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Internal Residual Stresses in Partially Crystallized Photo-Thermo-Refractive Glass

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Photo-thermo-refractive glass containing nanosized NaF crystals embedded in the glassy matrix shows a significant shift of X-ray diffraction (XRD) lines to lower angles resulting from large residual (tensile) stresses within the crystals. This is thus an excellent "model" system to test residual stresses models in glass–ceramics and composites because: the estimated stresses are high—about 1 GPa—the precipitates are nearly spherical, the NaF crystals structure is cubic and their volume fraction is quite small, which eliminates overlap between the stress fields of neighbor crystals. Samples treated at a sufficiently high temperature to develop larger (micrometer size) crystals revealed microcracking of the glassy matrix around the crystals, which partially relieved the residual stresses and decreased the shift of the XRD peaks. The experimental results for the magnitude of the residual stresses and the critical crystal diameter for microcracking agree with theoretical values calculated by the Selsing and the Davidge & Green models, respectively. These results suggest that these two models can be used for stress estimates and as a first approach for the design of tough glass–ceramics.

I. Introduction

Glass-ceramics are polycrystalline materials with one or more crystalline phases embedded in a glassy matrix. They are produced by controlled crystallization of glasses, which generally yields null porosity and micro- or nanosized crystalline particles of simple or complex shapes. Glass–ceramics encompass a vast range of applications, such as, for instance, opto-electronic devices, surgical implants, telescope mirrors, and cooking ware.[1]

One of the main issues concerning their mechanical performance is the type and magnitude of residual stresses around the crystalline precipitates. These stresses arise upon cooling down the material after crystallization due to the thermal and elastic mismatch between the crystalline precipitates and the glassy matrix. Residual stresses may or may not generate microcracks around the precipitates depending on their magnitude and crystal size. These stresses significantly affect the overall material's strength positively or negatively, depending on their type (tensile versus compressive) and magnitude.

Recently, there has been an increased interest in the study and development of glass–ceramics for advanced optical applications. Considerable effort has been dedicated to photo-thermo-refractive (PTR) glass, which is a sodium–potassium–zinc–aluminum–silicate glass doped with cerium, silver, fluorine, and bromine.[2,3] After proper thermal treatment, a very small volume fraction (<1%) of nanosized NaF crystals precipitate in the glass matrix. Exposure of PTR glass to UV laser light before thermal treatment boosts the crystallization process, leading to a local refractive index decrement with respect to the unexposed parts of the glass. This peculiarity of PTR glass enables the fabrication of high-efficiency volume holographic optical components with applications in lasers and other opto-electronic devices.[4,5]

The problem of residual stresses in PTR glass gained further interest as it has been considered the main mechanism of refractive index change.[6] It was demonstrated in Lumeau *et al.*[6] that redistribution of sodium and fluorine between NaF crystals and the silicate glass matrix during crystallization cannot explain the refractive index change, and that residual stresses are, most likely, the key factor determining the refractive index variation. Thus, proper characterization and control of residual stresses in PTR glass are crucial for the optimization of its optical and mechanical properties, and resulting applications.

The Selsing model[7] is often used to describe residual stresses in low volume fraction two-phase composites. It assumes that the precipitates are spherical, isotropic, and that their stress fields do not overlap. The hydrostatic pressure P inside the precipitates is

$$P = \frac{\Delta\alpha\Delta T}{\frac{(1+\nu_m)}{2E_m} + \frac{(1-2\nu_p)}{E_p}} \quad (1)$$

where E is the elastic modulus, ν is the Poisson ratio (the subscripts m and p refer to matrix and precipitate, respectively), $\Delta\alpha$ is the linear thermal expansion mismatch between the precipitate and the glass, and ΔT is the temperature difference between T_g (where the glass becomes elastic on cooling) and room temperature.

So far the Selsing model has mostly been tested for particle–matrix systems with precipitates having noncubic structure, which are affected by thermal expansion and elastic anisotropies.[8–13] Consequently, PTR glass is a promising choice to test

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this model because: (i) the NaF precipitates have a cubic structure, (ii) the glass matrix is very homogeneous and isotropic, (iii) the volume fraction of the crystalline phase is extremely low (0.2%–2%), which eliminates overlap between the stress fields around the crystals, (iv) the elastic, thermal and chemical properties of both precipitate and glassy matrix are well documented,[14–16] and (v) internal crystallization of nano- or micrometer size NaF precipitates can be achieved by controlled thermal treatment[17]

Furthermore, it has been recently shown[18] that the resistance to crack propagation of an alumina–zirconia composite with low volume fraction (1.8%) of uniformly dispersed nanosized ZrO_2 crystals reaches values comparable to those of covalent (single-phase) ceramics, and its toughness is higher. These optimized mechanical properties are quite likely due to the residual stress fields in the matrix and in the ZrO_2 particles (hydrostatic tensile stresses of about 1 GPa). Because a rough estimate indicates that PTR glass shows a similar level and type of residual stress, understanding this material may open new possibilities for the study and design of glass–ceramics having superior mechanical properties.[6,19]

II. Experimental Procedure

A glass with composition $15Na_20–5ZnO–4Al_2O_3–70SiO_2–5NaF–1KBr–0.01Ag_2O–0.01CeO_2$ (mol%) was melted at 1460°C, and annealed at about 460°C (near T_g) for 1 h. Some samples were UV-exposed at room temperature using a He–Cd laser at 325 nm (4 mW) and dosage of 0.9 J/cm^2. UV-exposed and unexposed samples were heat treated at 450°C—1 h for nucleation and at 520°C—2 h for growth of nanosized NaF precipitates. Some specimens were treated at 650°C—20 min to induce hypergrowth until micrometer-sized crystalline precipitates could be seen under an optical microscope. In this way we can also use such "model" composite material to test the equation of Davidge and Green,[20] which assesses the critical precipitate diameter for spontaneous cracking under a residual stress field.

Synchrotron radiation was used because of the very low volume fraction of the crystalline (precipitate) phase. X-ray diffraction (XRD) measurements were performed at room temperature at the XRD1 beam line of the Brazilian National Synchrotron Light Laboratory (LNLS). The used wavelengths (1.5408 and 1.9642 Å) were calibrated against a LaB_6 standard NIST-660a. The recorded angular 2θ range was 5°–6° around the most intense peaks of NaF in 0.01°–0.02° 2θ steps. The background was subtracted from every peak of the powder diffraction pattern. The uncertainty for each point was set as $(I_{obs}+I_{back})^{1/2}$, where I_{obs} and I_{back} are the observed profile and background intensities, respectively. The individual peaks were grouped into a single diffraction profile and Rietveld refinement was performed using the GSAS program.[21,22] The residual stress, σ, was calculated from the change Δa in the NaF lattice parameter a by $\sigma = E_p/(1–2\nu_p)\Delta a/a$. The lattice parameter of a stress-free sample was measured from XRD experiments with a 99.9% grade NaF powder.

III. Results and Discussion

PTR glass samples heat treated at 520°C, where NaF crystals of about 20 nm appear as indicated by arrows in Fig. 1(a), revealed single diffraction peaks as seen in Fig. 2(a). Peak positions are displaced to lower 2θ angles. It was shown in[19] that this shift appears because NaF crystals are strained in the glassy matrix, i.e. under tensile stress (stretched lattice parameters). On the other hand, samples heat treated at 650°C to produce "large" dendritic precipitates, as shown in Fig. 1(b) by reflected light optical microscopy, revealed two groups of diffraction peaks that could be ascribed to different types of crystals, one stressed and another under negligible stress (Fig. 2(b)).

Experimental, calculated and difference XRD patterns obtained for quantitative determination of the residual stress using Rietveld refinement are shown in Fig. 3. A residual stress of 970 ± 60 MPa was calculated for UV-exposed samples heat treated at 520°C. A similar stress of 1.0 ± 0.2 GPa was measured for an unexposed sample with same heat treatment.

Heat treatment at 650°C produced lower residual stress levels. The stresses in the two groups of crystals formed by heat treatment at 650°C were 660 ± 30 and 20 ± 40 MPa for UV-exposed samples and 620 ± 20 and -20 ± 20 MPa for unexposed samples. It should be noted that the nucleation kinetics of PTR glass is markedly higher at ~520°C, where a large number of very small, cuboidal NaF crystals are formed.[17] Conversely, heat treatment at 650°C promotes exaggerated growth of a small number of crystals, branched over seeds of cuboidal NaF, as the supply of Na and F in the surrounding glass becomes progressively scarcer.

Taking $E_m = 64$ GPa, $E_p = 77.6$ GPa, $\nu_m = 0.2$, $\nu_p = 0.23$, $\alpha_m = 8.4 \times 10^{-6}$ K^{-1}, $\alpha_p = 36 \times 10^{-6}$ K^{-1}, and $\Delta T = 440$°C,[23,24] a residual stress of 760 MPa (tensile) is calculated using Eq. (1). However, considering the changes in glass composition because of Na and F depletion in the glassy halo surrounding the NaF

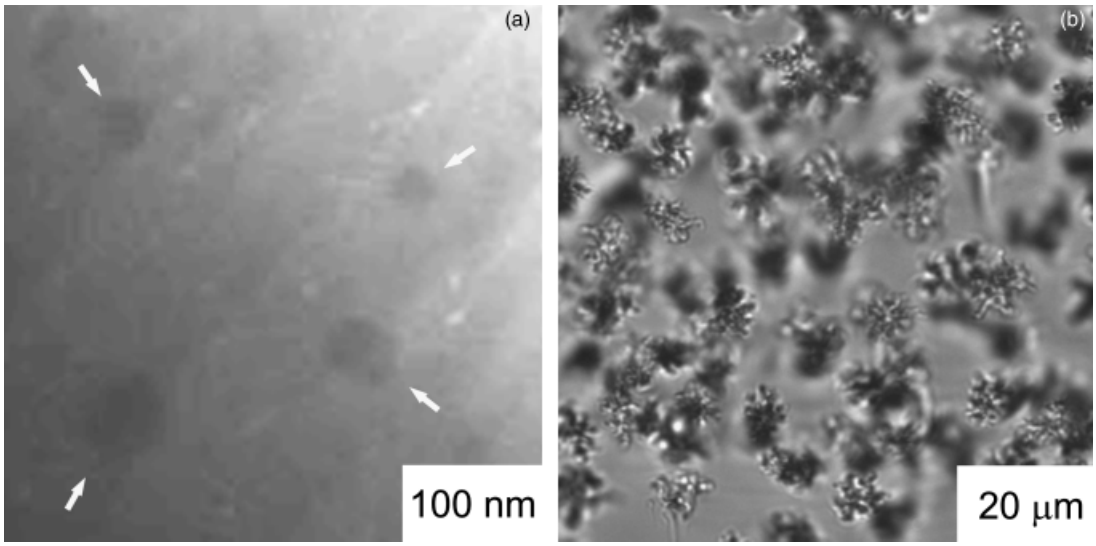

Fig. 1. (a) NaF precipitates (indicated by arrows) in a bright-field TEM image of UV-exposed PTR glass heat treated for 1 h at 483°C plus 1 h at 515°C; and (b) transmitted light optical micrograph of PTR glass UV-exposed, heat treated for 30 min at 650°C revealing a dendritic structure.

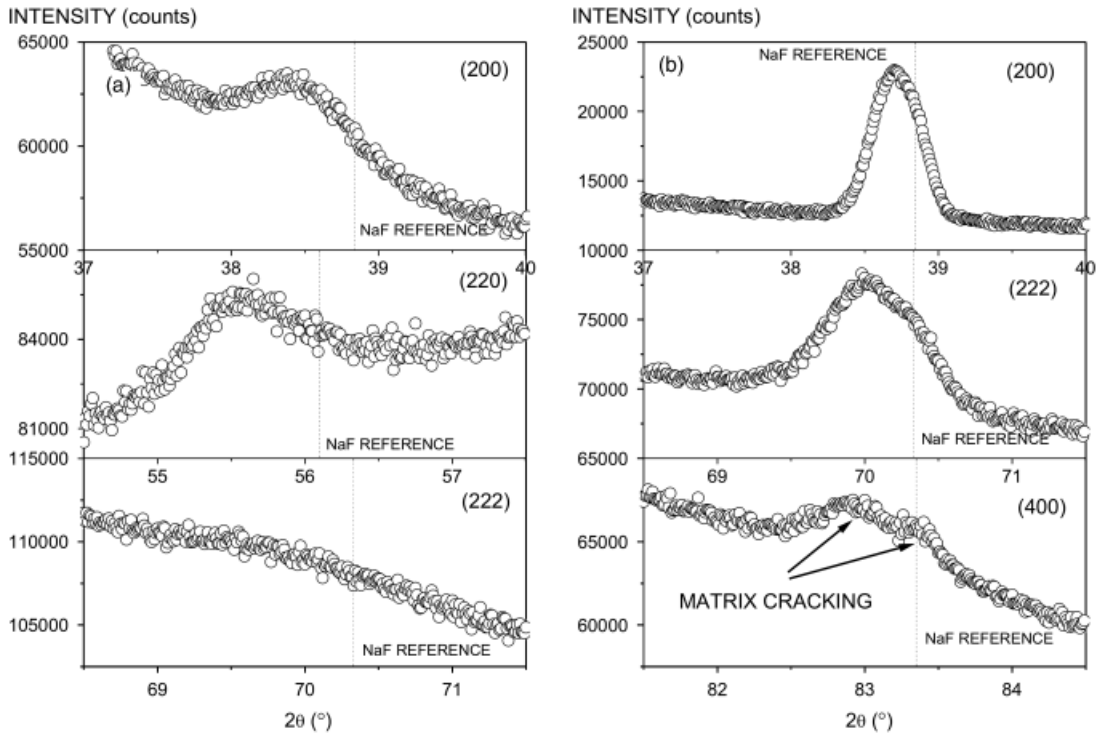

Fig. 2. Experimental X-ray diffraction patterns of UV-exposed samples heat treated for 1 h at 450°C plus: (a) for 2 h at 520°C; (b) for 20 min at 650°C. The peak positions are shifted to lower 2θ angles (larger interatomic spacing) due to tensile residual stresses. The 2θ peak positions for a stress-free NaF sample are indicated for reference.

precipitates, as those elements are consumed by the growing NaF crystals (previously described as the *courtyard effect* in Souza and colleagues[17,25]), the thermal expansion, α_m, should decrease (increasing $\Delta\alpha$) and the glass transition temperature, T_g, should increase. Therefore, this predicted residual stress is only a lower bound and the actual value should be >760 MPa.

This calculated stress level is similar to the measured residual stress of samples heat treated at 520°C in the present work (with cuboidal nanocrystals) and to previous measurements using nuclear magnetic resonance.[26] The lower stresses detected in the larger dendritic crystals (produced by heat treatment at a higher temperature) are caused by microcraking of the glass matrix around them, as revealed by scanning electron microscopy (Fig. 4). Therefore, microcracking partially relieves the residual stresses on the dendrites, causing the appearance of the second XRD peak. Rietveld refinement analysis demonstrated that the volume fractions of the "unstressed" NaF precipitates were approximately 1/4 and 1/3 of the total (crystallized) NaF in the glass for UV-exposed and unexposed samples, respectively. This result agrees with the fact that NaF precipitates are larger in unexposed samples for a given heat treatment (this was

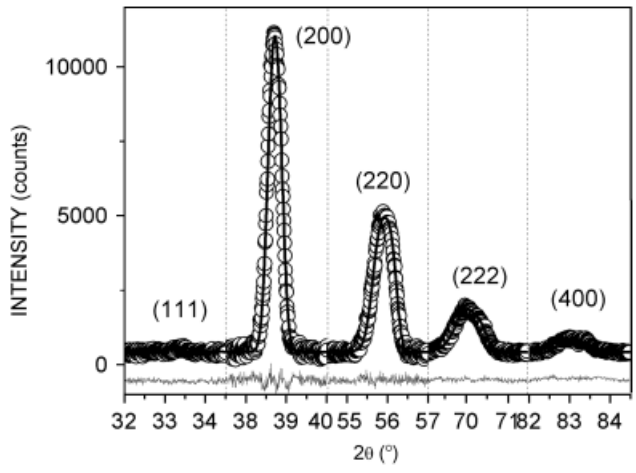

Fig. 3. Experimental, calculated and difference X-ray diffraction patterns after background subtraction of UV-exposed sample heat treated for 1 h at 450°C and for 20 min at 650°C. The observed intensity is represented by open circles, the calculated intensity and the difference curves are in bold black and light black, respectively.

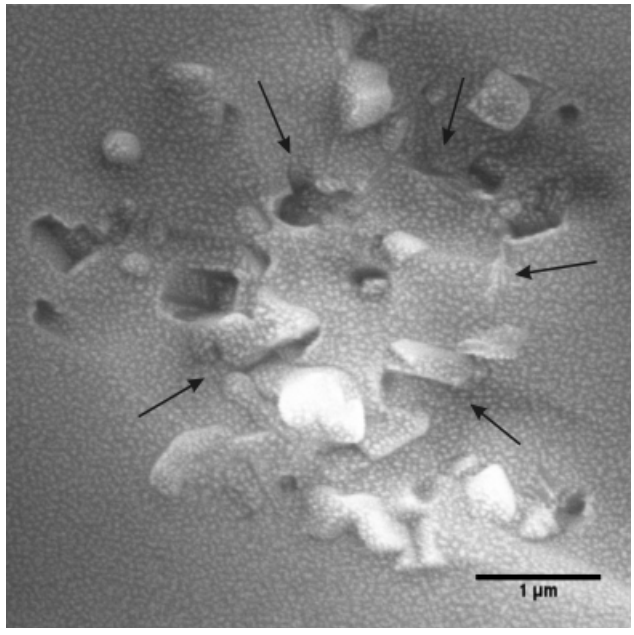

Fig. 4. Scanning electron microscopy image of fractured surface of a PTR sample unexposed, heat treated at 450°C—1 h/650°C—20 min showing a fractured NaF precipitate, and cracks in the surrounding matrix (indicated by arrows). Image obtained using a Philips XL30 TMP SEM (Eindhoven, the Netherlands) on a carbon-coated fractured surface.

investigated elsewhere), and therefore leads to a higher probability of matrix fracturing if a critical diameter is reached.

Davidge and Green[20] proposed an equation, based on an energy balance approach, for the critical diameter D_c above which spontaneous cracking should develop around a stressed precipitate:

$$D_c \geq \frac{8\gamma_S}{P^2\left[\frac{(1+\nu_m)}{2E_m}+\frac{(1-2\nu_p)}{E_p}\right]} \quad (2)$$

where γ_S is the glass surface energy, which is about 3.5 J/m^2 for PTR glass.[26] Calculations according to this equation reveal a critical diameter of 2.6 μm, which is about the size of the largest crystalline precipitates observed in samples heat treated at 650°C. Figure 4 shows a large precipitate in detail.

IV. Conclusions

In summary, the experimental 1.0 ± 0.2 GPa tensile residual stress in nanosized NaF crystals measured by XRD is not far from the prediction of Selsing's model for samples heat treated at 520°C, which have nanosized crystals. In addition, in samples heat treated at 650°C, which have hyperdeveloped crystalline precipitates with diameter above 2 μm, matrix microcracking around the precipitates partially relieved the residual stress, as predicted by the equation of Davidge and Green. Hence, these two models may be used as a guide to conceive glass–ceramics having a low volume fraction of crystals with a favorable residual compressive stress field in the matrix that may increase fracture strength and toughness,[27–30] and with nanosized precipitates that are below the critical diameter for cracking. Hence, these results may impact on the understanding and design of nanostructured glass–ceramics with superior strength and optical properties, as in the case of PTR glass.

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