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Journal of Non-Crystalline Solids 351 (2005) 149–157
JOURNAL OF NON-CRYSTALLINE SOLIDS
www.elsevier.com/locate/jnoncrysol

Crystallization behavior and microstructure of powdered and bulk $ZnO–Al_2O_3–SiO_2$ glass-ceramics

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Received 30 June 2003
Available online 25 November 2004

Abstract

The crystallization behavior of glass with the composition: 55.6 mol% SiO_2, 22.8 mol% Al_2O_3, 17.7 mol% ZnO and 3.84 mol% of TiO_2 as nucleating agent and with different particle sizes has been studied by differential scanning calorimetry (DSC), X-ray diffraction (XRD) and tranmission electron microscopy (TEM). In glass powders two crystalline phases: zinc–aluminosilicate s.s. with high-quartz structure, $Zn_{x/2}Al_xSi_{3-x}O_6$, (x varies dependent on heat-treatment temperature) and gahnite are formed. The ratio of these phases depends on particle sizes. In bulk glass, however, gahnite is the sole crystalline phase. The composition of initially formed zinc–aluminosilicate s.s. was determined by Rietveld refinement of XRD patterns to be $Zn_{0.69}Al_{1.38}Si_{1.62}O_6$. With temperature increase, the amount of zinc–aluminosilicate s.s decreased with simultaneous reduce of zinc and aluminum incorporated in the structure. Eventually at 1423 K almost pure high-quartz structure was formed. The activation energies of zinc–aluminosilicate s.s. and gahnite crystallization were determined by non-isothermal method to be 510 ± 18 and 344 ± 17 kJ mol^{-1}, respectively. The latter value matches well with those cited in literature for crystal growth of gahnite in similar glasses. That is attributed to the fact that the high-quartz structure acts as a precursor for gahnite crystallization.

PACS: 61.43; 81.10.a; 61.72.d; 81.70.p

1. Introduction

Transparent glass-ceramics based on spinel compositions with gahnite ($ZnAl_2O_4$) as the main crystalline phase can be prepared from glasses on the basis of $SiO_2–Al_2O_3–ZnO$ system, with ZrO_2 and/or TiO_2 as nucleating agents [1–6]. According to Beall and Pickney [3] nucleation of glasses with TiO_2 or with both nucleating agents is preceded by a highly uniform, ultrafine-scale phase separation into SiO_2-rich and TiO_2/Al_2O_3-rich areas. Gahnite ($ZnAl_2O_4$) then crystallizes and grows within the latter globular areas [3,4]. Studies conducted with powdered glasses [7] show that gahnite arises by two simultaneous mechanisms: growing on nuclei present in the whole glass, and from zinc–aluminosilicate solid solution with high-quartz structure that crystallizes on the surface of glass particles and acts as a precursor for gahnite. Which mechanism prevails depends on glass particle size. These glass-ceramics have excellent thermal stability. Potential applications of these materials include those where transparency and high use temperature are important, including flat panel displays and certain photovoltaic substrates [3]. Glazes containing gahnite are also interesting, since it is the crystalline phase of high scratch hardness and high refractive index [8].

In this work, the influence of particle size on phase development in $ZnO–Al_2O_3–SiO_2$ glasses with TiO_2 as nucleating agent has been studied. The composition of zinc–aluminosilicate s.s. in dependence of heat treatment temperature was studied by Rietveld refinement method

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doi:10.1016/j.jnoncrysol.2004.09.024

[9]. The activation energy for crystallization of zinc–aluminosilicate s.s (also called zinc-stuffed derivative of high-quartz) and gahnite was determined under non-isothermal conditions using Kissinger method [10].

2. Experimental procedure

2.1. Preparation of parent glass

The parent glass was prepared from reagent grade chemicals: SiO_2, $Al(OH)_3$, ZnO, and TiO_2. The batch was melted in Pt crucible in electrical furnace for 2 h at 1600 °C. Glass was crushed and remelted for another 2 h at the same temperature. Remelted melt was poured onto a heated steel plate to form a round discs about 5 mm thick. The glass was then annealed at about 925 K, and cooled down at the cooling rate of the furnace. The composition of the parent glass is shown in Table 1. The as-prepared glass was ground and sieved to produce 5 different fractions of glass powders (<63, 63–125, 125–250, 250–500 μm and ~5 mm) suitable for further analyses.

2.2. Characterization methods

Characteristic temperatures such as glass transition, T_g, onset of crystallization T_o and crystallization maximum T_p were determined by Netzsch STA 409 Simultaneous Thermal Analyser used in DSC mode. To investigate the crystallization mechanism of zinc–aluminosilicate and gahnite, the DSC scans were performed at the heating rates of 5, 10, 15, 20 and 25 K min^{-1}. The activation energies for crystallization of both phases (zinc–aluminosilicate s.s. and gahnite) under non-isothermal condition, E_a, were calculated from the relationship between the heating rate, β, and the temperature of the peak maximum, T_p, on DSC scans using Kissinger equation:

$$\ln\frac{\beta}{T_p^2} = -\frac{E_a}{RT_p} + \text{const.} \quad (1)$$

where R is the universal gas constant.

The thermally treated samples were analyzed by XRD to identify the crystalline phases formed during DSC runs. X-ray diffraction analysis was carried out on a computer-controlled diffractometer (Siemens D500/PSD) using CuKα radiation with α-quartz single-crystal monochromator, and a curved position sensitive detector. Samples were dispersed on a Si single crystal holder. Data were collected between 5 and 70° 2θ, with steps of 0.02° and counting time of 3 s per step. For the purpose of the Rietveld structure refinement [9], the XRD data were collected using a Philips X'Pert diffractometer with CuKα radiation. XRD patterns were scanned in steps of 0.02° (2θ) in the range from 15 to 120° with a fixed counting time of 30 s per step. The composition of metastable zinc–aluminosilicate s.s. differs from that cited in JCPDS-ICDD file No. 34-1455; therefore, the Rietveld refinement (TOPAS2 program [11]) was performed to determine its composition. The refinement of zinc–aluminosilicate structure was started using $P6_222$ space group [12] and the structure parameters for $LiAlSi_2O_6$ derived by Mueller et al. [13], since zinc prefers the tetrahedral coordination sites in silicates [14] and there is no data for zinc stuffed derivative structure of high-quartz in literature. The refinement for gahnite was started using Fm-3m space group derived by O'Neill [15]. The pseudo Voigt function was used for the modeling of diffraction profiles. In the final refinements the following parameters were refined: scale factor, 2θ zero, seven coefficients of Chebyshev polynomial to describe the background, peak profile parameters, unit cell parameters determined using Si as an standard, x, y, z atom positions, occupation factors

Table 1
Glass composition determined by EDX analysis

	SiO_2	Al_2O_3	ZnO	TiO_2
mol%	55.61	22.83	17.75	3.84

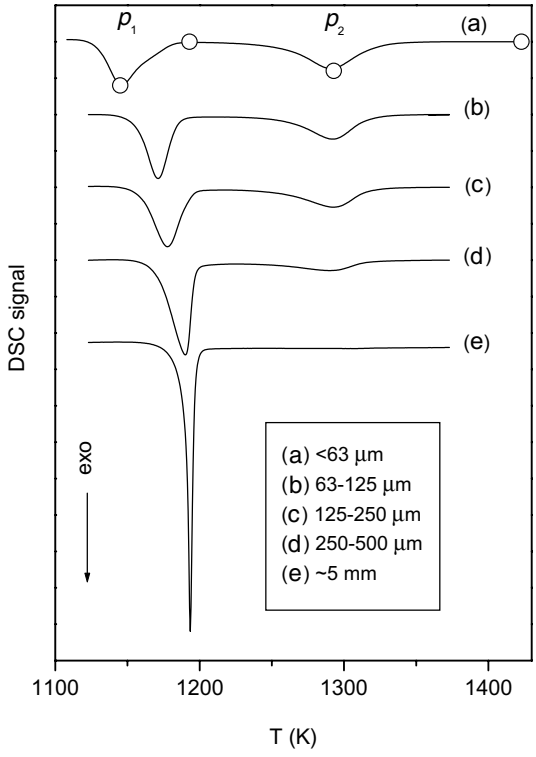

Fig. 1. DSC scans for non-isothermal crystallization of glasses as a function of particle size, (heating rate 10 K min^{-1}). (a) glass particles <63 μm; (b) glass particles 63–125 μm; (c) glass particles 125–250 μm; (d) glass particles 250–500 μm, (e) glass particles ~5 mm. Scans are shifted for visualization purposes. Circles on DSC scan (a) assign the quench temperatures for subsequent XRD analyses.