 {x=5, 10, 15, 20}
Series B: 20 Li_2O: (80-x) B_2O_3: (x) V_2O_5 {x=40, 45, 50, 55}
The choice of each series was done with a specific purpose for electrochemical applications.

Methodology: The starting chemicals lithium carbonate (Li_2CO_3), boric acid (H_3BO_3) and silica (SiO_2) with purity greater than 99.5% were procured from Aldrich Sigma Co., USA. The molecular weights along with the melting points of these ingredients are given in table1

Table1: **Molecular weights and melting points of the ingredients used**.

Compound	Molecular weight	T_m (°C)
Li_2CO_3	73.89	723
Li_2O	29.88	-
H_3BO_3	61.84	169
SiO_2	60.08	1610
B_2O_3	69.92	450
V_2O_5	*181.88*	*690*

$T_m \rightarrow$ melting temperature

Before going for the glass preparation, compositional parameter, *n* and *y*, are defined below to have a systematic variation in formers and modifier.

For Series: A

$$n = \frac{\text{Mixed Former}}{\text{Modifier}} = \frac{B_2O_3 + SiO_2}{Li_2O} = 2.33 \qquad y = \frac{\text{Former}}{\text{Mixed Former}} = \frac{B_2O_3}{B_2O_3 + SiO_2} = 0.7 \leq y \geq 0.9$$

The same procedure was adopted for preparation of series B.:

For Series: B

$$n = \frac{\text{Mixed Former}}{\text{Modifier}} = \frac{B_2O_3 + V_2O_5}{Li_2O} = 4 \qquad y = \frac{\text{Former}}{\text{Mixed Former}} = \frac{B_2O_3}{B_2O_3 + V_2O_5} = 0.3 \leq y \geq 0.5$$

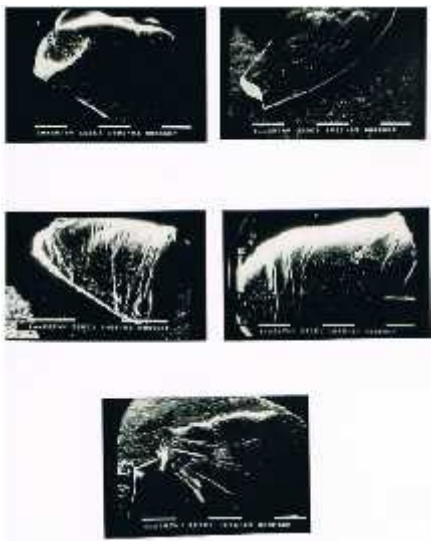
Preparations of Glass Ceramics

The glass of series A obtained by melt quenching techniques were heat treatment at 450^0C (Above Tg) for 12 hours so as to incorporating crystallization. Crystallization was seen to occur in all the samples as they turned opaque after sintering. The nucleation time was selected as 24, 36 and 48 hours so as to optimize the time to achieve highest conductivity, All the samples of glasses obtained as mentioned above, are subjected to a detailed structural characterization using X-ray powder diffraction (XRD); Differential thermal analysis (DTA), and scanning electron microscopy (SEM).

Result and Discussion:

2) Structural Characterizations:

X-ray Powder Diffraction Analysis (XRD):



X-ray powder diffraction patterns recorded for all the glass samples show a diffuse scattering over angles of several degrees, which confirm the amorphous. Samples of series A-B, shows amorphous nature, due to strong macromolecular network. These observations suggest that, before heat treatment, the sample was x-ray amorphous/non-crystalline solid. On the other hand a careful look, partial crystallization occurs due to heat treatment.

Differential Thermal Analysis (DTA): The glass transition temperature, T_g, obtained from the experimental thermo grams for glasses are given in table 2

Table 2: A comparison of T_g glasses belonging to series A-B

Series A	n	y	T_g (^{O}C)	Series B	n	y	T_g (^{O}C)
A1	2.33	0.9	405	B1	4	0.5	427
A2		0.85	433	B2		0.44	438
A3		0.78	437	B3		0.37	419
A4		0.71	423	B4		0.31	412

From this study it can be understood that the T_g strongly depends on *y* for all value of *n*.

Scanning Electron Microscopy:

$30Li_2O:60B_2O_3:15SiO_2$with highest glass transition temperature T_g **(**437^{o}C) of the series was also found to be the highest conducting one. Hence, this sample was subjected to controlled heat treatment for study of glass crystallization. When it was annealed at 400^{o}C for 24 hrs, no surface or bulk crystallization was observed as this is seen in SEM micrographs (Fig..a). This is in accordance with reported observations that glass do not provide any crystalline phase if heated below T_g. any crystalline phase if heated below T_g.

Figure (b-e) depicts SEM micrographs of the specimens heated at 450^{o}C for different time viz., 12hrs, 24hrs, 36hrs and 48hrs, respectively. From these figures it is seen that all temperatures show surface crystallization. In the present case the nucleation is attributed to B_2O_3 as a nucleation catalyst. The grain size on a surface varies in a systematic as the time was raised from 12hrs to 48hrs. It is worth mentioning here that, when the annealing time was increased above 48hrs the sample got melted.

3) Electrical characterization:

Following to approaches were opted for electrical characterization:

1. To determine the conductivity (AC and DC)
2. To determine contribution of ions and electrons to total conductivity of samples (Transport number)

Conductivity variation with temperature and concentration

The conductivity at various temperatures for all samples is calculated from the values of bulk resistance obtained from complex impedance analysis following formula $\pm = \frac{Gt}{A}$, Where G is the conductance; the *t/A* is the cell constant of sample having thickness *t* and cross section area *A.*

Table 3: The comparison of conductivity at 450ºC, T_g and activation enthalpy for $30Li_2O:55B_2O_3:15SiO_2$mixed farmer glass system

Series A	n	Composition	y	T_g (^OC)	± (Sòcm^{-1})	E_a (eV)
A1	2.33	$30Li_2O:65B_2O_3:5SiO_2$	0.9	405	9.26×10^{-4}	0.33
A2		$30Li_2O:60B_2O_3:10SiO_2$	0.85	419	2.17×10^{-4}	0.4
A3		$30Li_2O:55B_2O_3:15SiO_2$	0.78	437	1.5×10^{-3}	0.31
A4		$30Li_2O:50B_2O_3:20SiO_2$	0.71	423	2.25×10^{-3}	0.34

It can be seen from the table that composition ($30Li_2O:55B_2O_3:15SiO_2$) with n = 2.33 gives the highest conductivity (σ) of the order of 1.5×10^{-3} S/cm at 450ºC. This composition also exhibits the minimum activation energy amongst all samples under study.

Transport number measurement

The functional dependence of conductivity with time after the application of dc field across $30Li_2O:55B_2O_3:15SiO_2$ glass. The electronic conductivity (σ_e) due to the absence of polarization, zero time conductivity σ_0 is considered as total conductivity

$$\sigma_T = \sigma_i + \sigma_e \quad \text{and} \quad t_i = \frac{\pm_0 - \pm_\infty}{\pm_0}$$

The ionic transport number t_i is found to be 0.9999, which is nearly equal to unity. Hence, the ionic conductivity due to mobile Li ion carrier under study confirming that the present class of materials belongs to a glassy solid electrolyte.

Temperature and concentration dependent conductivity of Glass Ceramics

The values of conductivity (at 500ºC) and activation energy of all glass- ceramics summarized in following table.

Series	Composition	σ (S×cm^{-1})	E_a (eV)
A1	$30Li_2O:65B_2O_3:5SiO_2$	$7.54*10^{-4}$	0.98
A2	$30Li_2O:60B_2O_3:10SiO_2$	$3.24*10^{-3}$	0.79
A3	$30Li_2O:55B_2O_3:15SiO_2$	$9.4*10^{-3}$	0.72
A4	$30Li_2O:50B_2O_3:20SiO_2$	$6.294*10^{-4}$	0.81

Conclusion: The Li_2O-B_2O_3-SiO_2 glasses have

been studied from mixed former approach using particularly the combination of B_2O_3-SiO_2.Thus, development of lithium glasses possessing high T_g and high conductivity is expected to open a new gate for the researchers to engineer Li_2O - B_2O_3 - SiO_2 glass ceramic for all solid state electrochemical sensor applications. Also the Li_2O:B_2O_3:V_2O_5 glass system exhibits mixed conductivity. The electronic conductivity is due to semi-conducting properties associated with transition metal oxide. Such intercalating solid state reference electrode and electrolyte materials may provide a new route for the development of solid state electrochemical CO_X/SO_x gas sensor.

Scope of work:

1. These glasses have technological applications in the field of electrochemical gas sensors.
2. Lithium is lightest and most electropositive metal and therefore it offers good prospects in high energy density batteries and chemical applications.
3. This work may be useful in energy conversion devices, capacitors, timers and transducers
4. By using different intermediate former in these compositions, electrical properties may change and it could be helpful to prepare gas sensor and other application such as power sources employed in cardiac pacemaker and electronic appliances. Weak electronic conductivity and good stability of glasses are helpful properties for lithium battery application.

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