



Liquid–liquid transitions, crystallization and long range fluctuations in supercooled yttrium oxide–aluminium oxide melts

G.N. Greaves^{a,*}, M.C. Wilding^a, S. Fearn^a, F. Kargl^a, L. Hennet^{a,b}, W. Bras^c, O. Majérus^d, C.M. Martin^e

^a Centre for Advanced Functional Materials and Devices, Institute of Mathematics and Physics, Aberystwyth University, Aberystwyth SY23 3BZ, UK

^b CNRS-CEMHTI, 1d avenue de la Recherche Scientifique, 45071 Orléans cedex 9, France

^c DUBBLE CRG/ESRF, Netherlands Organisation for Scientific Research (NWO), P.O. Box 220, F38043 Grenoble cedex, France

^d Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre et Marie Curie, 75231 Paris, France

^e Synchrotron Radiation Source, STFC Daresbury Laboratory, Warrington, Cheshire WA4 4AD, UK

ARTICLE INFO

Article history:

Available online 10 April 2009

PACS:

61.10.Nz
61.43.Fs
61.72.Qq
64.60.70.Ja.Pf

Keywords:

Diffraction and scattering measurements
Synchrotron radiation
X-ray diffraction
Glass formation
Glass transition
Phases and equilibria
Structure
Fluctuations
X-rays
X-ray diffraction

ABSTRACT

Employing small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) combined with laser-heated aerodynamic levitation has enabled different transitions in supercooled yttrium oxide–aluminium oxide to be distinguished. These include liquid–liquid phase transitions as well as high temperature crystallization for different compositions. Prerequisites for avoiding crystallization in order to reveal polyamorphic phase separation in the supercooled state are established. We also show how the rise in SAXS intensity at low wavevectors can be used to identify correlation distances in long range fluctuations in high temperature melts. These distances appear to scale with melt viscosity and to extend temporarily during liquid–liquid transitions.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Where the traditional view of glass formation predicts an *infinite* variety of structures each dependent on the particular thermal history taken through the supercooled state, the discovery of phases of specific density and entropy but identical composition – polyamorphism – has brought considerable, if controversial, simplification [1,2]. For a liquid in thermodynamic equilibrium, though, abrupt changes in structure as a function of pressure and temperature are inadmissible. Below the melting temperature T_m , however, vibrational and diffusional relaxation processes in the supercooled state occur on different timescales. This promotes non-ergodicity which is accompanied by dynamic heterogeneity which affects structural order, especially on the nanoscale [3]. In the glass transition zone as the temperature falls the accompanying energy land-

scape develops into a *finite* collection of minima. If N is the number of atomic units these are far fewer than the $3N + 1$ configurations expected in thermodynamic equilibrium. Where each minimum is associated with different levels of configurational entropy, the fluctuating energy landscape is interrupted by the deep and narrow minima of crystalline phases for which the entropy is principally vibrational. Moreover, for the polyamorphic states reported so far [1–3], these often occur in low and high density pairs separated by phase boundaries akin to those between different crystalline phases in the solid state. In the supercooled state liquid–liquid phase boundaries also include the possibility of first order phase transitions and of critical points at higher temperatures above which different liquid phases become indistinguishable.

While the glass transition is governed by kinetic processes, melting is a thermodynamic phenomenon generally described by the Clausius–Clapeyron relation $\frac{dT}{dP} = \frac{\Delta V}{\Delta S}$. At ambient pressure the increase in entropy at the melting point ΔS_{config} equals H_{fusion}/T_m where H_{fusion} is the heat of fusion. As melting is usually accompa-

* Corresponding author. Tel.: +44 1970 622802; fax: +44 1970 622826.
E-mail address: gng@aber.ac.uk (G.N. Greaves).

nied by an increase in molar volume ΔV_m , the melting curve $\frac{dT_m}{dP}$ is generally positive. At the same time dense liquid phases, denser than their parent crystals at T_m are well-known in the case of water and result in negative melting curves. In other tetrahedral systems like Si [4,5] and Ge [6], SiO_2 [7] and GeO_2 [8] and also microporous zeolites [9,10], dense liquid phases have been linked with the dense glassy phases that result from high pressure amorphisation [3]. The antecedents for supercooled low density liquid (LDL) phases and high density liquid (HDL) phases are therefore melting point maxima. First order liquid–liquid transitions between HDL and LDL states at temperatures T_{LL} higher than the glass transition T_g are also expected to follow the Clausius–Clapeyron relation, driven by density and entropy [11]. Because the change in molar volume at such a transition $\Delta V_{LL} = V_{HDL} - V_{LDL}$ is negative while the entropy difference $\Delta S_{LL} = S_{HDL} - S_{LDL}$ is positive, the slope of the phase boundary $\frac{dT_{LL}}{dP}$ should be negative [1,3], mimicking the melting curve $\frac{dT_m}{dP}$ at higher temperatures, as illustrated in Fig. 1.

The two state model for liquid unmixing [11,12] has been very influential in the development of the physics and chemistry of polyamorphism. Predicting a melting point maximum overarching a critical point $T_c - P_c$ below which polyamorphic unmixing is expected, this model defines the phase boundary $T_{LL} - P_{LL}$ between HDL and LDL states in the supercooled region, as Fig. 1 illustrates. Phase coexistence is bounded by spinodal limits beyond which single phase HDL and LDL regions should occur. Liquid–liquid phase transitions will be encountered when T or P or both are traversed below the temperature and pressure, T_c and P_c , of the critical point. Another important aspect of the two state model is that the viscosities of the two liquids are likely to be quite different, with the LDL phase being stronger than the HDL phase and having a higher glass transition temperature T_g . Low density and high density amorphous phases – LDA and HDA – will be frozen in below their respective glass transition temperatures (Fig. 1).

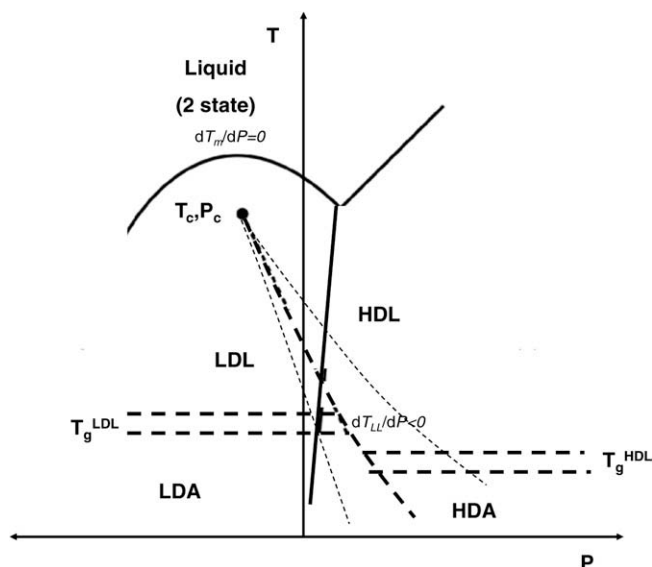


Fig. 1. Two state model [11,12] and the development of liquid–liquid and amorphous–amorphous transitions. A melting point maximum occurs if the high temperature liquid has the conformational flexibility to exist in two states characterized by different density and entropy. In the supercooled region a critical point T_c, P_c is expected below which a double minimum in the free energy comprising coexistence of a low density liquid (LDL) and a high density liquid (HDL) should occur, separated by a first order phase boundary. Below the glass transition both components become non-ergodic converting, respectively to a low density amorphous phase (LDA) and a high density amorphous phase (HDA). An LDL–HDL transition is possible above T_g^{LDL} and T_g^{HDL} and an LDA–HDA transition below these temperatures.

In practice polyamorphism at supercooled temperatures and high pressures is often masked by crystallization, which is why computer simulation has played such an important part in the search for new liquid phases, notably in water and other tetrahedral liquids [1,13–16]. However, an unexpected source of polyamorphism was discovered at high temperatures but at ambient pressures by Aasland and McMillan in studying $(\text{Y}_2\text{O}_3)_x - (\text{Al}_2\text{O}_3)_{100-x}$ or AYx melts [17]. They found that rapidly quenched glasses were optically heterogeneous, dependent on composition. Two different vitreous phases with identical composition were detected *ex situ*. With a small density difference $\Delta\rho/\rho$ of around 0.04, phase separation in the recovered glasses was consistent with a liquid–liquid HDL–LDL transition in the supercooled state [17].

In their original work Aasland and McMillan reported polyamorphism in AYx melts for compositions between AY24 and AY32. Subsequently this was extended to AY20 [18–22] and AY37.5 (YAG) [23]. Structural studies, particularly of AY20 and AY25 compositions, identified differences between HDA and LDA phases from neutron and X-ray diffraction structure factors $S(Q)$ – notably in the shape of the principal peak at around 2.2 \AA^{-1} [18–22]. Q is the scattering wavevector $4\pi\sin\theta/\lambda$, where 2θ is the scattering angle and λ the wavelength of the incident radiation. Reverse Monte Carlo (RMC) analysis [19,21,22] revealed that, rather like the case of the LDA and HDA phases of amorphous ice [24,25], the differences in AYx polyamorphs lie in inter-polyhedral arrangements, viz in Y–Y, Al–Al and Al–Y correlations. At the same time Molecular Dynamic (MD) simulations in the single liquid regime [1,26] identified random volume fluctuations comparable with the difference $\Delta\rho/\rho$ measured in phase separated glasses [17,19,22], with $S(Q)$ s in high and low density supercooled liquid zones sharing similarities with RMC modeling of HDA and LDA phases, respectively [1]. Taken together the interesting possibility emerges that, as the single phase melt enters the supercooled state and the temperature falls below T_c , these fluctuations might seed first the HDL and LDL phases and then the HDA and LDA glasses obtained by rapid quenching through the glass transitions [17–23], as shown schematically in Fig. 1.

When the quench rate from the supercooled state is reduced crystallization usually occurs with precipitation of garnet YAG (AY37.5) and perovskite YAP (AY50) phases from yttria-rich melts [27,28], with corundum Al_2O_3 featuring for alumina-rich compositions [29]. For rapid quenching the interpretation of liquid unmixing for AYx melts in the composition range $24 < x < 30$ [17] has been challenged by arguing that these phase transformations might be attributable to nanocrystalline nucleation [27–29]. Evidence comes mainly from optical microscopy and calorimetry. At the same time the Debye–Scherrer patterns are reported to be “X-ray amorphous” [29]. For this to be consistent with nanocrystalline nucleation the sizes of crystallites need to be so small that Scherrer broadening leaves diffraction peaks undetectable above the thermal diffuse scatter.

In this paper we first describe the application of contactless aerodynamic levitation furnace methods [30–32] to the study of polyamorphism and crystallization in high temperature liquids. We use combined X-ray detector techniques [33], nanostructure and atomic structure being obtained simultaneously from SAXS and WAXS, respectively [34]. As a result of these methods it has been possible to identify and fully characterize first order liquid–liquid transitions in supercooled $(\text{Y}_2\text{O}_3)_x - (\text{Al}_2\text{O}_3)_{1-x}$ melts for the first time *in situ*, substantiating the conclusions of Aasland and McMillan from their *ex situ* studies [17]. These results were presented in a recent paper [35]. In this paper further details of the novel experimental arrangement are given. Furthermore the affects of crystallization under levitated conditions are described and distinguished from polyamorphic transitions. Finally we demonstrate how the Ornstein–Zernike approximation can be used to estimate

Download English Version:

<https://daneshyari.com/en/article/1484240>

Download Persian Version:

<https://daneshyari.com/article/1484240>

[Daneshyari.com](https://daneshyari.com)