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

Effect of low NiO doping on anomalous light scattering in zinc aluminosilicate glass-ceramics

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ARTICLE INFO

Keywords:
Glass-ceramics
Nanocrystals
Light scattering
Interference effects
Structure of glass-ceramics

ABSTRACT

The effect of low NiO doping (0–0.15 mol%) on the extinction coefficient of zinc aluminosilicate glass-ceramics prepared by five different two-stage heat treatments was studied experimentally. Extinction coefficient vs wavelength presented as a log-log plot was separated into scattering and absorption coefficients. The NiO addition drastically changes not only values of the scattering coefficient at a given wavelength of visible light (effect 1), but also the type of wavelength dependence of this coefficient (effect 2). These effects do not correlate with variation of sizes and volume fractions of nanocrystals determined by Rietveld refinement of X-ray diffraction data. They cannot be described in the model of independent Rayleigh scatterers. These effects are characteristic features of anomalous light scattering by inhomogeneous glasses and can be explained by interference of light scattered by different nanocrystals. To calculate interference effects, the detailed information on mutual arrangement of nanocrystals is required, which unlikely can be determined experimentally for multiphase polydisperse system of nanocrystals. Instead, simplified models for systems of nanocrystals in glass-ceramics can be considered. And finally, we cannot explain the mechanism of the effect of small NiO additions on light scattering and hence, on structure of glass-ceramics.

1. Introduction

Several types of optical materials based on glasses, i.e., glass-ceramics (GCs) and phase-separated glasses, have inhomogeneous structure, which inevitably results in light scattering by these materials. Light scattering is the property that determines the applicability of materials for fabrication of diffuse reflection standards, diffuse reflectors, etc. For transparent optical elements, scattering is a negative factor that should be reduced to minimum. Thus experimental study and theoretical modeling of light scattering in optical materials prepared on the basis of glasses is important for optical materials science.

Below we will consider unpolarized incident light. The light extinction (attenuation) coefficient (EC) of a material, α, is presented as a sum of the absorption and scattering coefficients, α_a and α_s. EC is identical with the scattering coefficient (SC) in the spectral range wherein absorption is negligible.

Spectral behavior of the EC for non-absorbing glass-based materials was analyzed in the literature beginning with the early papers [1,2] (see also review [3]) and up to now [4–9]. It was found that the dependence of the EC on wavelength λ in some particular spectral range (e.g., in the range of visible light [4]) is given by

$$\alpha(\lambda) = \alpha_s(\lambda) = a\lambda^{-p}, \quad (a, p = \text{constant}). \tag{1}$$

The value $p = 4$ is typical for independent Rayleigh scatterers [10]. For GCs, it was stated that $p = 4$ [11,12] or $p \leq 4$ [13]. The values $p \approx 4$ were experimentally observed for several GCs [5,7–9].

However, some inhomogeneous glasses and GCs demonstrate the so-called anomalous light scattering[1] characterized by predominant scattering into the backward semi-sphere [3] and the p values considerably > 4 [3,4,6,8,9]. These phenomena are connected with interference effects in scattering [3]. For example, at the Ostwald ripening stage of phase separation, anomalous scattering is interpreted as a result of interparticle interference (interference of light scattered by different particles). This interpretation is based on the original idea by Kolyadin [15]. Such a behavior of scattering for the phase-separated

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[1] The anomalous light scattering in inhomogeneous glasses [3,4,6,8,9] should not be confused with anomalous light scattering by small particles (see [14] and references therein).

http://dx.doi.org/10.1016/j.jnoncrysol.2017.08.012
Received 10 March 2017; Received in revised form 3 August 2017; Accepted 7 August 2017

glass at the Ostwald ripening stage was observed in Ref. [6] (for the glass G2, $p = 6.9 \pm 0.1$).

When precipitation of crystalline phases in GC is completed, crystals are distributed in a homogeneous matrix, and the structure of the GC is somewhat similar to, but more complicated than a binodal structure of phase-separated glass at the Ostwald ripening stage. Indeed, particles in phase-separated glass prepared at isothermal conditions have the same composition and almost spherical shape, while GCs frequently contain irregularly shaped crystals of several crystalline phases with different refractive indices. Meanwhile, GCs, as well as phase-separated glasses, can exhibit anomalous light scattering [4,8,9].

The theoretical treatment of interparticle interference was carried out using the interference approximation [16] for a system of identical spherical particles distributed in a homogeneous matrix [17–19]. Interference leads to a decrease in the SC in comparison with the case of independent scatterers (effect 1) [19] and to the wavelength dependence (1) with value of $p > 4$ (effect 2) [17,18]. These effects are connected with the short-range ordering in mutual arrangement of particles. The effects are determined by the structure factor of the system of particles. Effect 2 is closely related to a predominant scattering into the backward semi-sphere (effect 3). Interference effects 1–3 were observed experimentally. Effect 1 was observed for a suspension of latex particles in water ([16], Fig. 1, $x \leq 3.5$, where x is the size parameter [10] – see Section 4.3.2 below) and for GCs [20]. Effect 2 was detected for phase-separated glasses [3,6] and GCs [4,8]. Effect 3 was studied for phase-separated glasses [3,15].

Let us also note that the interference effects are observed in small angle X-ray scattering (SAXS): a dependence of scattering intensity on scattering angle in some cases shows a maximum, the position of which is associated with characteristic interparticle distance [21,22].

In most cases particles are not identical (polydisperse spherical particles in phase-separated glasses, crystals of several crystalline phases with different shapes, sizes and refractive indices in GCs). Then the explanation for the interference effects becomes greatly complicated.

The interference approximation [16] was used in the theoretical study of effects of polydispersity on SC of the system of spherical Rayleigh particles [23]. On the assumption that the pair correlation function of particles is independent of their sizes, it was shown that the interference effects decrease, and the scattering increases with an increase in the degree of polydispersity. However, analysis of the scattering properties of phase-separated sodium borosilicate glass in connection with data on its structure has shown that this assumption is not adequate, and the pair correlation function which depends on sizes of particles in pair should be used [6]. It was also noted [6] that experimental determination of such a function is impossible, at least at present. So the conclusion was drown that there is only one way to theoretically analyze the polydispersity effects – to apply the interference approximation with pair correlation functions dependent on sizes of particles in pair and calculated in appropriate models.

For the more complicated case of GCs, progress towards understanding the scattering laws is modest, and practical recommendations are based largely on empirical facts (see, for example, [24]). With certainty we can only say that the scattering properties depend not only on refractive indices, sizes and shapes of the crystals, but also on their mutual arrangement, which determines the nature of interference effects in the scattering. Therefore, a further study of the relation between structure of GCs and light scattering is necessary.

In previous paper [8] we reported the results of preliminary study of the EC and the structure of gahnite-based zinc aluminosilicate GCs with low nickel oxide doping. This work continues the study for GCs prepared by several heat treatment (HT) schedules and includes theoretical estimation to show anomalies in light scattering.

Table 1
Heat treatment schedules for the GC preparation.

Heat treatment schedule	Designation
750 °C, 6 h + 1000 °C, 6 h	HT1
800 °C, 6 h + 950 °C, 6 h	HT2
800 °C, 6 h + 1000 °C, 6 h	HT3
800 °C, 6 h + 1025 °C, 6 h	HT4
800 °C, 6 h + 1050 °C, 6 h	HT5

2. Experimental

2.1. Sample preparation

The zinc aluminosilicate glass of the composition 25ZnO, $25Al_2O_3$, $50SiO_2$ (mol%) was doped by a mixture of $5TiO_2$ and $5ZrO_2$ as nucleation agents [25] and 0.0–0.15 mol% NiO, all introduced above total 100%.

Batches to produce 300 g of glass were melted in crucibles made of quartz ceramics in a laboratory electric furnace at 1580 °C for 5 h with stirring and poured onto a metal plate. The glasses were annealed at 670 °C. According to previous studies [25], to prepare GCs, initial glasses were subjected to two-stage HTs listed in Table 1.

2.2. Methods of structural study of GCs

The structure of prepared GCs was studied by X-ray diffraction (XRD), SAXS and transmission electron microscopy (TEM).

2.2.1. XRD

XRD patterns of powdered samples of GCs were measured using Shimadzu XRD-6000 diffractometer, CuK_α radiation with a Ni filter (wavelength $\lambda_X = 1.54$ Å). For the estimation of volume fractions of crystalline phases and the mean crystal sizes (diameters), Rietveld refinement of the patterns [26] was performed using the MAUD program [27]. The XRD patterns were collected in a step-scanning mode with steps of $\delta(2\theta) = 0.02°$ in the 2θ range 10–120° and with the preset time of 1.00 s. Pure cubic Y_2O_3 powder standard sample was used to correct the data for instrumental broadening. For modeling the residual glass [28], the cristobalite SiO_2 was used. As a result, lattice constants and volume fractions of crystalline phases were determined.

2.2.2. SAXS

Plane-parallel polished GC samples with thickness of 0.2 mm prepared using HT1 were studied by SAXS.

The potentialities of SAXS in the study of inhomogeneous media have been described in detail elsewhere [29–31], while application of SAXS to the analysis of GCs structure was described in detail in Ref. [22]. Let us specify some details important for obtaining the results given below. The SAXS intensity $I(\varphi)$ was measured with a home-made instrument in the range of scattering angles φ from 3 to 400 arc min. CuK_α radiation ($\lambda_X = 1.54$ Å) was used with an “infinitely” high primary beam (“infinitely” high slit).

A degree of structural inhomogeneity of the multiphase GCs structure is characterized by the mean square of the electron densities difference $\langle(\Delta\rho)^2\rangle$ [30,22][2]. For the geometry of “infinitely” high primary beam used in our study, $\langle(\Delta\rho)^2\rangle$ is proportional to the area under the curve $s\,I(s)$ versus s where $I(s)$ is the SAXS intensity,

$$s = 4\pi \sin(\varphi/2)/\lambda_X \quad (2)$$

is the magnitude of the scattering vector, and φ is the scattering angle (the angle between the primary and the scattered beam).

[2] The right-hand side of expression (41) for $\langle(\Delta\rho)^2\rangle$ on page 92 of Ref. [30] should contain an additional factor 1/2 (see Eq. (39) on the same page and Eq. (9) on page 82).