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Spectroscopy study on the nucleation kinetics of $ZrTiO_4$ in a lithium alumosilicate glass

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ABSTRACT

The nucleation kinetics of zirconium titanate $ZrTiO_4$ in a multi-component lithium alumosilicate (LAS) glass was quantified by analysis of spectroscopic data from the UV–Vis-region. Using Mie theory the scattering power of nano-sized $ZrTiO_4$ crystals embedded in the glassy matrix as well as their absorptive properties were determined and separated from the individual absorbance of various dilute Fe- and Ti-species in nucleated LAS glasses. Extinction coefficients, elaborated with the assumption of constant crystal size ($\approx$4 nm) revealed that the $ZrTiO_4$ volume fraction reached its final value for a dwell time of $\approx$120 min at 1018 K. The power of the transformation rate ($\approx$1.3) as analyzed by JAMK equation was attributed to a steady state crystal nucleation process. For a final crystal volume fraction of 1% $ZrTiO_4$, the maximum number density $N_v \approx 3 \times 10^{23}$ m^{-3} and the stationary nucleation rate $I_{ss} \approx 5 \times 10^{19}$ m^{-3} s^{-1} was determined.

1. Introduction

In the industrial glass production nucleating agents are used to catalyze the crystallization in glass, forming glass–ceramics with nano-grained crystals [1–3]. Depending on the type of the nucleating agent, the optical properties of glass–ceramics can be differently modified due to changes in the absorption and scattering mechanisms. For glasses in the $Li_2O–Al_2O_3–SiO_2$ (LAS) systems, absorption is dominated by various dilute Fe- and Ti-species in the residual glass whereas scattering stems from the existence of crystalline phases.

In the past, the analysis of optical scattering phenomena turned out to be a great challenge, since process- and chemistry-driven differences of scattering intensities very often interfered with equal or greater variations of the absorption phenomena within the same material. Therefore, studies had been confined to model systems with vanishing contents of polyvalent impurities, namely of iron [4]. This study aims in extending analyses of scattering to technical glass compositions bearing regular amounts of impurities and in deducing subtle changes in the crystal volume fraction of zirconium titanate ($ZrTiO_4$), which is used for analysis of the underlying kinetic parameters.

Modeling of absorbance is limited by the correct calculation of species concentrations. These demands for the simultaneous balancing of all internal reactions, namely of the redox interactions of the ionic species of iron, titania and of the fining component (i.e. of arsenic, antimony or tin) have to be considered.

The notion of ion-clustering was used to explain cooperative absorption phenomena such as ilmenite-type chromophore [5–8]. Studies in crystalline compounds proved that only the immediate neighborhood of both diluted ferrous iron and titania guarantees the operation of an intensive charge transfer absorption band [9]. Its intensities increase from corner over edge to face sharing symmetries, i.e. with the cluster size and the number density, agglomerations should be more efficient than chain- or plane-like structures. In most titania-bearing LAS glasses, Fe is a sub-minor component opposed to a hundred-fold majority of titania species. Therefore, one expects that the smaller and probably one-dimensional cluster geometries dominate the spectral character of the Fe–Ti interactions. One expects the sensitivity of specific absorption coefficients to changes in concentrations of iron or titania to be small, the total intensity of the ilmenite absorption to depend more or less linearly on the concentration of ferrous iron.

In regular ceramization processes of LAS glasses the nucleation of rutile (TiO_2) or zirconium titanate ($ZrTiO_4$) is followed by a crystallization of a high quartz solid solution (HQ-ss). Since the composition of the LAS glass departs from HQ-ss, a glass–ceramic with about 30 vol.% residual glass phase is formed. Typically, the residual glass is high in silica and bears an excess amount of titania, not used for nucleation. Given the anisotropic character of HQ-ss crystals, up to three scattering mechanisms may operate: crystal/crystal, crystal/glass and nuclei/glass, their scattering cross sections depending on geometric parameters as well as on the differences of the pertinent refractive indices [3,10]. In nano-sized glass–ceramics all geometric scales are much smaller than the wavelength of visible light, which is the domain of Rayleigh or Rayleigh–Gans scattering [11,12]. A most careful analysis of scattering intensities revealed that the scattering cross

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sections of many LAS glass–ceramics show coherency effects [13] and Rayleigh–Gans theory has to be modified by a factor regarding the high packing density of HQ-ss crystals [14,15]. For instance, Sakamoto et al. [4] used this correction for an experimental analysis of minor refractive index differences between residual glass and crystal phases. However, a complete theoretical analysis of the glass–ceramic transmittance is most demanding and up to now, lacking coherent models.

Reducing complexity may start from avoiding the HQ-ss crystallization. In contrast to HQ-ss crystals, $ZrTiO_4$ crystals are much smaller, less densely packed and randomly distributed within the glassy matrix. Therefore, their contribution to the total scattering of nucleated glasses should be of a simpler incoherent character. On the other hand, several studies were carried out to monitor the nucleation in terms of crystallinity in LAS glass–ceramics [16–23]. In particular, it has been shown that $ZrTiO_4$ grows in less than 30 min at 1023 K to an average diameter of $\approx$4 nm and during the further nucleation and crystallization their size did not change significantly [24]. Furthermore, $ZrTiO_4$ crystal fraction and stoichiometry under these heating conditions were determined using Raman spectroscopy [18].

Despite, the numerous nano-structural and kinetic studies on $ZrTiO_4$ nucleation in LAS glasses, its role on the evolution of optical properties of transparent glass–ceramics is less understood. In this study we present a new approach to determine the effect of $ZrTiO_4$ nano-crystal formation from optical transmittance. In particular, the optical spectra are deconvoluted to separate the intensity of absorbing and scattering of $ZrTiO_4$ crystals from the individual absorbance of various dilute Fe- and Ti-species in nucleated LAS glasses.

2. Methods

2.1. Deconvolution of optical extinction spectra

In order to deconvolute the optical extinction spectra for the contributions of the individual absorbing and scattering species, the internal transmittance for normal incidence of light of a coplanar glass plate of refractive index n and thickness d has to be considered. According to Neuroth [25] the intensity of the light after reflection at the entrance surface I_e is given by $I_e = I_0 \cdot (1 - R)$, with I_0 = initial intensity and R = reflectivity ($R = ((n - 1)/(n + 1))^2$). Inside the glass the intensity is attenuated exponentially as $I_d = I_e \cdot \exp(-\varepsilon d)$, with I_d = intensity at the inside of the exit surface and ε = natural extinction coefficient. At the exit surface another reflection occurs. Thus, the transmitted intensity I_t is given by $I_t = I_0 \cdot (1 - R)^2 \cdot \exp(-\varepsilon d)$. Taking multiple reflections into account the transmission through the glass plate can be derived as:

$$\frac{I_t}{I_0} = P\frac{I_d}{I_e} = P\exp(-\varepsilon d), \tag{1}$$

with P = correction factor for multiple reflections = $2n/(1 + n^2)$. We note that the reflection factor P is a function of the wavelength-dependent refractive index. We further note that the natural extinction coefficient ε of this study is 2.303 times larger than taking the ratio of the common extinction $E = \log(I_0P/I_t)$ to the thickness of the glass plate, which is also used in optical spectroscopy:

$$\varepsilon = \frac{1}{d}\ln\frac{I_0P}{I_t} = \frac{\ln(10)}{d}\log\frac{I_0P}{I_t} = 2.303\frac{E}{d}. \tag{2}$$

The natural extinction coefficient ε given by the sum of contributions from absorption and scattering, i.e.

$$\varepsilon = \varepsilon_{spe} + \varepsilon_{par} \tag{3}$$

with ε_{spe} = extinction due to ionic species, and ε_{par} = extinction due to particles. The individual extinctions are assumed to be linear functions of the number densities of absorbing species (c_i) and scattering centers (N_{vi}), respectively

$$\varepsilon_{spe} = \sum \varepsilon_i c_i \tag{4}$$

$$\varepsilon_{par} = \sum C_i(m,x)N_{vi}. \tag{5}$$

The cross sections ε_i and $C_i(m,x)$ are material parameters and have to be determined from theory or experiment. The number densities result from the interaction of chemical species, i.e. they depend on glass composition and on the thermal history of the material. In the following sections the modeling of the individual cross sections will be derived.

2.2. Modeling the extinction of absorbing species

Absorption of light by ionic species i is best described by a Gaussian function of the form:

$$\varepsilon_{spe,i} = c_i\varepsilon_i = c_i\alpha_i\exp\left[-\frac{1}{2}\left(\frac{\nu-\nu_i}{\Delta\nu_i}\right)^2\right] \tag{6}$$

with ε_i = absorption cross section of species i, ν = wavenumber (cm^{-1}), α_i = normalized peak height (cm^{-1} $mol\%^{-1}$), ν_i and $\Delta\nu_i$ = peak position and peak width (both in cm^{-1}), respectively. The glass specific parameters α_i, ν_i and $\Delta\nu_i$ were taken from the literature. For the Fe- and OH-species the data of Volotinen [26], Glebov [27] and Ehrt [28] were used. Ti^{3+} has been analyzed thoroughly by Bates [29] and Ti^{4+}-data are best from Smith and Cohen's [30] comprehensive study.

Charge-transfer bands are generally most sensitive to variations in glass chemistry. Therefore, the modeling of the ilmenite-type-cluster poses greater problems. Again, there are only data for peak position and half width. Carl [8] and Burns [5] as well as Nolet [7] offered reasonable data for a first approximation — in the end, our own analysis of the non-nucleated green glass sample proved to be the most reliable data source.

Among the crystalline compounds, rutile and zirconium titanate should contribute to extinction both by absorption as well as scattering. The modeling will be explained in the following part.

2.3. Theory of absorption and scattering by nuclei

When a particle surrounded by a medium is illuminated by a beam of light, the amount of light scattered by the particle, as well the amount absorbed, depend on the nature of the particle and on the surrounding medium [12]. Light absorbed and scattered by spherical particles has been investigated by Mie [31]. Starting with Maxwell's equations he has developed the extinction cross section C_i of a crystal i as a function of the size parameter ($x = \pi Na/\lambda$), the refractive indices of the spherical particle (n) and the surrounding medium (N). λ is the wavelength in vacuum and a the diameter of the particle.

$$\begin{aligned} C_i(m,x) &= C_i^{abs}(m,x) + C_i^{scatt}(m,x) \\ &= \pi a^2 x \mathrm{Im}\left\{\frac{m^2-1}{m^2+2}\left[1+\frac{x^2}{15}\left(\frac{m^2-1}{m^2+2}\right)\frac{m^4+27m^2+38}{2m^2+3}\right]\right\} \\ &\quad + \frac{2}{3}\pi a^2 x^4 Re\left\{\left(\frac{m^2-1}{m^2+2}\right)^2\right\} \end{aligned} \tag{7}$$

with C_i^{abs}, C_i^{scatt} = the absorption and scattering cross sections of the particle i, respectively, m = relative refractive index ($m = n^*/N$). *Im* and *Re* denote the imaginary and real part of the complex term in bracket, respectively. In the case that the incident light is not only