Anisotropic residual stresses in partially crystallized Li$_2$O–2SiO$_2$ glass-ceramics

Valmor R. Mastelaro $^1$, Edgar D. Zanotto $^*$

Vitreous Materials Laboratory (LaMaV), Department of Materials Engineering (DEMa), Federal University of São Carlos (UFSCar), CEP 13565-905, São Carlos, SP, Brazil

Abstract

Levels of residual stresses in partially crystallized Li$_2$O–2SiO$_2$ glass-ceramics were calculated for several crystallographic planes. The stresses were also determined by an X-ray diffraction method (XRD) using synchrotron radiation. The linear thermal expansion coefficient ($\alpha_{hkl}$) of a fully crystallized, stress-free, powdered sample, was measured in situ using a hot-stage XRD technique. The thermal expansion coefficient depends on the crystallographic (hkl) direction. For some direction, the thermal expansion coefficient of the crystalline phase is greater than that of the glass matrix, while for other direction the inverse is observed. The average thermal expansion coefficient calculated from the unit cell expansion with temperature $\alpha_{uc}=(10.1\pm0.5)\times10^{-6}\degree C^{-1}$ was close to that obtained by a dilatometric method for a polycrystalline sample $\langle\alpha\rangle=(10.8\pm0.5)\times10^{-6}\degree C^{-1}$. The theoretical residual stresses were calculated by the Selsing model using experimental data for the elastic constants combined with the thermal expansion coefficient for each crystallographic plane. Experimental determinations of residual stresses were made using an XRD technique for six different sets of (hkl) planes in two partially crystallized specimens. The type of experimental residual stresses (tensile or compressive) for each crystallographic plane was in agreement with the predicted type. Regarding the stress magnitude, the experimental results vary from $-58/-117$ MPa (compressive) to $60/149$ MPa (tensile), whereas the calculated magnitudes vary from $-192$ MPa (compressive) to $16/102$ MPa (tensile). These magnitudes were confirmed by micro-Raman spectroscopy. The differences between the theoretical and experimental stress magnitudes are within the limits of experimental errors. Therefore, the Selsing model can give a reasonable estimate of residual stresses for real (anisotropic) materials. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Glass-ceramics are polycrystalline materials produced by controlled crystallization of glass having one or more crystal phases embedded in a glassy matrix. The ability to produce complex shapes, coupled to their lack of porosity and microstructure control make glass-ceramics unique for both domestic and advanced applications, such as microwave and opto-electronic devices [1], surgical implants [2] and large telescope mirrors [3]. Their mechanical performance is a major issue in such applications.

The mechanical properties of these materials are dependent on microstructural parameters and also on the level and type (tensile vs. compressive) of residual stresses around the crystals. These stresses increase on cooling specimens from the
vicinity of the glass transition temperature, $T_g$, to room temperature due to the thermal and elastic mismatch between the constituent phases. While the effects of microstructure on mechanical properties are well established, much less is known on the effects of residual stresses. Recently we reported an experimental test of two models often used describe the residual stresses in duplex materials, using a partially crystallized soda–lime–silica glass [4]. The experimental stresses were in good agreement with those calculated using the Selsing model [5]. To generalize the findings of [4], we extend that study here to another silicate system: partially crystallized Li$_2$O–2SiO$_2$ glass-ceramics.

2. Theory of residual stresses

The deduction of and popularization of the effects of residual thermal stresses in composites containing particulate inclusions was attributed to Selsing [5]. For the particular case of a spherical inclusion of radius, $R$, embedded in an infinite matrix, subjected to a temperature variation, $\Delta T$, the analytical expression for the stresses in the matrix and in the inclusion can be easily deduced. The stresses in the matrix, for an isotropic, elastic material are given by the following equations:

$$\sigma_r = P \cdot \frac{R}{x^3},$$

$$\sigma_\theta = -P/2 \cdot \frac{R}{x^3},$$

where $\sigma_r$ is the radial stress, $\sigma_\theta$ the tangential stress, $P$ the hydrostatic pressure on the particle, $R$ the particle radius and $x$ the distance from the center of the inclusion. Thus, these stresses are maximum at the crystal/glass interface ($x = R$) and drop to only 3.7% of the maximum for $x = 3R$.

The hydrostatic thermal stress, $P$, can be obtained using the following equation [5]:

$$P = \Delta x \cdot \Delta T / K_e,$$

where $K_e = [(1 + v_m)/2E_m + (1 - 2v_p)/E_p]$, $E$ and $v$ being respectively the elastic modulus and the Poisson ratio, and the subscripts, m and p, refer to the matrix and particle, respectively. $\Delta x = x_p - x_m$ is the thermal expansion mismatch and $\Delta T$ the difference between the temperature at which the glass ceases to flow on cooling ($\approx T_g$) and the ambient temperature.

For an isotropic system containing several particles in a matrix, Eq. (3) should still hold if the stress fields around each particle do not overlap. This situation is expected to be valid if the volume percentage of the second phase does not exceed approximately 15% [4]. However, as real materials are seldom isotropic, we will test the validity of Eq. (3) to estimate residual stresses in anisotropic materials, using a Li$_2$Si$_2$O$_5$ glass-ceramic.

3. Literature review

Recently we carried out a literature review about residual stresses in glass-ceramics [4] and observed that a controversy remains on this subject. For instance, in the works of Fulrath [6] and Zevin et al. [7], the experimental residual stresses were dependent on the particle size, however, according to Davidge and Green [8] they should not be. In addition, in the papers published by Borom et al. [9] and Miyata et al. [10] the experimental internal stresses were smaller than the calculated stresses (using Eq. (3)). Although there are several new publications on residual stresses in other materials, a literature search, using the ‘Web of Science’ database of the Institute of Scientific Information (ISI), which includes all periodicals indexed by the ISI, did not reveal any recent paper about residual stresses in glass-ceramics.

4. Materials and methods

4.1. Sample preparation

The Li$_2$O–2SiO$_2$ system was chosen because it presents favorable conditions for the residual stresses study, principally concerning the facility of microstructure control, and also due to the fact that this system has been extensively studied by our research group [11].

A glass of Li$_2$O–2SiO$_2$ composition was melted at 1350°C in a Pt crucible in air. The liquid was then cast between two cold steel plates, with an
estimated cooling rate of 400°C/min. To obtain partially crystallized glasses (glass-ceramics), some specimens, 10 × 25 × 3 mm, were submitted to isothermal treatments at 460°C ($T_g \sim 450°C$) for two different periods, 86 and 100 h. The heat treatments were carried out in an electric furnace with a temperature control within ±1°C. A fully crystallized polycrystalline sample, used for thermal expansion measurements, and a powdered sample, used as a stress free standard, were obtained by nucleating one specimen at 450°C for 24 h and then heating it at 600°C for 10 min to allow crystal growth. Only the stable Li$_2$Si$_2$O$_5$ crystalline phase was detected after these heat treatments.

4.2. Microstructure and physical properties

After polishing and etching glass-ceramic plates by a diluted solution of HF/HCl (0.08%/0.04%) for 30 s, they were observed by reflected light microscopy (RLM) coupled to an image analyzer system. The experimental crystallized fraction of the samples were about 8% for the sample heat-treated for 86 h, and 10% for the sample heat-treated for 100 h.

The crystal morphology was observed by RLM. Fig. 1 shows an RLM micrograph of the specimen heat-treated for 100 h at 460°C. For this treatment, the Li$_2$Si$_2$O$_5$ crystals have an ellipsoidal geometry and a maximum size of approximately 12 μm. We did not observe the formation of crystal branches, reported for specimens heat-treated in different conditions [12]. The lack of branches in the individual crystals coupled to small fractions of crystallinity were important microstructural features of our specimens to ensure that the stress fields did not overlap.

4.3. Physical properties

Fig. 2 shows the thermal expansion data for the glass sample and for fully crystallized samples obtained by a dilatometer (STA 409 Netzsch). To calculate their linear thermal expansion coefficients ($\alpha$), the curves presented in Fig. 2 were fit by a linear function (Microcal Origin software, the correlation coefficients were $r=0.998$ and $r=0.999$ for the glass and fully crystallized samples, respectively) in a temperature range between 200°C and 400°C. The following are the average linear thermal expansion coefficients: $\alpha_g = 12.8 \times 10^{-6}°C^{-1}$ for the glass and $\langle \alpha_c \rangle = 10.8 \times 10^{-6}°C^{-1}$ for the fully crystallized sample. Typical errors are about ±0.5 × 10^{-6}°C^{-1}. The $\alpha$s are similar to those found by Freiman and Hench [13] in the same temperature range (12.5 × 10^{-6}°C^{-1} and 10.0 × 10^{-6}°C^{-1} for the glass and fully crystallized samples, respectively).

As $\alpha_g$ is larger than $\langle \alpha_c \rangle$, at first sight these results indicate that, if the embedded crystals are isotropic, they should be under compression. However, our experimental X-ray results indicated that, for some crystallographic planes, the embedded crystals were under tension. Thus we

---

Fig. 1. RLM micrograph of the specimen heat-treated for 100 h at 460°C.

Fig. 2. Thermal expansion data for the glass and totally crystallized samples.
measured the linear thermal expansion coefficient for each $(hkl)$ plane $(\alpha_{hkl})$ through a hot stage X-ray diffraction camera. The measurements were made with a fully crystallized, stress-free, powdered specimen using an X-ray diffractometer (D-5000 Siemens). Both room and high ($\approx 400^\circ$C) temperature experiments were made using a platinum-substrate heater attachment. The substrate was used as an internal standard. The diffraction peaks were recorded under the following conditions: Cu-K$_\alpha$ radiation, X-ray tube operated at 40 mA and 40 kV and a scintillation counter as detector. The diffraction peaks were collected at 25°C, 250°C and 400°C over the range of 20.0–75.0 (20) using a 0.01° step interval and a step time sufficient to give a signal to noise ratio. At each temperature, the substrate/sample assembly was heated for 10–20 min before measurement to ensure thermal equilibrium.

The linear thermal expansion coefficient, $\alpha_{hkl}$, for each crystallographic plane was obtained by fitting linear functions to each $d_{hkl}$ versus temperature curve (Microcal Origin software, $r$ varied from 0.942 to 0.999). The results presented in Table 1 show that $\alpha_{hkl}$ is dependent on the $(hkl)$ plane. For some crystallographic planes, the thermal expansion coefficient of the crystalline phase is larger than that of the glass matrix, while for other planes the inverse is observed. To compare these results with dilatometric data, we calculated the volume expansion.

For the lithium disilicate samples, we found an average $E$ equal to 75 GPa for the glass and 122

### Table 1

<table>
<thead>
<tr>
<th>$(hkl)$</th>
<th>$2\theta$</th>
<th>$\alpha_{hkl}$ ($\times 10^{-6}$ °C$^{-1}$)</th>
<th>$\Delta \alpha = (\alpha_{hkl} - \alpha_g) \times 10^{-6}$°C$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 0 0</td>
<td>16.41</td>
<td>20.0</td>
<td>7.2</td>
</tr>
<tr>
<td>1 3 0</td>
<td>23.77</td>
<td>9.5</td>
<td>-3.3</td>
</tr>
<tr>
<td>0 4 0</td>
<td>24.39</td>
<td>5.3</td>
<td>-7.5</td>
</tr>
<tr>
<td>1 1 1</td>
<td>24.82</td>
<td>11</td>
<td>-1.8</td>
</tr>
<tr>
<td>2 0 0</td>
<td>30.69</td>
<td>17</td>
<td>4.2</td>
</tr>
<tr>
<td>0 0 2</td>
<td>37.57</td>
<td>8.3</td>
<td>-4.5</td>
</tr>
<tr>
<td>2 2 1</td>
<td>38.19</td>
<td>12.7</td>
<td>0.1</td>
</tr>
<tr>
<td>3 3 0</td>
<td>50.60</td>
<td>16.0</td>
<td>3.2</td>
</tr>
<tr>
<td>1 1 -3</td>
<td>60.56</td>
<td>13.5</td>
<td>0.5</td>
</tr>
<tr>
<td>2 8 -1</td>
<td>63.14</td>
<td>13.6</td>
<td>0.8</td>
</tr>
<tr>
<td>0 1 0</td>
<td>63.68</td>
<td>6.8</td>
<td>-6.0</td>
</tr>
<tr>
<td>3 3 2</td>
<td>64.54</td>
<td>13.9</td>
<td>1.1</td>
</tr>
<tr>
<td>3 7 0</td>
<td>68.66</td>
<td>14.1</td>
<td>1.3</td>
</tr>
</tbody>
</table>
GPa for the glass-ceramic. According to the literature, the Young modulus of Li$_2$O–2SiO$_2$ glass varies from 72 to 82 GPa [16,17]. Young’s modulus data for the Li$_2$O–2SiO$_2$ glass-ceramic are scarce. Freiman and Hench [13] reported that the Young modulus for a 90% crystallized Li$_2$O–2SiO$_2$ glass-ceramic is 127 GPa.

The Poisson ratios of the glass and fully crystallized glass-ceramic were taken from the literature [17,18]. The glass has a Poisson ratio, $\nu$, between 0.22 and 0.23, whereas the fully crystallized (polycrystalline) material has an average Poisson ratio of 0.19. Since we did not find elastic properties data for single crystal Li$_2$Si$_2$O$_5$, these average $E$ and $\nu$ were used in our calculations to estimate the magnitude of both theoretical and experimental residual stresses.

4.4. Residual stress measurements

The XRD for measuring strains and stresses in crystalline solids is well established [19,20]. The method relies on using the crystal lattice as an absolute strain gauge [20]. XRD is based on Bragg’s Law, which relates the interplanar spacing of atomic planes, $d$, to the angle peak position, $\theta$, of a diffracted beam of monochromatic X-ray [15]. The residual strain determined by XRD is based on the displacement of the peaks in the XRD pattern, i.e., on the relative change in the interplanar distance of the crystalline phase under study when subjected to mechanical stresses. The relative deformation can be assessed from the displacement of the diffracted peaks as follows [20]:

$$\varepsilon_{hkl} = -0.5\Delta(2\theta) \cot(\theta) = \Delta d_{hkl}/d_{hkl},$$  \hspace{1cm} (6)

where $\varepsilon_{hkl}$ is the relative deformation of the crystal lattice normal to the $(hkl)$ plane, $\Delta(2\theta)$ the displacement of the diffraction peak caused by the strain in the crystal, $2\theta$ the Bragg angle and $d_{hkl}$ the interplanar distance related to the $(hkl)$ reflecting plane. The experimental residual strain can be determined by Hooke’s Law:

$$\sigma_{exp} = \varepsilon_{hkl}E_{hkl},$$  \hspace{1cm} (7)

where $E_{hkl}$ is the direction dependent elastic modulus of the crystal.

X-ray diffraction measurements were carried out at the Synchrotron Light National Laboratory (LNLS-Campinas, Brazil) at 1.35 GeV, with a current between 70 and 120 mA. The experiments were made at room temperature and the X-ray beam was monochromatized using a Si(1 1 1) double-crystal. A scintillation counter was used as detector. Data for the glass-ceramic monolithic samples and for the fully crystallized sample were collected over a $2\theta$ range of 45.0–75.0$^\circ$, using a 0.02$^\circ$ ($2\theta$) step interval. Due to the volume fraction of crystals in the partially crystallized glass-ceramics (~10%), each XRD spectra was collected during 4 h. It was possible to measure the position of six different interplanar spacings with a reasonable signal to noise ratio (5) in this $2\theta$ range.

As an example, we present X-ray curves for the fully crystallized sample and for a partially crystallized glass-ceramic (100 h treatment) in Figs. 3 and 4. The X-ray diffraction spectrum of the sample heated for 100 h shows that, due to the quality of the crystals, some peaks are detected. Both spectra present only the Li$_2$Si$_2$O$_5$ crystalline phase (JCPDS 17-447). The internal residual strain and stresses presented in Table 2 were calculated using Eqs. (6) and (7). The type of experimental residual stress show that the crystals embedded in the glass matrix are in tension for $\alpha_{ac}$ larger than $\alpha_g$ and in compression for $\alpha_{ac}$ smaller than $\alpha_g$. Regarding the stress magnitude, the experimental

![Fig. 3. X-ray curve for the fully crystallized sample (24 h at 450°C and 20 min at 600°C). The diffraction peaks in the figure are identified with their respective $(hkl)$ plane.](image-url)
The stresses at the particle/matrix interface were calculated using Eq. (1) and the Selsing formula (3). The following data were used: $\Delta z = (2\theta_{hkl} - \theta_g)$ for each crystallographic plane (presented in Table 1); $\Delta T = 425^\circ$C (we consider a temperature range in which the matrix plasticity is negligible, from $T_g$ to room temperature); $v_m = 0.23$; $v_p = 0.19$, $E_m = 7.5 \times 10^4$ MPa and $E_p = 12.2 \times 10^4$ MPa. Due to the lack of single crystal data for the elastic constants, averages $v_p$ and $E_p$ (obtained for polycrystalline samples) were used. Substituting these averages into Eq. (3), we found that the calculated $\sigma$ vary from $-58/-117$ MPa (compressive) to $60/149$ MPa (tensile).

5. Residual stress calculations

The stresses at the particle/matrix interface were calculated using Eq. (1) and the Selsing formula (3). The following data were used: $\Delta z = (2\theta_{hkl} - \theta_g)$ for each crystallographic plane (presented in Table 1); $\Delta T = 425^\circ$C (we consider a temperature range in which the matrix plasticity is negligible, from $T_g$ to room temperature); $v_m = 0.23$; $v_p = 0.19$, $E_m = 7.5 \times 10^4$ MPa and $E_p = 12.2 \times 10^4$ MPa. Due to the lack of single crystal data for the elastic constants, averages $v_p$ and $E_p$ (obtained for polycrystalline samples) were used. Substituting these averages into Eq. (3), we found that the calculated $\sigma$ vary from $-192$ MPa (compressive) to $16/102$ MPa (tensile). As the experimental errors in these measurements are about 20%, the differences between the theoretical and experimental stress magnitudes are within the error limits. The results for each crystal plane are presented in Table 2.

An attempt was made to estimate the magnitude of residual stresses using micro-Raman spectroscopy technique [21]. The residual stresses can be obtained by measuring the shifts of the Raman lines of the polycrystalline samples. Raman spectra were obtained with a Raman micro-probe consisting of a microscope (Olympus BH-2) equipped with a holographic beam splitter and a super nutsch filter. A nominal $10$ mW HeNe laser was used as the excitation source. Pressure was generated in a diamond anvil cell (DAC) and measured with the ruby fluorescence technique.

### Table 2

<table>
<thead>
<tr>
<th>Sample form</th>
<th>Sample form</th>
<th>$(hkl)$</th>
<th>$\theta$</th>
<th>$d$ (Å)</th>
<th>$\epsilon \times 10^{-3}$</th>
<th>$\sigma_{\exp}$ (MPa)</th>
<th>$\sigma_{\text{Thco}}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder</td>
<td>Powder</td>
<td>3 3 0</td>
<td>53.27</td>
<td>1.7935</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Powder</td>
<td>Powder</td>
<td>1 1 –3</td>
<td>63.71</td>
<td>1.5234</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Powder</td>
<td>Powder</td>
<td>2 8 –1</td>
<td>66.46</td>
<td>1.4672</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Powder</td>
<td>Powder</td>
<td>0 10 0</td>
<td>66.96</td>
<td>1.4576</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Powder</td>
<td>Powder</td>
<td>3 3 2</td>
<td>68.14</td>
<td>1.4352</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Powder</td>
<td>Powder</td>
<td>3 7 0</td>
<td>69.08</td>
<td>1.4181</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Plate</td>
<td>Plate</td>
<td>3 3 0</td>
<td>53.20</td>
<td>1.7957</td>
<td>1.22</td>
<td>149</td>
<td>102</td>
</tr>
<tr>
<td>Plate</td>
<td>Plate</td>
<td>1 1 –3</td>
<td>63.66</td>
<td>1.5245</td>
<td>0.72</td>
<td>88</td>
<td>16</td>
</tr>
<tr>
<td>Plate</td>
<td>Plate</td>
<td>2 8 –1</td>
<td>66.40</td>
<td>1.4686</td>
<td>0.81</td>
<td>98</td>
<td>25</td>
</tr>
<tr>
<td>Plate</td>
<td>Plate</td>
<td>0 10 0</td>
<td>66.99</td>
<td>1.4569</td>
<td>-0.48</td>
<td>-58</td>
<td>-192</td>
</tr>
<tr>
<td>Plate</td>
<td>Plate</td>
<td>3 3 2</td>
<td>68.06</td>
<td>1.4366</td>
<td>0.97</td>
<td>118</td>
<td>35</td>
</tr>
<tr>
<td>Plate</td>
<td>Plate</td>
<td>3 7 0</td>
<td>69.04</td>
<td>1.4188</td>
<td>0.49</td>
<td>60</td>
<td>42</td>
</tr>
<tr>
<td>Plate</td>
<td>Plate</td>
<td>3 3 0</td>
<td>53.22</td>
<td>1.7951</td>
<td>0.89</td>
<td>108</td>
<td>102</td>
</tr>
<tr>
<td>Plate</td>
<td>Plate</td>
<td>1 1 –3</td>
<td>63.63</td>
<td>1.5252</td>
<td>1.18</td>
<td>143</td>
<td>16</td>
</tr>
<tr>
<td>Plate</td>
<td>Plate</td>
<td>2 8 –1</td>
<td>66.38</td>
<td>1.4686</td>
<td>0.95</td>
<td>116</td>
<td>25</td>
</tr>
<tr>
<td>Plate</td>
<td>Plate</td>
<td>0 10 0</td>
<td>67.03</td>
<td>1.4562</td>
<td>-0.96</td>
<td>-117</td>
<td>-192</td>
</tr>
<tr>
<td>Plate</td>
<td>Plate</td>
<td>3 3 2</td>
<td>68.08</td>
<td>1.4364</td>
<td>0.83</td>
<td>101</td>
<td>35</td>
</tr>
<tr>
<td>Plate</td>
<td>Plate</td>
<td>3 7 0</td>
<td>69.02</td>
<td>1.4192</td>
<td>0.77</td>
<td>94</td>
<td>42</td>
</tr>
</tbody>
</table>

$^a$ Fully crystallized = 24 h at 450°C, 10 min at 600°C.
Experiments with the powder sample were performed with silicon oil. A more detailed description of Raman experiments can be found in Ref. [23]. A calibration curve was constructed with the fully crystallized Li$_2$O–2SiO$_2$ powder, which indicated that the detection limit of the equipment used was about 150 MPa. As no detectable shift was observed in the micro-Raman lines of our monolithic glass-ceramics when compared to the spectrum of a fully crystallized (stress free) powder, we conclude that the magnitude of residual stress in the glass-ceramics was <150 MPa.

Taking into account the fact that the thermal expansion coefficient of the crystal is anisotropic, our experimental results and theoretical calculations concerning the type of residual stress agree. As can be noted in Table 2, however, there are differences between the theoretical and experimental stress magnitudes for each crystallographic plane. On the other hand, these differences are within the limits of experimental error. Due of the lack of data for single crystals, we assumed in our calculations that the Young modulus and the Poisson ratio of the crystalline phase are isotropic. If we take into account the uncertainty which results from this approximation, the overall magnitude of the theoretical and experimental residual stress are consistent with the Raman spectroscopy estimate.

Mathematical solutions for anisotropic stresses adjacent to odd-shaped crystals in commercial glass-ceramics containing a volume fraction $\geq$ 15% of crystals are complex and should be solved using finite element computer simulations.

6. Conclusions

It is necessary to take into account the anisotropy of the thermal expansion coefficient and elastic constants of silicate crystals to make a proper evaluation of residual stresses in glass-ceramics. For the lithium silicate glass-ceramic studied here, these stresses were compressive or tensile, depending on the crystallographic direction, and varied from about –120 MPa to +150 MPa. The theoretical and experimental stresses agreed within experimental error, therefore, the Selsing model can give a reasonable estimate of residual stresses even for real, anisotropic, materials.

These stresses have an effect on the mechanical properties of glass-ceramics and should be taken into account by researchers interested in their mechanical properties.

Acknowledgements

We are indebted to Professors Richard Bradt, Luis N. Oliveira and Walter Libardi for stimulating discussions. We also thank Professor João A.H. da Jornada for the Raman spectroscopy measurements. The financial help of FAPESP and PRONEX are fully appreciated. This research was partially performed at LNLS National Synchrotron Light Laboratory, Brazil.

References


