

Electric properties of phosphate glasses

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Results of d.c. conductivity studies of glasses and glass-ceramics from $\text{Li}_2\text{O}-\text{P}_2\text{O}_5-\text{SiO}_2-\text{TiO}_2-\text{Al}_2\text{O}_3$ system are presented. The main crystalline phase in devitrificates is lithium titanium phosphate ($\text{LiTi}_2(\text{PO}_4)_3$), but the phase composition strongly depends on chemical composition of the glass. Activation energy of conduction process is very low being characteristic of superionic conductors and equals ~ 0.25 eV. The d.c. conductivity at room temperature is about 1×10^{-6} [Scm^{-1}]. The highest conductivity has been observed for glasses containing 2.5 wt % Al_2O_3 .

1. Introduction

There is a growing demand for solid state materials with high ionic conductivity and good chemical stability. The best material should exhibit high ionic conductivity but low electronic conductivity, good mechanical properties and thermal stability. Many kinds of oxide and non-oxide ceramics as well as glasses and glass-ceramic materials with different chemical compositions were studied in the last two decades [1]–[4]. Much attention has been given to lithium titanium phosphate because of high conductivity reported for this phase [5]–[7]. Conductivity of $\text{LiTi}_2(\text{PO}_4)_3$ can be enhanced by partial substitution of Ti by M^3 [8]. The structure of $\text{LiTi}_2(\text{PO}_4)_3$ is built with TiO_6 octahedra and PO_4 tetrahedra connected by corners and forming three-dimensional network. Titanium is present as Ti^{3+} and Ti^{4+} [9], [10]. Spatial orientation of these structural units leads to the structure with tunnels suitable in size for lithium migration, *i.e.*, fast diffusion paths. The tunnels have cavities where the lithium ion can stay and bottlenecks throughout which lithium migrates. To optimise conductivity, the bottleneck must be just the right size, not too small to allow lithium migration, and not too large. Dimension of the bottleneck can be changed by substituting titanium with three valence ions. One of the most serious difficulties connected with practical application of the lithium-titanium phosphate phase is its poor sinterability and low mechanical strength. An alternative way utilising good ionic properties of $\text{LiTi}_2(\text{PO}_4)_3$ is to produce glass-ceramic material with lithium-titanium phosphate as a major phase. The aim of

this work was to study the influence of lithium and aluminium ion on conductivity of selected glasses and glass-ceramics. The chemical compositions of glasses were chosen to obtain $\text{LiTi}_2(\text{PO}_4)_3$ phase as the predominant phase after crystallisation.

2. Experimental procedure

Glasses were prepared using a conventional melting method. Baths were prepared with pure reagents: Li_2CO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, SiO_2 , Al_2O_3 and TiO_2 . The synthesis was carried out in a covered alumina crucible in air. In all the cases the melting temperature was 1473 K and melting time 30 min. The melting conditions are very important in the case of phosphate glasses as different melting temperature may result in different structures of the final glass. The melt was then poured out on a stainless-steel plate and samples of 3 mm in thickness were formed. Then glasses were annealed at the temperature 20 °C above T_g during 2 hours. The annealing temperature was established on the base of DTA measurements. The thermal treatment was conducted at crystallisation temperature T_c during 5 hours. Cold samples were kept in an exsiccator to avoid water vapour attack. Chemical and phase composition of all the samples was examined by wet chemical analysis and the X-ray diffraction method (diffractometer SEIFERT XRD7 with Cu K_α radiation). Two series of glasses with different amount of Al_2O_3 and Li_2O were selected to establish influence of these oxides on the electric properties of glasses. Their chemical composition is shown in Tab. 1. Samples for electric measurements were prepared in the form of square 2×2 cm and about 1 mm thick by grinding and polishing glass plates. Electrodes were prepared by painting with colloidal graphite

Table 1. Chemical composition of glasses under study.

Code	Chemical composition [wt%]				
	SiO_2	Al_2O_3	P_2O_5	Li_2O	TiO_2
A0	9.4	—	62.7	12.9	15
A1	9.4	1	62.7	11.9	15
A2	9.4	2	62.7	10.9	15
A4	9.4	4	62.7	8.9	15
L1	9.5	0.5	63.5	13	13.5
L2	9.5	0.5	64.5	12	13.5
L3	9.5	0.5	67	9.5	13.5

Ted Pella Inc. The d.c. conductivity was measured as the sample was heated at 5 Kmin^{-1} . Samples were polarised by 1.5 V d.c. bias and resulting current was measured. The d.c. conductivity was calculated from equation: $\sigma = Id/Va$, where I – current, V – applied d.c. voltage, d – thickness of the sample, a – electrode area.

3. Results and discussion

Thermal properties of the glasses under study and phase composition of the glass-ceramics obtained by crystallisation of glasses are summarized in Tab. 2. Phosphate glasses usually exhibit low transformation temperature T_g . For the compositions studied $350 < T_g < 400$ °C. Crystallisation temperature is correlated with T_g . Although two or more phases crystallise, only one peak on the DTA curve is observed. A rapid volume crystallisation is observed. The phase composition of the glass-ceramics strongly depends on the chemical composition of the glass. Lithium-titanium phosphate crystallises when its lithium content exceeds 12 wt% (A0, L1).

Table 2. Thermal properties of glasses and phase composition of glass-ceramics.

Code	T_g	T_c	Phase composition
A0	350	500	LiTi ₂ (PO ₄) ₃ , Li ₄ P ₄ O ₁₂
A1	360	520	LiTi ₂ (PO ₄) ₃ , cristobalite
A2	380	560	LiTi ₂ (PO ₄) ₃ , cristobalite, eucryptite
A4	390	580	LiTi ₂ (PO ₄) ₃ , AlPO ₄ , TiP ₂ O ₇
L1	350	500	LiTi ₂ (PO ₄) ₃ , Li ₄ P ₄ O ₁₂
L2	360	530	LiTi ₂ (PO ₄) ₃ , cristobalite
L3	390	580	LiTi ₂ (PO ₄) ₃ , TiP ₂ O ₇ , tridymite

When lithium content is less than 10 wt%, the A4, L3 titanium phosphate phase is observed. Glass with 4 wt% of Al₂O₃ results in AlPO₄ crystallisation (A4). The d.c. conductivity versus temperature for most of the glasses obeys the Arrhenius behaviour

$$\sigma_{dc} \cdot T = \sigma_0 \exp(-E_a/kT)$$

where: σ_{dc} – d.c. conductivity, T – temperature, σ_0 – parameter, E_a – activation energy of ion transport, k – Boltzmann constant (8.617×10^{-5} eV K⁻¹). The glasses being studied also fit this equation very well. Figure 1 shows results for the A series of glasses. The lowest conductivity has been observed for glasses with no Al₂O₃ and is growing with the Al₂O₃ content up to ~2.5 wt%. Further increase in the Al₂O₃ content leads to a decrease in conductivity. The relation between conductivity and the Al₂O₃ content is shown in Fig. 2. Maximum conductivity has been observed at ~2.5 wt%. Similar effect has been reported in literature for Li_{1-x}M_xTi_{2-x}(PO₄)₃ ceramics [11]. For glass-ceramics Al₂O₃ substitution also improves conductivity but the effect is much weaker. Figure 3 shows a comparison of glass and glass-ceramic conductivity as a function of temperature for selected compositions. In all the cases the observed conductivity is lower for glass-ceramics than for glass. This is connected with higher mobility of lithium ions in glass. Lithium in glass-ceramics is much more strongly chemically bounded. The microstructure of glass-ceramics is polycrystalline with variously oriented crystals and some porosity is usually observed. This is the reason for the conductivity of devitrificates being lower compared to that of

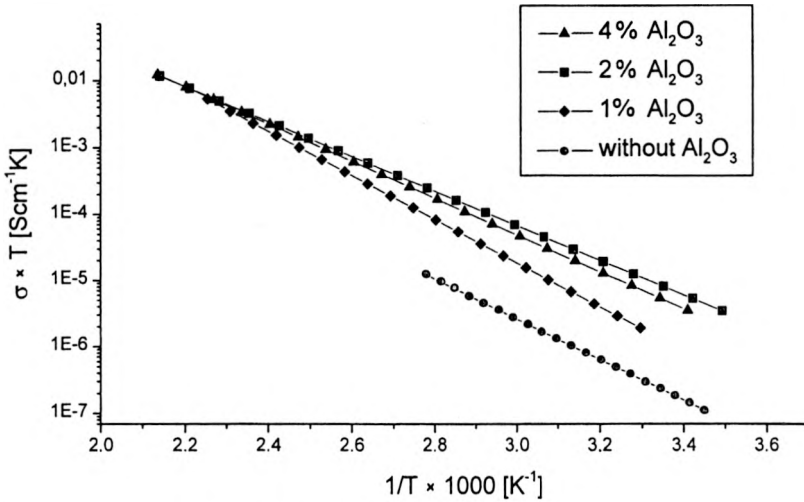


Fig. 1. Conductivity versus $1/T$ for glasses of A series.

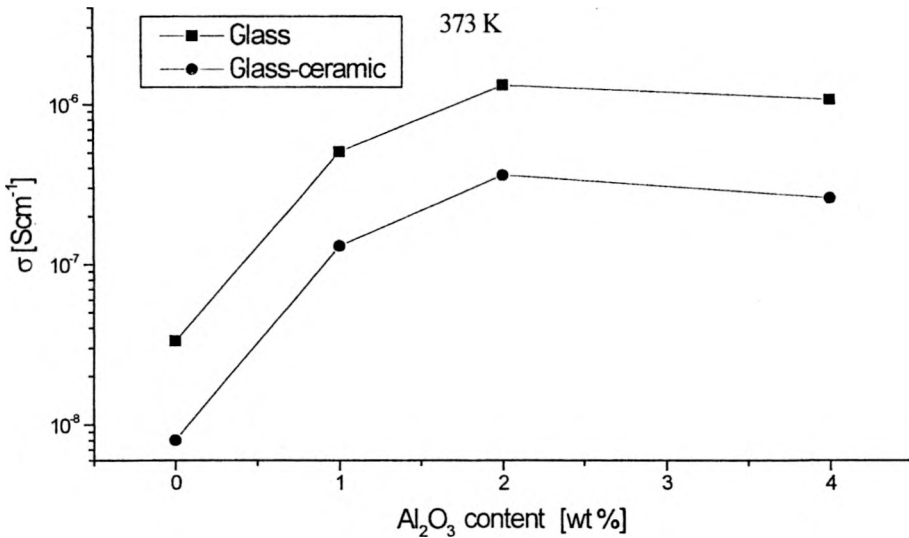


Fig. 2. Conductivity at 373 K as a function of Al_2O_3 content.

glasses. The influence of lithium content on conductivity of glasses and glass-ceramics is shown in Figs. 4 and 5. A logarithmic relationship is observed between conductivity and the Li_2O content (see Fig. 5). Increased lithium concentration gives higher concentration of conducting species and higher conductivity. However, higher lithium concentration also results in poor chemical durability of glasses and glass-ceramics — the $\text{Li}_4\text{P}_4\text{O}_{12}$ phase is formed. Activation energy of the analysed glasses and glass-ceramics is very low (see Tab. 3), being usually

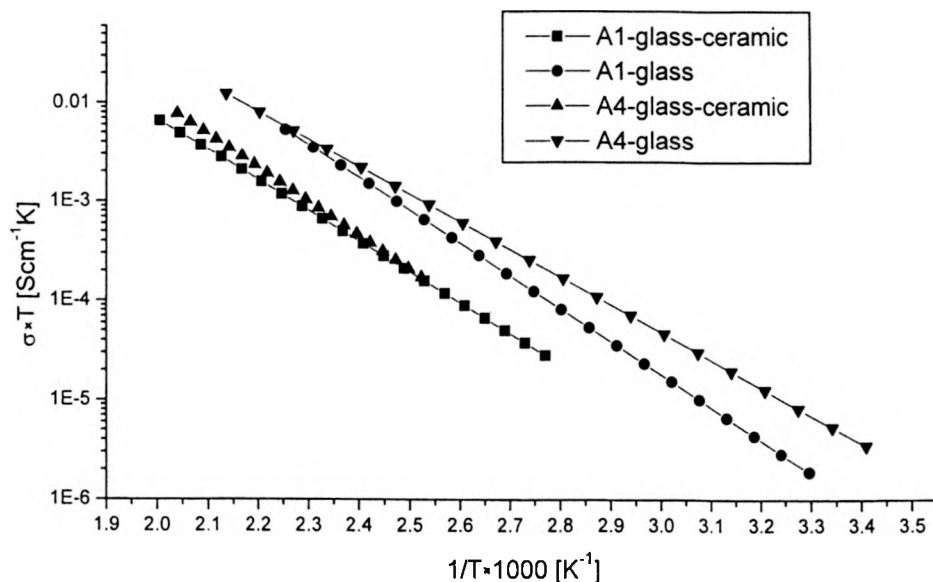


Fig. 3. Comparison of conductivity of glasses and glass-ceramics for selected compositions.

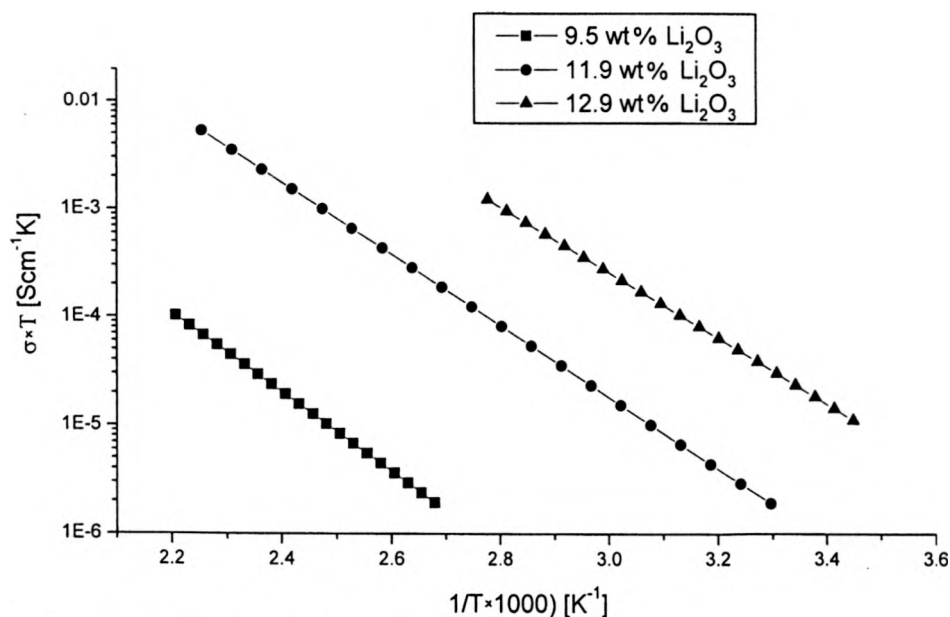


Fig. 4. The d.c. conductivity of glasses with different Li_2O content.

observed for superionic conductors. Conductivity at 373 K for all the samples is also presented in Tab. 3. Conductivity of our glasses as well as glass-ceramics is two orders of magnitude lower than that reported for a similar system [12].

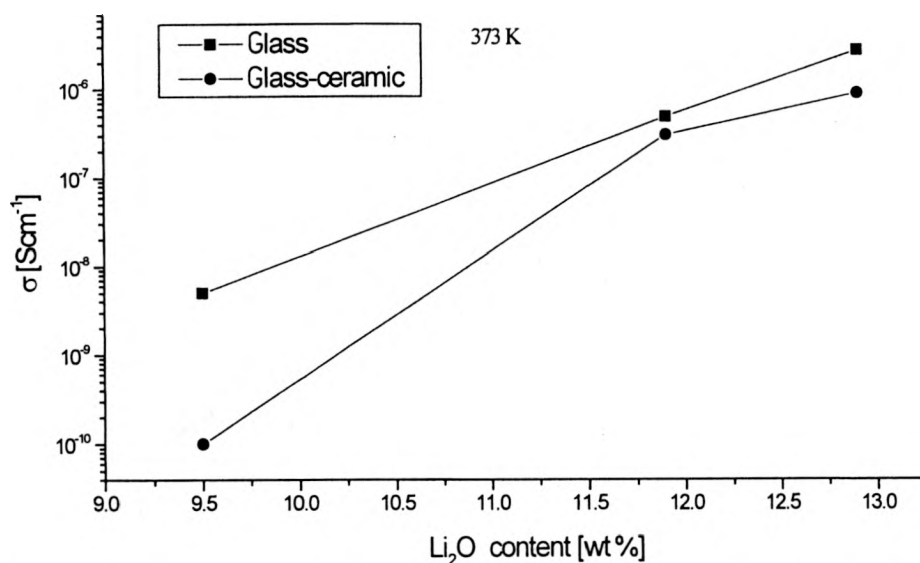


Fig. 5. Conductivity at 373 K for glasses and glass-ceramics for different Li₂O content.

Table 3. Activation energy and conductivity at 373 K for glasses and glass-ceramics.

Code	Glass		Glass-ceramic	
	E_a [eV]	$\sigma_{(373\text{ K})}$ [S cm ⁻¹]	E_a [eV]	$\sigma_{(373\text{ K})}$ [S cm ⁻¹]
A0	0.26	3.3E-8	0.18	0.8E-8
A1	0.28	5.05E-7	0.27	1.3E-7
A2	0.22	1.3E-6	0.33	0.16E-6
A4	0.24	1.07E-6	0.29	0.26E-6
L1	0.26	2.68E-6	0.28	8.8E-7
L2	0.30	4.8E-7	0.30	8E-7
L3	0.31	5E-9	0.33	1E-10

4. Conclusions

Phase composition of phosphate glasses is very sensitive to chemical composition. Partial substitution of Ti⁴⁺ for Al³⁺ up to 2.5 wt% leads to an increase in conductivity. Activation energy observed for glasses and glass-ceramics is similar and is very low (0.18–0.33 eV), which is characteristic of superionic conductors. The studied glasses can be used as conductors at 373 K and above up to 773 K.

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