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Bulk and surface crystallisation of lead tetragermanate glass.
A DTA study

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Abstract

The surface and bulk crystallisation of lead tetragermanate glass has been studied by differential thermal analysis. The influence of the specific surface area of the sample and the nucleation heat-treatment on the crystallisation is pointed out. Infrared spectroscopy measurements suggest that the addition of PbO to germanium oxide leads to a change in the coordination number of germanium atoms from 4 to 6. The phases which crystallise during the DTA runs were identified by X-ray diffraction as hexagonal and monoclinic $PbGeO_4O_9$. The activation energy of crystal growth was also evaluated from DTA curves. A value of about $300\,kJ\,mol^{-1}$ was calculated from surface and bulk crystallisation.

Keywords: Crystallisation; DTA; Glass; IRS; Lead tetragermanate; XRD

1. Introduction

The properties and the structures of lead germanate glasses have been widely studied [1–3], while poor attention has been devoted to the study of their devitrification mechanisms. An exception is the study by Mukherjee [4] who investigated the kinetics of crystallisation of gel, gel-derived glass and conventional oxide glass with $10PbO \cdot 90GeO_2$ molar composition. Topping et al. [1] found, by light scattering and electron microscopy, that lead germanate glasses are phase-separated in the range from 10 to 27 mol% PbO. In the glass compositions ranging from 30 to 25 mol% PbO, a large minimum was observed on the diagram of the deviation from ideality of molar

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volumes versus composition. This behaviour, as for alkali germanate glasses, has been attributed to the change in the coordination number of Ge atoms from 4 to 6 as PbO is added to the GeO_2. The range of phase separation was extended by Shelby [2] up to about 3 mol% PbO, as its DSC measurements showed two glass transition temperatures; he did not observe any crystallisation for glasses containing less than 45 mol% PbO. These results do not agree with the data of Nassau and Chadwick [3] who reported only one value of glass transition temperature and the values of crystallisation temperature for the glasses in the range from 10 to 50 mol% PbO. Moreover the glasses prepared by Mukherjee [4] do not show any inhomogeneity in the glassy matrix in either the gel glass or the conventional glass.

The aim of the present study was to evaluate the crystallisation mechanism and the kinetic parameters for crystal growth of a lead germanate oxide glass containing 20 mol% PbO ($PbO \cdot 4GeO_2$).

2. Experimental

The $PbO \cdot 4GeO_2$ glass was prepared using reagent-grade lead and germanium oxides in a batch sized to yield 10 g of glass. The glass was melted in a Pt crucible in an electric oven at 1200°C for 4 h. The melt was cast at high cooling rate between two brass plates. Although this resulted in fracture of the glass, pieces of sufficient size for the experimental measurements were obtained by this technique.

To check the lead content in the glass, a finely powdered glass sample (155 mg) was dissolved in concentrated boiling HNO_3 solution, diluted with bidistilled water and then analysed for lead content by atomic absorption analysis (AAS) using a Varian SpectrA-A 10 plus spectrophotometer. The analysed PbO content (33.9 wt%) and the theoretical value (34.8 wt%) are in fairly good agreement.

The non-isothermal crystallisation of the investigated glass was studied by differential thermal analysis (DTA). DTA curves were recorded in air at different heating rates (2, 5, 10, 15, 20 K min^{-1}) on powders (−350−+400 mesh), as-quenched bulk, and nucleated bulk specimens (about 50 mg) from room temperature to 800°C. Powdered Al_2O_3 was added to improve heat transfer between bulk samples and sample holder. A Netzsch thermoanalyser High-Temperature DSC 404 was used with Al_2O_3 as reference material.

To investigate the amorphous nature of the as-quenched glass and of the nucleated glass, and to identify the crystalline phases grown during the DTA runs, the thermally processed samples were finely ground and analysed in a computer-assisted X-ray (Cu Kα) powder diffractometer (XRD) using a Philips diffractometer model PW1710, with a scan speed of 1° min^{-1}. The X-ray diffraction patterns were matched to JCPDS data and corresponding phases were identified.

3. Results and discussion

The DTA curves, recorded at 20 K min^{-1} of: (a) a powdered sample of the as-quenched glass (QP), (b) a bulk sample of the as-quenched glass (QB), and (c) a bulk sample of the glass nucleated for 16 h at 490°C (NB) are shown in Fig. 1. All curves exhibit a slope change at about 470°C that can be attributed to the glass transition, followed by an exothermic peak of crystallisation.

The phases which crystallise during the DTA runs were identified by X-ray diffraction. The XRD patterns of QP, QB and NB samples show the same reflections. All these reflections were assigned to the two polymorphic phases (monoclinic and hexagonal) of lead tetragermanate (see Table 1). The intensity of the reflections indicate that more monoclinic crystals are grown in nucleated samples than in as-quenched samples. The structures of lead tetragermanate contain Ge_3O_9 rings consisting of three GeO_4 tetrahedra; these rings are connected by GeO_6 octahedra forming a three-dimensional network [5]. The structure of both polymorphs of $PbO \cdot 4GeO_2$ can be characterised by the formula $PbGe(Ge_3O_9)$.

The presence of Ge atoms in six-fold coordination (GeO_6 groups) in the as-quenched glass is confirmed by IR measurements. The highest frequency band at about 880 cm^{-1}, due to Ge–O–Ge bond stretching in GeO_2 glass, is shifted in the investigated glass to

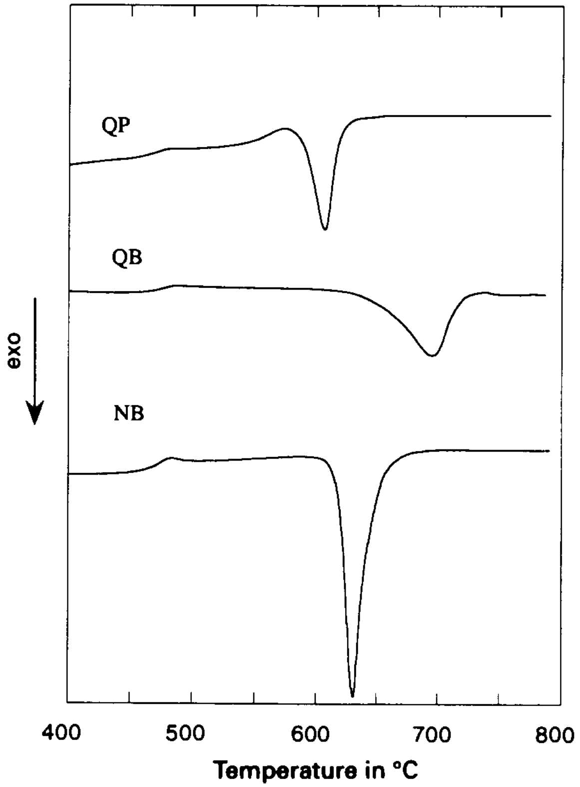

Fig. 1. DTA curves recorded in air at 20 K min^{-1} of: as-quenched powders (QP), as-quenched bulk (QB), and nucleated bulk (NB) samples.

Table 1
X-ray diffraction data

QB heated up to the first DTA exo peak d spacing/Å	NB heated up to the first DTA exo peak d spacing/Å	$PbGe_4O_9$ hexagonal JCPDS N. 13-153 d spacing/Å	$PbGe_4O_9$ monoclinic JCPDS N.32-516 d spacing/Å
$5.734_{22.7}$	$5.756_{38.5}$		$5,745_{40}$
$4.199_{22.7}$	$4.207_{62.0}$		$4,203_{70}$
3.647_{100}	3.658_{100}	3.65_{100}	
$3.426_{9.3}$		3.42_{6}	
$3.396_{21.9}$	$3.399_{47.3}$		3.394_{55}
$3.291_{26.3}$	$3.296_{24.4}$	3.29_{25}	
	$3.314_{30.8}$		3.311_{35}
$2.932_{46.6}$	$2.934_{77.4}$	2.932_{20}	2.9263_{50}
$2.914_{58.5}$	$2.912_{99.7}$		2.9164_{100}
$2.876_{45.3}$	$2.880_{70.4}$		2.8768_{50}
$2.851_{78.3}$	$2.857_{71.2}$	2.851_{60}	2.8634_{25}
$2.710_{77.5}$	$2.710_{69.9}$	2.704_{80}	
$2.374_{23.2}$	$2.379_{29.3}$	2.373_{10}	2.3745_{40}
	$2.262_{14.6}$		2.2596_{15}
$2.193_{17.6}$	$2.193_{20.3}$	2.190_{12}	
$2.172_{9.2}$	$2.173_{14.5}$		2.1776_{5}
$2.158_{15.0}$	$2.159_{8.5}$	2.155_{10}	
$2.048_{12.1}$	$2.052_{17.1}$		2.0486_{20}
	$1.979_{17.9}$		$1,9750_{12}$
$1.965_{26.8}$	$1.967_{17.4}$	1.9628_{25}	
$1.927_{9.3}$		1.9255_{10}	
$1.826_{27.1}$	$1.830_{27.3}$	1.8239_{20}	1.8274_{10}
$1.776_{14.0}$	$1.776_{23.2}$		1.7748_{25}
$1.767_{23.4}$	$1.769_{17.9}$	1.7647_{25}	
$1.648_{19.6}$		1.6464_{14}	1.6559_{10}

a lower frequency, as shown in Fig. 2. This shift can be related, as in alkali germanate glasses [6], to the change in the coordination number of Ge from 4 to 6. The minus-two charge of the GeO_6 octahedron is balanced by the localisation of a Pb^{2+} ion. In both the crystalline phases of lead tetragermanate, all oxygen atoms are of the bridging type. The lack of non-bridging oxygen atoms makes the glass devitrification rather hard. The rearrangement of the network, involved in the crystallisation processes, requires a rather low viscosity of the glass, as confirmed by the high lag between T_g and T_p, and, from the appearance of the powdered samples after the DTA runs, as coherent blocks.

The differences among the DTA peak temperatures of the three (QP, QB, NB) specimens can be attributed to three different nucleation mechanisms. Glass devitrification is the result of two individual processes: nucleation and crystal growth. The total number of nuclei per unit volume N is the sum of the surface nuclei, N_s (proportional to the specific surface area of the sample), the bulk nuclei formed during the DTA run N_h (proportional to the reciprocal of the heating rate β) and the bulk nuclei formed during the heat treatment of nucleation N_n (proportional to the duration of the heat treatment) [7]

$$N = N_s + N_h + N_n$$

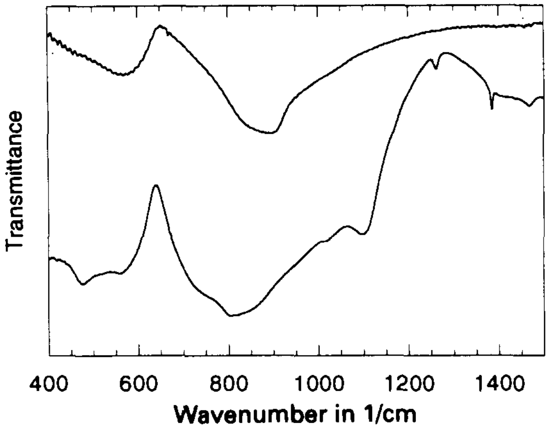

Fig. 2. Infra-red spectra of vitreous GeO_2 (upper curve) and $PbO{\cdot}4GeO_2$ glass (lower curve).

As a glass usually crystallises at temperatures well above the temperatures of high nucleation rates, in all cases, the crystal grow from an almost fixed number of nuclei.

When the crystallisation proceeds in a glass, the heat of crystallisation is evolved and an exothermic peak appears on the DTA curve, as shown in Fig. 1. If the DTA runs are carried out at the same heating rate, the higher the number of nuclei N the lower the temperature of the DTA crystallisation peak according to the equation [8]

$$\ln N = a\left(\frac{1}{T_p}\right) + b \tag{1}$$

where a and b are constants.

In finely powdered samples of the as-quenched ($N_n = 0$) glass, surface nucleation is dominant due to the high specific surface of the samples and the short time (DTA run) of bulk nucleation, i.e. $N_s \gg N_h$. In bulk samples of the as-quenched glass the small number of bulk nuclei, formed during the DTA run, is comparable with that of surface nuclei due to the very low specific surface area of the samples. The crystals grow from the surface and in the bulk of the samples from a small number of nuclei. The DTA peak is therefore shifted, according to Eq. (1), towards a higher temperature than that of the powdered sample (Fig. 1). The high number of bulk nuclei formed during the long (16 h) heat treatment of nucleation at the temperature of 490°C (very close to T_g) makes bulk nucleation dominant in the bulk sample and the number of nuclei is much higher than that in the as-quenched bulk samples. The DTA crystallisation peak is therefore shifted towards a lower temperature than that of the as-quenched glass (Fig. 1).

The activation energy E of crystal growth has been evaluated from a set of DTA curves recorded at different heating rates by the equation [9]

$$\ln \beta = \left(-\frac{E}{RT_p}\right) + \text{const} \tag{2}$$

Table 2
Activation energy of crystal growth.

Glass samples	E/kJ mol^{-1}
As-quenched powders (QP)	308
As-quenched bulk (QB)	164
Nucleated bulk (NB)	302

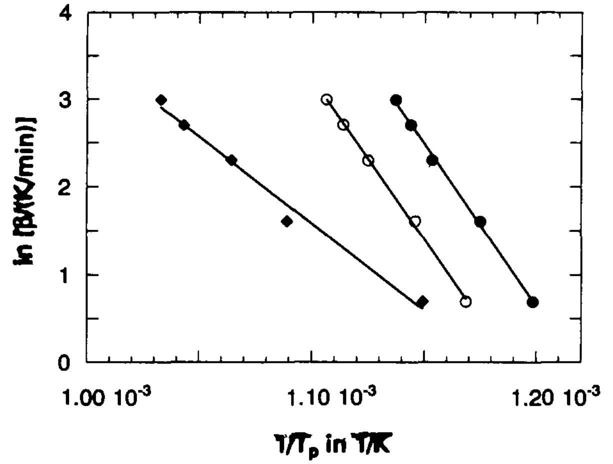

Fig. 3. Plots of ln β vs. $1/T_p$: (●) as-quenched powders, (◆) as-quenched bulk, (○) nucleated bulk samples.

This equation is based on two assumptions: (a) at the peak temperature T_p, the degree of crystallisation reaches the same specific value and it is not dependent on the heating rate β; and (b) the crystals grow at each heating rate from the same number of nuclei [7].

The values of E, reported in Table 2, were calculated from the slope of the straight lines obtained by plotting ln β against $1/T_p$ (Fig. 3). The values of the activation energy of crystal growth in QP and NB samples are nearly the same; the lower value of E in QB sample is not real. In the as-quenched bulk sample, the number of nuclei formed during the DTA run cannot, as in the other two cases, be neglected. The crystals grow at each heating rate from a different number of nuclei so that the peak temperature is shifted not only by the change in the heating rate but also by the change in the number of nuclei. In this case, assumption (b) of Eq. (2) fails.

4. Conclusions

From the experimental results the following conclusions can be drawn.

(a) During a DTA run, the lead tetragermanate glass devitrifies into two polymorphic crystalline phases whose structural formula is $PbGe(Ge_3O_9)$.

(b) The nature of the crystallising phases is not affected by the heat treatment of nucleation, even if in a nucleated bulk sample there are more in the monoclinic phase than in as-quenched bulk sample.

(c) Bulk and surface crystallisation have the same values of activation energy for the crystal growth.

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