ARTICLE IN PRESS

Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Electrical conductivity and viscosity of phosphate glasses and melts

Doris Ehrt*, Sylvia Flügel

Otto-Schott-Institut, Friedrich-Schiller-Universität Jena, Fraunhoferstr. 6, D-07743 Jena, Germany

ARTICLE INFO

Keywords:
Electrical conductivity
Impedance spectroscopy
Viscosity
Phosphates
Glasses
Melts

ABSTRACT

Phosphate glasses are of great interest for basic research and for special applications in various fields as technical and optical glasses. Metaphosphate compositions with PO_4-chain structure are mostly used. The cations have a significant effect on the properties of the glasses and melts. This was studied in more details. High purity metaphosphate glasses, $M^n(PO_3)_n$ with M = Na^+, K^+, Zn^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+} and Fe^{3+}, were prepared and the optical and thermal properties were measured with different methods. The electrical conductivity of glasses and melts is the property of great practical importance. It was determined by impedance spectroscopy in a wide temperature range from 300 to 1250 °C in frequency range of 0.1 Hz to 6 MHz. The electrical conductivity of alkaline earth phosphate glasses and melts increases with increasing ion radius of the cation. $NaPO_3$ and KPO_3 glasses and melts have much higher conductivity. Viscosity measurements were carried out from transformation temperature, T_g, to the melt. The measured data were fitted and the activation energies of the conductivity and viscosity were calculated. Simple exponential behavior was found at temperatures below T_g, but above T_g only in very narrow temperature range. The relation between conductivity and viscosity was considered.

1. Introduction

Electrical conductivity of glasses and melts is a property of great practical importance. It determines the use of glass in electrical engineering applications at ambient temperature and high-temperature conductivity is important for special methods of electrical melting of glass. Phosphate glasses do not have the importance of silicate or borosilicate glasses, because of their lower chemical stability. Their application is limited to special requirements with high importance, e.g. for high performance optics, active laser and amplifier materials.

The formation of phosphate glasses has been well known for a very long time and many scientific papers have been published by many authors. Phosphate glasses are of great interest for basic research and for special applications in various fields, e.g. as biomaterials, fertilizer, technical and optical glasses [1–6]. Metaphosphate compositions with PO_4-chain structure are mostly used. The cations have a significant effect on the properties of the glasses and melts. Glasses for high performance optics, e.g. laser glasses, need extremely high purity and optical homogeneity [2,3]. Phosphate glass melts are very corrosive against various crucible materials leading to impurities. With a new 'inductive skull melting technique' (ISMT) high temperature induction melting is suitable without a crucible. A solid layer of the initial material around the melt is formed by strong cooling of a coil. This protects the melt against corrosion and impurities from the container material [7].The efficiency of this technique is very high. But special electrical conductivity, crystallization and viscosity behavior of the glasses and melts are necessary. The aim of this work was the investigation of this behavior with simple metaphosphate glasses and melts.

2. Experimental

High purity simple metaphosphate glasses, $M^n(PO_3)_n$ with M = Na^+, K^+, Zn^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+} and Fe^{3+}, were prepared and the optical and thermal properties were measured with different methods. Metaphosphate glasses were prepared by melting $M^n(PO_3)_n$ or P_2O_5 with MCO_3 of high purity in amorphous SiO_2 crucibles as 200–300 g batches in a resistant heated furnace at different temperatures, 800 to 1600 °C (Table 1). Glasses were obtained by pouring the melts into a preheated graphite mould. After annealing from T_g + 50 K to room temperature at 3 K/min, the glasses were cut, ground and polished to produce samples for different measurements. The refractive indices in the visible range were measured with a refractometer with an error $\Delta n \pm 2 \times 10^{-5}$. The density was determined using Archimedes' principle with an error ± 0.002. DTA (heating rate 10 K/min) and dilatometer measurements (heating rate 5 K/min) were carried out to obtain values for the thermal properties, T_g and thermal expansion coefficient (TEC). The viscosity η as a function of

* Corresponding author at: Rudolf-Breitscheid-Str. 51, D-07747 Jena, Germany.
E-mail address: doris.ehrt@uni-jena.de (D. Ehrt).

https://doi.org/10.1016/j.jnoncrysol.2018.01.047
Received 1 December 2017; Received in revised form 18 January 2018; Accepted 31 January 2018

Please cite this article as: Ehrt, D., Journal of Non-Crystalline Solids (2018), https://doi.org/10.1016/j.jnoncrysol.2018.01.047

Table 1
Measured properties of glasses.

Glass	Melting T_m (°C)	T_g (°C) (5 K/min) ± 3 °C	TEC (ppm/K) (5 K/min) ± 0.1	Density (g/cm^3) ± 0.01	Refractive index n_e (546.07 nm) ± 0.0001	ABBE[a] umber ν_e ± 1	[OH] (cm^{-1}) ± 0.1/ ± 3 (ppmw)	Ionic radius (Å)/CN [26]	T_{k100} value (°C) ± 5	Viscosity VFT – fit parameter *A*	*B*	T_o
$NaPO_3$	800	265	24.0	2.51	1.4858	65	~15/450	1.02/6	150	−1.30	864	220
KPO_3	900	~265	nm	2.41	Crystals	nm	nm	1.51/8	200	nm		
$Zn(PO_3)_2$	1150	400	7.3	2.88	1.5260	62	7.5/225	0.60/4	nm	−2.77	4373	487
$Mg(PO_3)_2$	1300	520	7.5	2.43	1.4974	71	5.2/156	0.57/4	425	−1.92	2698	256
$Ca(PO_3)_2$	1300	500	11.0	2.65	1.5469	66	5.5/165	1.00/6	365	−1.26	2191	391
$Sr(PO_3)_2$	1300	485	13.0	3.15	1.5591	66	5.7/171	1.26/8	340	−2.78	2140	401
$Ba(PO_3)_2$	1200	460	14.2	3.66	1.5899	64	5.0/150	1.42/8	340	−0.92	1250	418
NaSrP	1300	400	15.7	3.08	1.5468	66	5.5/165	1.02/1.26	340	−1.83	1788	313
$Fe(PO_3)_3$	1350	590	6.7	2.80	nm	nm	< 2/ < 60	0.55/6	nm	−3.37	4552	307
$Al(PO_3)_3$	1600	765	6.0	2.60	1.5310	70	1.4/42	0.54/6	nm	−1.44	1275	390

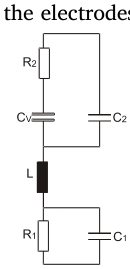
nm = not measurable.

[a] ABBE number = dispersion coefficient $\nu_e = (n_e - 1)/(n_{F'} - n_{C'})$ with F′ = 479.99 nm (blue), C′ = 643.85 nm (red), e = 546.07 nm (green).

temperature *T* was determined with two different methods. The low viscosity range of the melts was measured in a Pt crucible with rotating Pt cylinder method in the η range, $10^{1.5}$–10^5 dPa s, and the high viscosity range with the beam bending method in the range 10^9–10^{13} dPa s with solid glass rods. The electrical conductivity σ of the glasses and melts was determined as electrical resistance ρ by impedance measurements [8–14] in the temperature range 300–1250 °C. Solid glass samples were measured to a temperature where the viscosity was about 10^4 dPa s. Cylindrical samples with a diameter 10 mm and thickness 5 mm contacted with Pt plates were used (Fig. 1a). The contact between glass sample and Pt plates was obtained by heating to temperature T_g + 50 K in a first step. Than the equipment was cooling down and the measurement was started in heating and cooling modus. Low viscosity melts were measured with a high accuracy coaxial Pt/Rh10 crucible/cylinder technique (Fig. 1b) starting at 1300 °C and cooling down [10].

The electrical resistance ρ was measured depending on dipping depth of the cylinder in the melt and variation of the temperature [9]. Impedance spectra were recorded with a Zahner IM5d electrochemical workstation, with an ac voltage of 20 or 50 mV, and variable frequencies in the range of 0.1 Hz to 6 MHz, normally in steps of 20–50 K. Most liquid samples were also measured with suitable fixed frequency from high to lower temperature. The measurements of the solid samples were carried out during heating and cooling with a rate of 1 K/min. The melts were measured starting from 1250 °C cooling down to ~700 °C or lower. The *dc* (*direct current*) potentials of the measured impedance spectra were always 0 mV (Bode plots Fig. 2).

Than the impedance is mainly caused by the ionic resistivity *R* of the sample. The following equivalent circuit was used for fitting, with R_1 and C_1 as bulk properties of the sample, R_2, C_2 and C_V as phenomena of the electrodes, and *L* for wires:



The following equations were used:

$$\hat{Z} = \frac{\hat{U}}{\hat{I}} = \frac{U_0}{I_0} \cdot e^{-i\phi} = \left|\hat{Z}\right| \cdot e^{-i\phi} \quad (1)$$

$$\sigma = \frac{1}{R} \cdot G \quad (2)$$

Z: impedance, *U*: voltage, *I*: current, *Φ*: phase angle, *σ*: specific electrical conductivity, *R*: electrical resistance, *G*: geometric factor.

The error of the resistance values was < 5%. More details are given in Ref. [10].

3. Results

This paper concentrates on investigations of the electrical conductivity of alkaline metaphosphate glasses and melts, $M(PO_3)_2$ with M = Mg, Ca, Sr, Ba, in comparison with $NaPO_3$ and KPO_3 and the influence of Na^+ in $Sr(PO_3)_2$ (NaSrP), and the effect of different cations on the viscosity, as well as the relation between electrical conductivity and viscosity.

The main results on characteristic properties of simple metaphosphate glasses that we have investigated from time to time during a long period, are given in Table 1 [2,3]. The cations have a very large effect on the properties, due to different bonding and structure. Various melting temperatures, between 800 °C and 1600 °C were necessary to prepare glasses. The values for the glass transition temperature, T_g, vary between 265 °C for $NaPO_3$ and 765 °C for $Al(PO_3)_3$, and for the thermal expansion coefficients, TEC, between 24 ppm/K for $NaPO_3$ and 6 ppm/K for $Al(PO_3)_3$. All metaphosphates, excepting KPO_3, have shown good glass-forming abilities. It was possible to obtain large samples without crystals by normal melting and cooling technique. KPO_3 melts were clear without visible crystals but showed strong crystallization tendency during cooling. Only glass samples with few small crystals were