

# The infrared and Raman spectra of $\text{ZrO}_2\text{-SiO}_2$ glasses prepared by a sol-gel process

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Infrared and Raman spectra were measured and interpreted on the basis of structure for various  $\text{ZrO}_2\text{-SiO}_2$  glasses that were prepared by a sol-gel process involving zirconium nitrate. Interpretation of the spectra indicates the presence of both Zr-O-Si and Si-O-H linkages depending upon heat treatment conditions, and the evidence of zirconium atoms with eight fold coordination for glasses with high  $\text{ZrO}_2$  contents. The crystalline products formed during glass devitrification were monitored by vibrational spectra. The formation and detection of tetragonal  $\text{ZrO}_2$ , zircon, monoclinic  $\text{ZrO}_2$  and  $\alpha$ -cristobalite depended upon the conditions of devitrification.

## 1. Introduction

Zirconia-containing silicate glasses have attracted much attention because of their excellent resistance to alkali corrosion and their low thermal expansions [1, 2]. Changes of such properties with changes in glass composition intimately depend upon related changes in glass structure. Infrared and Raman spectroscopy are two techniques that can provide such structural information.

Bihuniak and Condrate [3] have investigated the changes in glass structure for  $\text{ZrO}_2\text{-SiO}_2$  glasses containing less than 2 wt %  $\text{ZrO}_2$  with changes in glass composition, using the changes in vibrational spectra and related physical properties. Their glasses were prepared by reacting colloidal silica with zirconium chloride in an aqueous slurry. They related infrared and Raman bands at ca.  $950\text{ cm}^{-1}$  to vibrational modes involving Si-O-Zr linkages. However, there is some question of this assignment due to the low concentration of  $\text{ZrO}_2$  in the glasses. Zhu *et al.* [4] investigated the infrared spectra of glasses containing 30 mol %  $\text{ZrO}_2$  prepared by a sol-gel process. They assigned the observed above-mentioned band due to an Si-OH stretching mode. Nogami [5] also investigated the infrared spectra of  $\text{ZrO}_2\text{-SiO}_2$  glasses prepared by a sol-gel process which contained up to 50 mol %  $\text{ZrO}_2$ . He also assigned the infrared band in the  $900$  to  $1000\text{ cm}^{-1}$  region to Si-OH linkages. A band at  $600\text{ cm}^{-1}$  was assigned to  $\text{ZrO}_8$  units that do not enter into the total anionic framework structure of the glass. D'yakonov *et al.* [6] studied the infrared spectra of silicate glasses containing 20 wt %  $\text{ZrO}_2$ , varying the heat treatment temperature from 20 to  $1000^\circ\text{C}$ . They suggested that the band at ca.  $950\text{ cm}^{-1}$  was due to Si-O-Zr linkages. They also suggested that the infrared band at  $610\text{ cm}^{-1}$  for glasses treated above  $700^\circ\text{C}$  was generated by crystalline zircon ( $\text{ZrSiO}_4$ ).

Apparently, there is still some controversy concerning the structural information that has been obtained from infrared spectra of these glasses that are prepared by sol-gel processes. Therefore, both infrared and Raman spectra were used together in this current study in order to obtain a consistent glass structural picture concerning the formation of  $\text{ZrO}_2\text{-SiO}_2$  glasses by the sol-gel process with varying glass compositions and under varying conditions of heat treatment. Also, the nature of the different crystalline forms that were generated under different conditions of devitrification of the glasses were investigated using vibrational spectroscopy.

## 2. Experimental techniques and procedure

Zirconia-containing silica gels were prepared by a sol-gel process which was similar to that used earlier by Zhu *et al.* [4], and is described elsewhere in detail [7]. Tetraethyl orthosilicate (TEOS) and zirconium nitrate were used as precursor materials. Silica gels containing 7.4 to 64.0 mol %  $\text{ZrO}_2$  were formed. They were then dried at  $50^\circ\text{C}$  for seven days, and were heat-treated to remove organic and nitrate compounds. The heat-treatment schedule for these gels is listed elsewhere [7]. Samples containing 42.4 and 64.0 mol %  $\text{ZrO}_2$  were also heat-treated on different schedules in order to investigate the effect of the heat-treatment schedule on their devitrification.

Infrared spectra ( $4000$  to  $350\text{ cm}^{-1}$ ) were measured on a double-beam grating infrared spectrometer with an air purging system, using the KBr pellet technique. Raman spectra were measured using the green line ( $514.5\text{ nm}$ ) of an argon-ion laser. Raman spectra were collected using  $90^\circ$  optics and photon counting. Samples were mounted after various stages of heat treatment in the laser beam for analysis. X-ray diffraction patterns were measured for the treated gels on a powder

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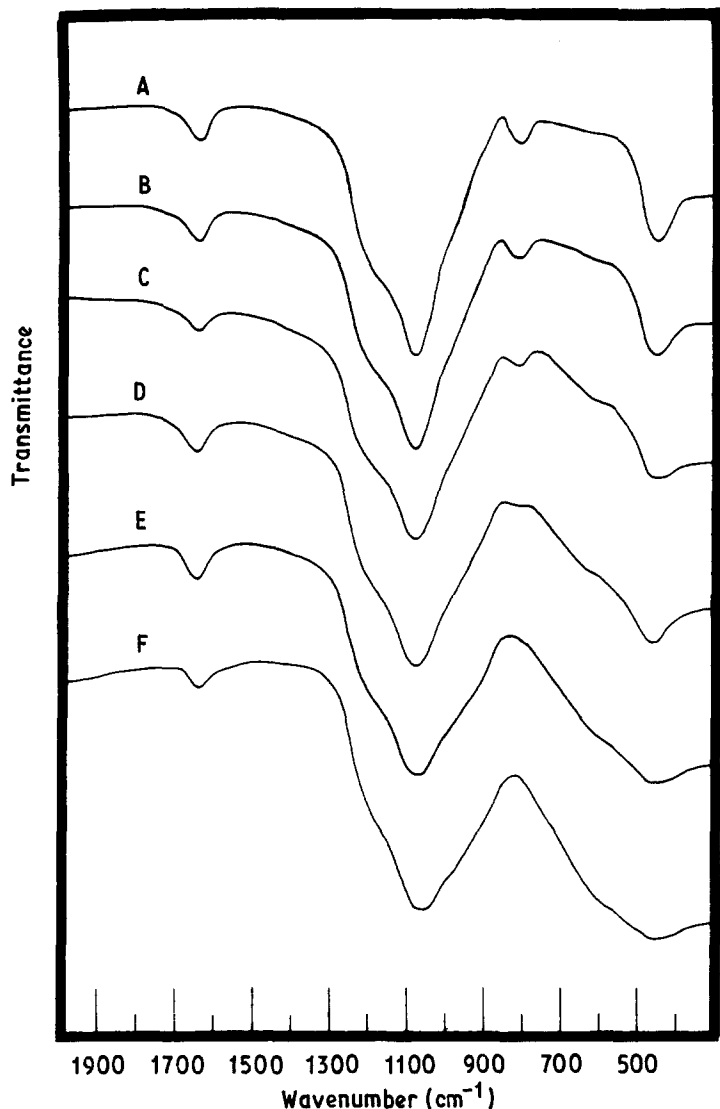


Figure 1 Infrared spectra of  $x\text{ZrO}_2-(100-x)\text{SiO}_2$  gels heat-treated at  $500^\circ\text{C}$ . (A)  $x = 7.4$ ; (B)  $x = 14.1$ ; (C)  $x = 27.2$ ; (D)  $x = 42.4$ ; (E)  $x = 55.0$ ; (F)  $x = 64.0$ .

X-ray diffractometer using  $\text{CuK}\alpha$  radiation with a single-crystal graphite monochromator.

### 3. Results and discussion

#### 3.1. Samples heat-treated at 500 and $700^\circ\text{C}$

Figs 1 to 3 illustrate the infrared and Raman spectra for various gels which were heat-treated at 500 and  $700^\circ\text{C}$ . X-ray diffraction analysis indicates that most of these materials were non-crystalline except for gels containing 55 and 64 mol %  $\text{ZrO}_2$  fired at  $700^\circ\text{C}$ .

The vibrational modes generated by the Si-O stretching and related bending vibrations associated with the pure silica network can be observed in the infrared spectra of the  $\text{ZrO}_2\text{-SiO}_2$  glasses (Figs 1 and 2). In addition to these bands, several other infrared bands can be observed at 1640, 975 and  $600\text{ cm}^{-1}$ . The band at ca.  $1640\text{ cm}^{-1}$  is associated with bending vibrations of  $\text{H}_2\text{O}$  in the glass phase. Bands associated with the silica network can also be seen in the Raman spectra (Fig. 3). The Raman band observed at ca.  $440\text{ cm}^{-1}$  can be assigned to a symmetric silicate bending vibration. Also, the Raman bands observed for materials containing low  $\text{ZrO}_2$  contents at 600 and  $490\text{ cm}^{-1}$  can be assigned to defects described by earlier investigators for pure silica [8-12]. In addition, Raman bands are observed at 975, 954 and  $550\text{ cm}^{-1}$ . The additional bands in the Raman and infrared

spectra of  $\text{ZrO}_2\text{-SiO}_2$  glasses are related to the presence of zirconium ions in the glass structure, and will be discussed in the following paragraphs in detail.

Fig. 1 specifically illustrates the infrared spectra of gels which were heat-treated at  $500^\circ\text{C}$ . As the zirconia content increases, the band at ca.  $800\text{ cm}^{-1}$  which is related to the silica network decreases in intensity. This infrared intensity change was observed earlier by Nogami [5], and indicates that the silicate network is broken down by introducing  $\text{Zr}^{4+}$  ions into the glass structure.

As mentioned earlier, an infrared band can be observed in the infrared spectra at  $975\text{ cm}^{-1}$ . This band is also observed at  $975\text{ cm}^{-1}$  in the Raman spectra of the gels treated at  $500^\circ\text{C}$ . For these materials, the band can be assigned mainly to a vibrational mode involving Si-OH stretching motion. This band assignment is consistent for the material heated at  $500^\circ\text{C}$  because there is no change in its wavenumber, and no increase in its intensity as the zirconia content increases. The intensity of the Raman band decreases rather than increases as the zirconia content increases. This decrease apparently occurs because the activation energy for dissociation of hydroxyl groups decreases when zirconia is introduced into silicate glasses, so that the rate of dissociation of hydroxyl groups during the formation of Si-O-Zr and Si-O-Si linkages

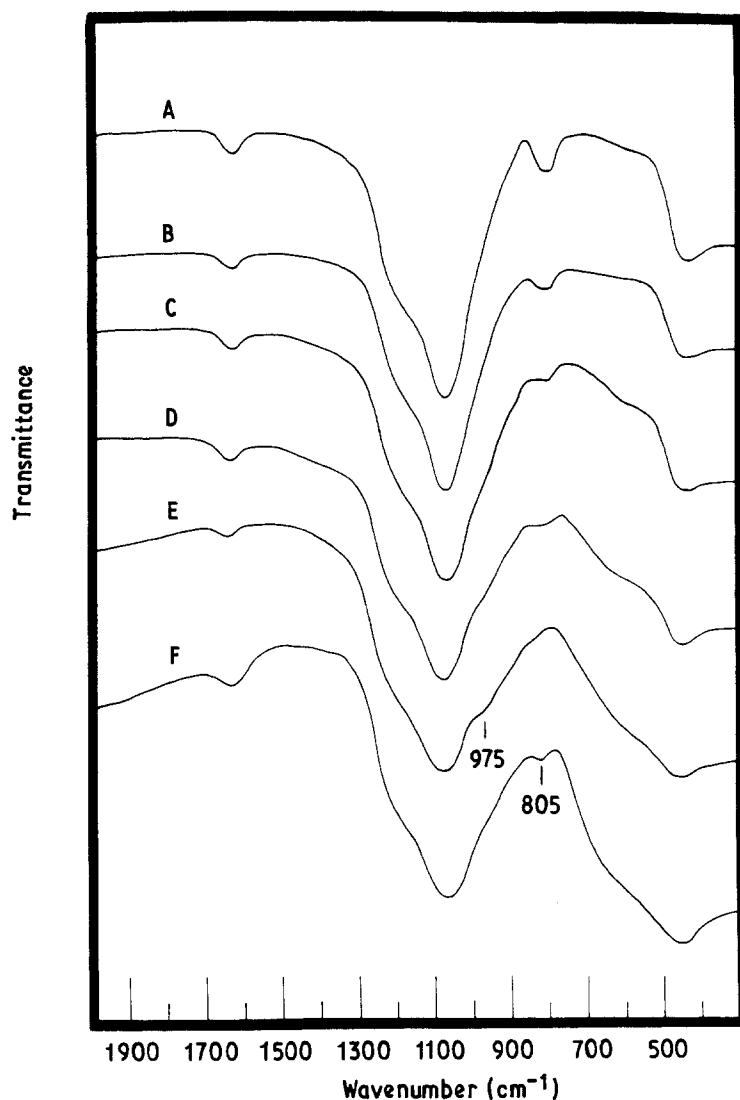


Figure 2 Infrared spectra of  $x\text{ZrO}_2-(100-x)\text{SiO}_2$  gels heat-treated at  $700^\circ\text{C}$ . (A)  $x = 7.4$ ; (B)  $x = 14.1$ ; (C)  $x = 27.2$ ; (D)  $x = 42.4$ ; (E)  $x = 55.0$ ; (F)  $x = 64.0$ .

increases as the  $\text{ZrO}_2$  concentration increases. Nogami [13] has calculated the activation energy for the dissociation of hydroxyl groups by measuring the shrinkage of gels during heat treatment, and assuming that the shrinkage was due only to hydration and condensation. However, the shrinkage of the gels is not only due to hydration and condensation mechanisms. This point has been mentioned earlier by Brinker and co-workers [14–16]. Two other possible mechanisms for gel shrinkage are capillary contraction due to increasing surface energy as the pore surfaces are dehydroxylated, and structural relaxation which occurs by diffusive motions of the polymeric network, resulting in reduced excess free volume without the expulsion of water or other products. Even though Nogami's assumption is a rough approximation neglecting these other contributions to gel shrinkage, his predictions are consistent with the Raman data that are obtained in this study. In other words, the spectral results in this study seem to indicate that the major shrinkage upon heat treatment of the gels at the lower applied temperatures may be due to the hydration and condensation processes.

One may note that there is a band at ca.  $900\text{ cm}^{-1}$  in the Raman spectra of several gel samples (for example, see Fig. 3). This band has been reported earlier by Bertoluzza *et al.* [17] in a study of silica glasses prepared by a sol-gel process. However, they

did not make any band assignments. This band may be due to either the silica structure of the glass or the capillary tube which was used as a sample holder.

Fig. 2 illustrates the infrared spectra of gels treated at  $700^\circ\text{C}$  after treatment at  $500^\circ\text{C}$ . In these cases, the resulting spectral data seem to indicate that the band at  $975\text{ cm}^{-1}$  is mainly due to a vibrational mode involving Si–O–Zr linkages. There are two different infrared spectral details that appear to argue this probability. First, the change in the intensity of this band with increasing treatment temperature is consistent. The gel containing 55 mol %  $\text{ZrO}_2$  which was treated at  $700^\circ\text{C}$  possesses a more intense infrared band than the same gel treated at  $500^\circ\text{C}$ . The concentration of Si–O–H linkages should decrease at the higher temperature due to the formation of either Si–O–Zr or Si–O–Si linkages. An infrared band observed at  $3440\text{ cm}^{-1}$  is associated with stretching vibrations involving OH groups. The intensity of this band decreases as the heat-treatment temperature increases, suggesting the gradual evaporation of water and the progressive condensation of the gel during heating. On this basis, the intensity of the band at  $975\text{ cm}^{-1}$  should decrease during treatment at  $700^\circ\text{C}$  if it is generated by a vibrational mode involving Si–OH stretching motion. Therefore, since the intensity increases, the band at  $975\text{ cm}^{-1}$  can be more reasonably assigned mainly to a vibrational mode involving

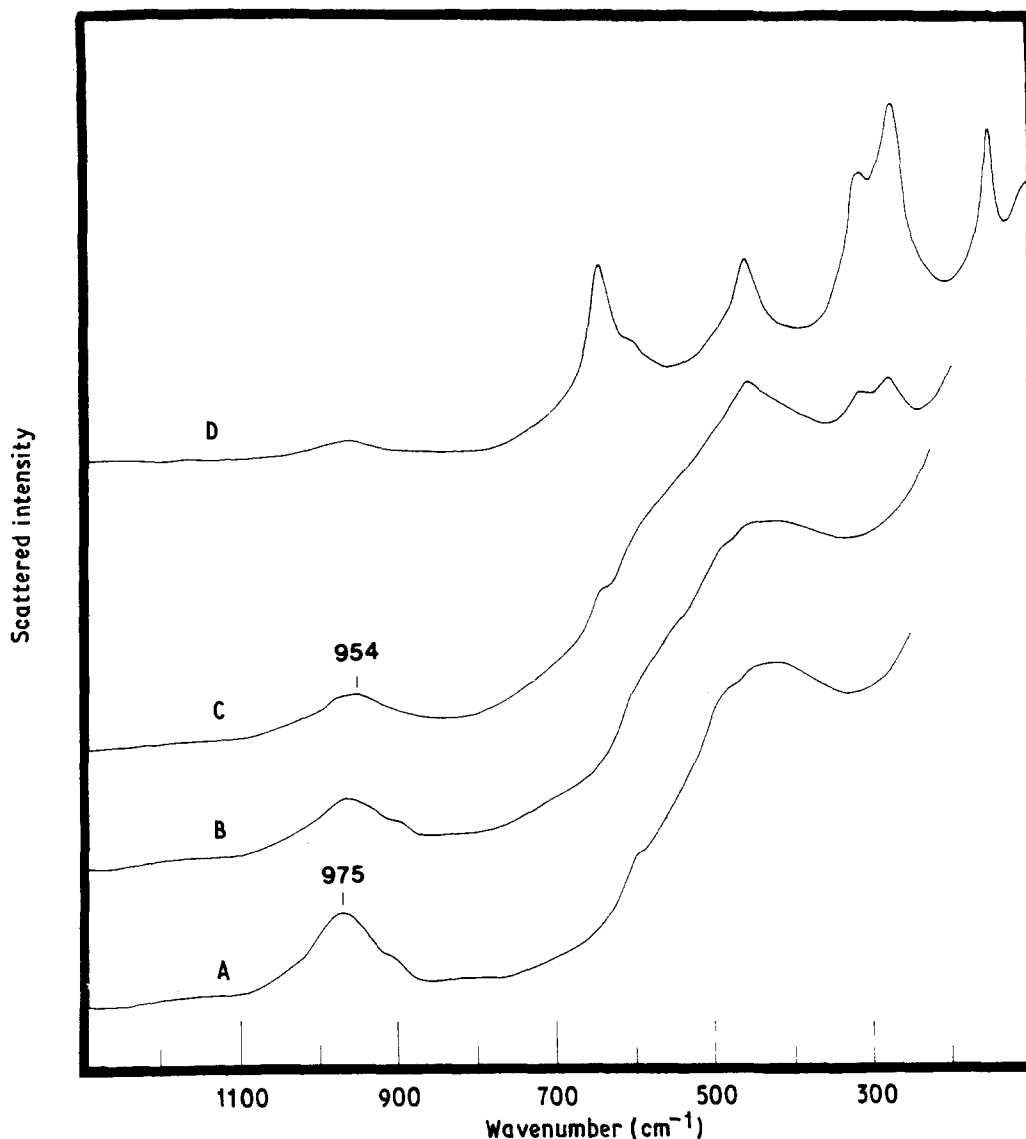


Figure 3 Raman spectra of  $x\text{ZrO}-(100-x)\text{SiO}_2$  gels heat-treated at  $700^\circ\text{C}$ . (A)  $x = 27.2$ ; (B)  $x = 42.4$ ; (C)  $x = 55.0$ ; (D)  $x = 64.0$ .

Si-O-Zr linkages rather than Si-O-H linkages. The intensity changes should follow the concentration change of Si-O-Zr linkages if the band is mainly associated with their vibration. Earlier studies [18, 19] have observed similar bands at ca.  $975\text{ cm}^{-1}$  for related silicate glasses, and assigned them to vibrational modes involving Si-O-M linkages (M = metal).

A second infrared detail that argues for the above-mentioned assignment is the lower intensity of this band for the gel containing 64 mol %  $\text{ZrO}_2$  heated at  $700^\circ\text{C}$ , as compared to that of the gel containing 55 mol %  $\text{ZrO}_2$ . X-ray diffraction analysis indicates that the former material possesses significant amounts of devitrified tetragonal zirconia. The infrared intensity decreases for this material can be explained by the decrease of Si-O-Zr linkages due to the exsolution of  $\text{ZrO}_2$ . An intensity increase is also observed for the band at  $800\text{ cm}^{-1}$  along with the intensity decrease for the band at  $975\text{ cm}^{-1}$ . This intensity increase occurs because of the formation of the new Si-O-Si linkages due to exsolution of  $\text{ZrO}_2$ . These observed features in the infrared spectra cannot be explained if the band at  $975\text{ cm}^{-1}$  for the treatment at  $700^\circ\text{C}$  is generated mainly by a vibrational mode involving Si-O-H linkages.

The infrared interpretation is also consistent with the analysis of the observed Raman spectra for the related materials. Fig. 3 illustrates the Raman spectra of the gel containing 55.0 mol %  $\text{ZrO}_2$  treated at  $700^\circ\text{C}$ . Comparing its spectra to the spectra of gels treated at  $500^\circ\text{C}$ , a shifted band can be observed at ca.  $954\text{ cm}^{-1}$ . This shifted band can be assigned mainly to a vibrational mode involving Si-O-Zr linkages, because the intensity of this band increases as the zirconia content increases up to 55.0 mol %, following the intensity changes for the infrared band at  $975\text{ cm}^{-1}$ . The intensity of this Raman band decreases for the gel containing 64 mol %  $\text{ZrO}_2$ , as with the related infrared band. As mentioned earlier for the infrared band, this intensity decrease can be explained by the break-up of Si-O-Zr linkages due to the exsolution of  $\text{ZrO}_2$  as tetragonal zirconia. Parallel to the intensity change, the Raman band at  $954\text{ cm}^{-1}$  for the sample containing 55.0 mol %  $\text{ZrO}_2$  also shifts back to higher wavenumbers with increase in  $\text{ZrO}_2$  content upon heating at  $700^\circ\text{C}$ . This band shift seems to indicate that Si-O-H linkages are making a larger contribution to the intensity of the band in this wavenumber region for the sample containing 64.0 mol %  $\text{ZrO}_2$ .

Broad bands can be observed at ca.  $600\text{ cm}^{-1}$  in the

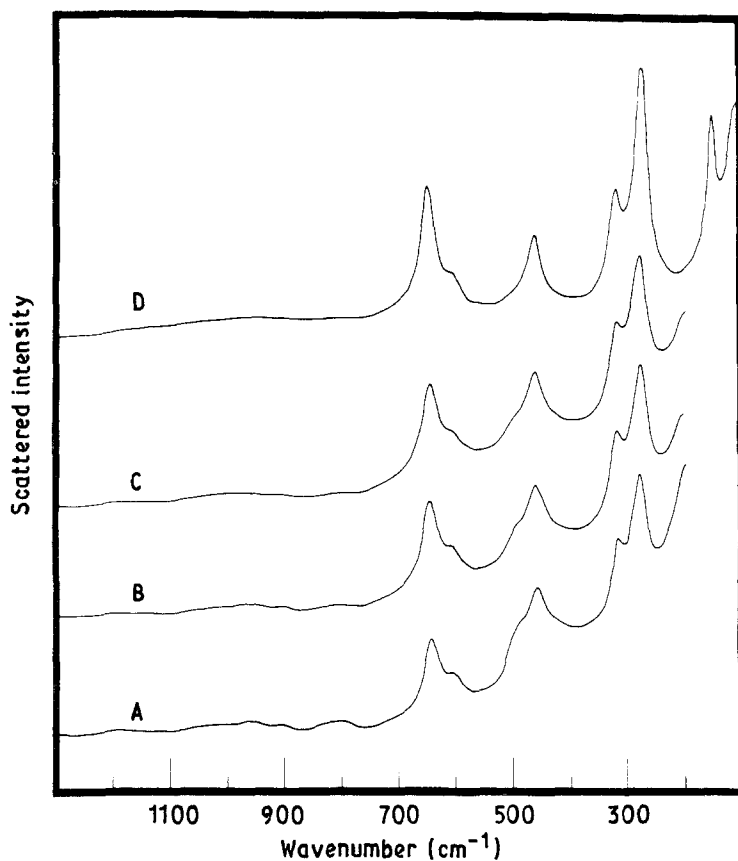


Figure 4 Raman spectra of  $x\text{ZrO}_2-(100-x)\text{SiO}_2$  gels heat-treated at  $900^\circ\text{C}$ . (A)  $x = 27.2$ ; (B)  $x = 42.4$ ; (C)  $x = 55.0$ ; (D)  $x = 64.0$ .

infrared spectra, and at ca.  $550\text{ cm}^{-1}$  in the Raman spectra of gels treated at either  $500$  or  $700^\circ\text{C}$ . Previous investigators have related the intensity increase of the infrared band to the generation of a crystalline phase in the gels upon heat treatment [6, 20]. However, these bands are observed both in the infrared and Raman spectra for such gels without any indication of a crystalline phase in their powder X-ray diffraction patterns. This result suggests that bands in this region of the spectra can be related to the structural features in the  $\text{ZrO}_2\text{-SiO}_2$  glasses before devitrification as well as the crystalline phases that are present after heat treatment of the gels. D'yakonov *et al.* [6] assigned the infrared band to crystalline zircon because the most intense infrared band for zircon appears at ca.  $600\text{ cm}^{-1}$  [21]. Since this band was observed in the infrared spectra, the zircon-type atomic arrangement was considered as a possibility in the glass structure. However, this type of atomic arrangement in the glass can be excluded on the basis of the Raman spectra. Crystalline zircon does not have a Raman band in the  $550$  to  $600\text{ cm}^{-1}$  region [21–23], whereas gels treated at  $500$  and  $700^\circ\text{C}$  possess a broad Raman band at  $550\text{ cm}^{-1}$  whose intensity increases with  $\text{ZrO}_2$  content. This spectral observation suggests either that this Raman band may not involve similar modes involving vibrations of silicon atoms, or that the contribution of silicon atoms to this band for the  $\text{ZrO}_2\text{-SiO}_2$  glass structure may be very small. Therefore, it appears that this band is mainly generated by vibrational motions involving Zr–O bonds in the  $\text{ZrO}_2$ -rich phase in the glass.

The wavenumber and/or intensity of vibrational modes involving Zr–O bonds will vary depending upon the arrangement of oxygen atoms around zirconium atoms. Several zirconium–oxygen structural

units can be considered with respect to the Zr–O stretching modes: (i)  $\text{ZrO}_4$  units, (ii)  $\text{ZrO}_6$  units, (iii) monoclinic zirconia-type  $\text{ZrO}_7$  units, (iv) tetragonal zirconia-type  $\text{ZrO}_8$  units, and (v) cubic zirconia-type  $\text{ZrO}_8$  units.

Conzalez-Vilchez and Griffith [24] reported the vibrational spectra of  $\text{Li}_2\text{ZrO}_4$  in which zirconium atoms are coordinated by four oxygen atoms. No Raman band was observed in their spectra at ca.  $550\text{ cm}^{-1}$ , suggesting that the band in this region for the glass is not due to  $\text{ZrO}_4$  units. Another spectral argument supporting the absence of large concentrations of such structural units involves the consideration of the intensity of the Raman band at  $954\text{ cm}^{-1}$ . This band is significantly less intense for  $\text{ZrO}_2\text{-SiO}_2$  glasses than the related band for  $\text{TiO}_2\text{-SiO}_2$  glasses containing comparable molar amounts of metal oxide [18]. Both zirconium and titanium atoms should contribute to the intensity of this type of mode. If  $\text{ZrO}_4$  units exist in  $\text{ZrO}_2\text{-SiO}_2$  glasses, the intensity of the band should be higher than for  $\text{TiO}_2\text{-SiO}_2$  glasses which possess  $\text{TiO}_4$  units. One would expect this intensity trend because the polarizabilities of zirconium atoms and ions are larger than those for titanium atoms and ions.

Pasto and Condrate [25] have studied the Raman spectra of several perovskite zirconates, which contain zirconium atoms coordinated by six oxygen atoms. They found bands at ca.  $550\text{ cm}^{-1}$  for all investigated materials, which were assigned to vibrational modes involving Zr–O stretching motion. However, the intensities of these bands were very low. The intensity of this feature for perovskite zirconates implies that the Raman band observed for the glasses may not be generated by such  $\text{ZrO}_6$  units. The observed Raman

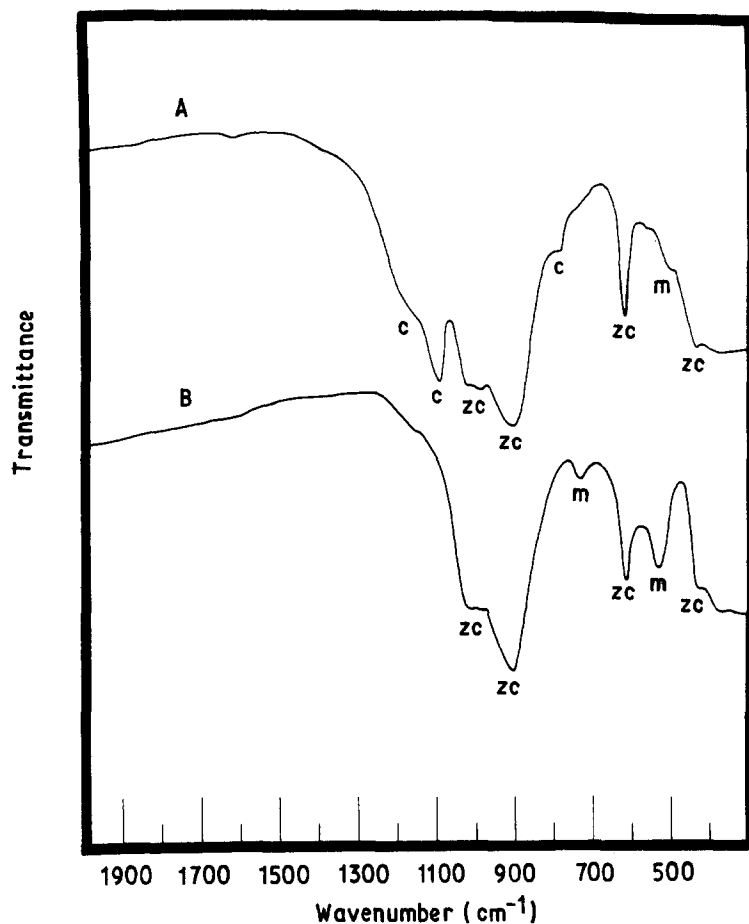


Figure 5 Infrared spectra of  $x\text{ZrO}_2-(100-x)\text{SiO}_2$  gels heat-treated at  $1100^\circ\text{C}$ . (A)  $x = 42.4$ ; (B)  $x = 64.0$ . In this and the following figures, zc = zircon, m = monoclinic  $\text{ZrO}_2$ , t = tetragonal  $\text{ZrO}_2$  and c =  $\alpha$ -cristobalite.

band at  $550\text{ cm}^{-1}$  for the treated gels possesses considerable intensity which was not observed for the above-mentioned crystalline material.

There are three other structural units which can generate the above-mentioned bands. For instance, monoclinic zirconia possesses bands in the  $550$  to  $600\text{ cm}^{-1}$  region [26]. However, those bands are considerably weak, and it also possesses stronger Raman bands at ca.  $614$  and  $637\text{ cm}^{-1}$  which are not observed for the glass phases. These observations imply that the Raman band in the  $550$  to  $600\text{ cm}^{-1}$  region may not be generated by  $\text{ZrO}_7$  units similar to those in monoclinic zirconia.

Fig. 3 illustrates the Raman spectra of the gels treated at  $700^\circ\text{C}$  after treatment at  $500^\circ\text{C}$ . The spectra of the gel containing  $64\text{ mol}\%$   $\text{ZrO}_2$  indicate the beginning stages of the crystallization of tetragonal zirconia. Bands observed at  $280$ ,  $316$ ,  $462$  and  $644\text{ cm}^{-1}$  are characteristic Raman bands for tetragonal zirconia [27]. None of these bands are located in the  $550$  to  $600\text{ cm}^{-1}$  region. The lack of bands in this region for the above-mentioned crystalline phase indicates that the Raman bands in this region for the glass material may not be associated with glass structural units similar to those in crystalline tetragonal zirconia.

Keramidas and White [28] reported the Raman spectra of amorphous zirconia. They observed four bands ( $148$ ,  $263$ ,  $476$  and  $550\text{ cm}^{-1}$ ) for the material. They argued that the local atomic arrangement of amorphous zirconia is similar to that of tetragonal zirconia because the first three bands are the characteristic bands for crystalline tetragonal zirconia. However, they did not make any comment concerning the band

at  $550\text{ cm}^{-1}$ . Phillipi and Mazdiyasi [29] reported the Raman spectrum of metastable cubic zirconia. They found only one band at  $490\text{ cm}^{-1}$  for this material. Thackeray [30] suggested that this band is appropriate for cubic zirconia because factor group analysis predicts only one Raman active band for the cubic phase of zirconia, assuming a fluorite structure. There have been many studies of the Raman spectra of dopant-stabilized zirconia including a stabilized cubic phase [31–33]. One band at  $600\text{ cm}^{-1}$  was reported for this latter material which is consistent with factor group theory. Therefore, the band at  $550\text{ cm}^{-1}$  reported by Keramidas and White [28] may be due to the vibrational mode for a cubic-type atomic arrangement for the zirconium and oxygen atoms in amorphous  $\text{ZrO}_2$ .

The same interpretation can possibly be applied to the Raman band observed in the  $550$  to  $600\text{ cm}^{-1}$  region for the glasses investigated in this study containing more than  $42.4\text{ mol}\%$   $\text{ZrO}_2$  (Fig. 3). This band can be due to a similar arrangement of atoms in the glass for the reasons that have been applied in interpreting the spectra of Keramidas and White [28]. Therefore, this Raman band may be associated with the vibration of  $\text{ZrO}_8$  units in an atomic arrangement that may follow the cubic arrangement observed for crystalline zirconia at high temperatures. As mentioned before, this mode may not involve major contributions from vibrations of silicon atoms. These clustered cubic groups are probably found in the zirconia-rich glass phase in the amorphous phase-separated glasses. The opaqueness of the gels containing higher than  $27.2\text{ mol}\%$   $\text{ZrO}_2$  indicates such a phase separation.

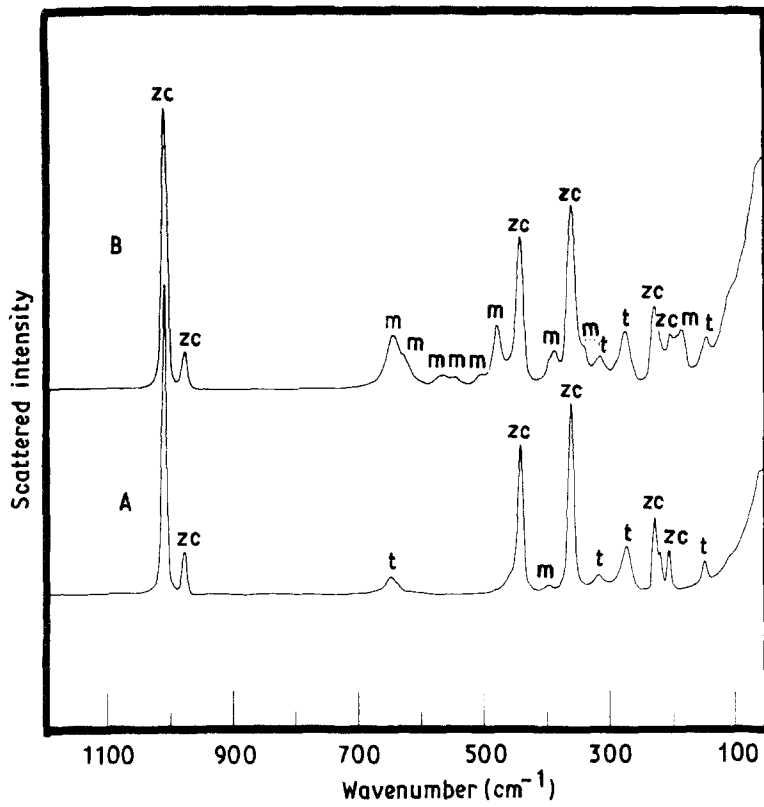


Figure 6 Raman spectra of  $x\text{ZrO}_2-(100-x)\text{SiO}_2$  gels heat-treated at  $1100^\circ\text{C}$ . (A)  $x = 42.4$ ; (B)  $x = 64.0$ .

### 3.2. Devitrified materials heat-treated at higher temperatures

The nature of the heat treatment and the compositions of the  $\text{ZrO}_2\text{-SiO}_2$  gel determines which crystalline phases devitrify. The dominant bands in the infrared

spectra of the gels treated at  $900^\circ\text{C}$  after treatment at  $700^\circ\text{C}$  are associated with the glass phase. The infrared band at  $600\text{ cm}^{-1}$  increases in intensity as the zirconia content increases. This band is now generated by the crystalline phase of tetragonal zirconia which is

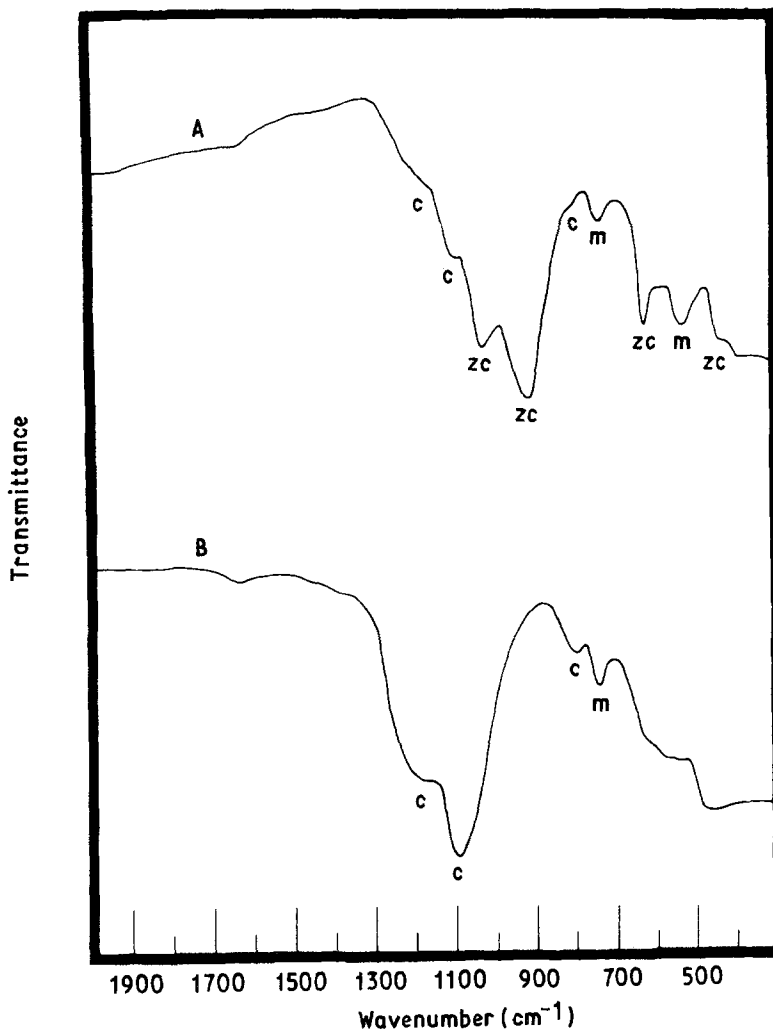


Figure 7 Infrared spectra of (A)  $64.0\text{ZrO}_2-36.0\text{SiO}_2$  gel heat-treated at  $1350^\circ\text{C}$  for 19 h; (B)  $42.4\text{ZrO}_2-57.6\text{SiO}_2$  gel heat-treated at  $1300^\circ\text{C}$  for 2 h.

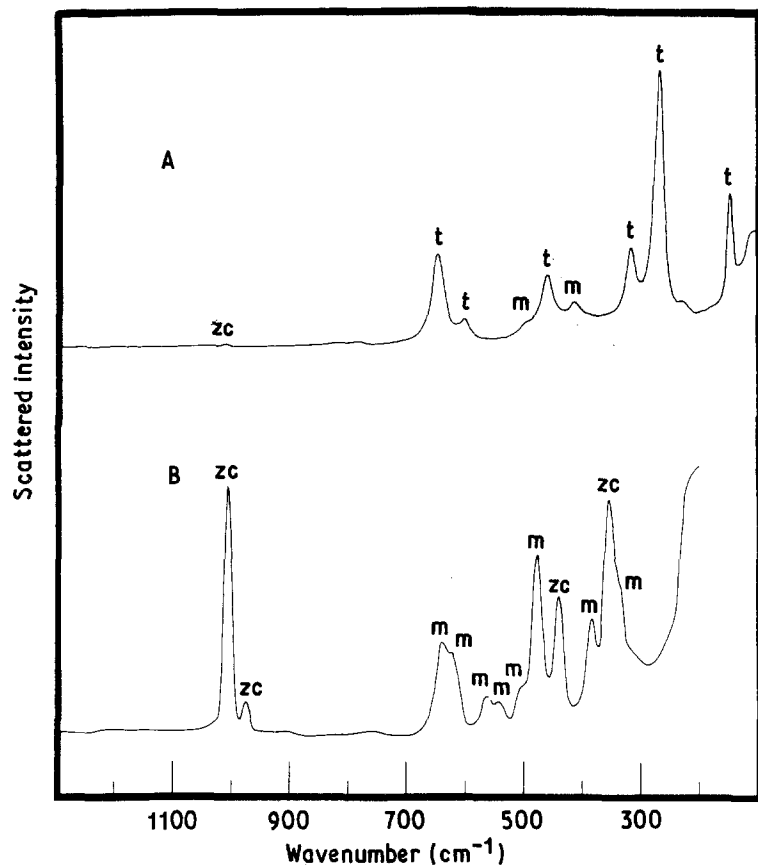


Figure 8 Raman spectra of (A) 42.4ZrO<sub>2</sub>-57.6SiO<sub>2</sub> gel heat-treated at 1300°C for 2 h; (B) 64.0ZrO<sub>2</sub>-36.0SiO<sub>2</sub> gel heat-treated at 1350°C for 19 h.

detected by X-ray diffraction analysis. Raman spectra of the same treated gels are illustrated in Fig. 4. All Raman bands except for the bands at 490 and 800 cm<sup>-1</sup> which are generated by the glass matrix can be assigned to the tetragonal phase of zirconia. The characteristic bands in Raman spectra for the glass are not as strong as the related bands for crystalline zirconia. This intensity trend is not true for the related infrared bands. This spectral difference probably occurs because the polarizabilities of zirconium atoms or ions are much larger than the polarizabilities of silicon atoms or ions.

The wavenumbers of the vibrational modes of tetragonal zirconia observed in this study are somewhat different from the observed values for zirconia stabilized by adding stabilizing ions [27, 31-33]. This difference may be due to differences in structural parameters, especially to differences in the force constants for Zr-O bonds and related bond angles occurring in zirconia stabilized by the addition of stabilizing ions such as yttrium, as compared to those in zirconia stabilized by particle size. There have been many studies which investigated the stabilization of tetragonal zirconia due to the crystalline particle size effect [34-39]. Recently, Nogami and Tomozawa [40] studied the crystallization behaviour of zirconia-silica gels upon heat treatment. They noted that the radius of devitrified tetragonal zirconia particles increased as the heat-treatment temperature and/or the heat-treatment period increased. They also showed that the particles of tetragonal zirconia were stable below  $\approx 40$  nm. They found that the critical size for their ZrO<sub>2</sub> particles was closer to the critical size of free particles ( $\approx 30$  nm) than the critical particle size for constrained particles such as ZrO<sub>2</sub> particles in Al<sub>2</sub>O<sub>3</sub> ( $\approx 600$  nm), even

though the particles of tetragonal zirconia were precipitated in an SiO<sub>2</sub> matrix [37, 39]. In this study, the critical size for tetragonal zirconia was not measured. However, it is obvious in this study that tetragonal zirconia was stabilized for gels treated at lower temperatures by the particle size effect.

Tetragonal zirconia will transform to the monoclinic phase if the particle size for crystalline zirconia exceeds the critical size for tetragonal zirconia. The effect of this transformation (martensitic transformation [38]) can be noted in the infrared and Raman spectra of gels treated under appropriate conditions. Figs 5 and 6 illustrate the infrared and Raman spectra of the gels also treated at 1100°C for 48 h after treatment at 900°C. As may be noted, vibrational bands associated with monoclinic zirconia are present in both spectra [26]. The sizes of the crystals of tetragonal zirconia increase by increasing the devitrification temperature, and the martensitic transformation temperature increases. For such sufficiently large crystals, the transformation occurs to monoclinic zirconia during cooling. The gel containing 64 mol % ZrO<sub>2</sub> contains more monoclinic zirconia because it has a higher zirconia content. Therefore, the size of their ZrO<sub>2</sub> particles is larger after heat treatment of this gel than for the gel containing 42 mol % ZrO<sub>2</sub>. Additionally, the infrared and Raman spectra indicate the presence of the zircon phase for both gels at this treatment temperature, while the  $\alpha$ -cristobalite phase is only detected for the gel containing 42 mol % ZrO<sub>2</sub> [21-23, 41]. One may further note that infrared spectroscopy is more sensitive for detecting  $\alpha$ -cristobalite in these materials than Raman spectroscopy.

Figs 7 and 8 illustrate the infrared and Raman spectra of gels heated at 1300 or 1350°C using a



different heat-treatment schedule. These samples had not been preheated at 900 and 1100°C. Analysis of the spectra for the gel containing 42 mol % ZrO<sub>2</sub> which was heat-treated at 1300°C for 2 h indicates mainly tetragonal zirconia with a small amount of monoclinic zirconia. This phase distribution occurs because the heat-treatment period was not enough for most particles of tetragonal zirconia to grow up to the critical size, at which they transform to monoclinic zirconia. In contrast, the vibrational spectra of the gel containing 64 mol % ZrO<sub>2</sub> which was heat-treated at 1350°C for 19 h indicates large amounts of monoclinic zirconia. The latter treated material contains more monoclinic zirconia because it was heat-treated at a higher temperature for a long period of time, and it contains more zirconia. Also, the spectra of the latter material indicate the presence of crystals of zircon and  $\alpha$ -cristobalite. Again, infrared spectroscopy is more sensitive for detecting  $\alpha$ -cristobalite in these materials than Raman spectroscopy.

#### 4. Conclusions

The infrared and Raman spectra of heat-treated ZrO<sub>2</sub>-SiO<sub>2</sub> gels can be interpreted on the basis of the crystalline and glass phases present. The band observed at ca. 975 cm<sup>-1</sup> in both the infrared and Raman spectra for gels treated at 500°C can be assigned to a vibrational mode involving mainly Si-O-H linkages in the glass. In contrast, the shifted Raman band at 954 cm<sup>-1</sup> and the infrared band at 975 cm<sup>-1</sup> for the gels further treated at 700°C can be assigned to a vibrational mode involving mainly Si-O-Zr linkages. The Raman band at 550 cm<sup>-1</sup> and the infrared band at ca. 600 cm<sup>-1</sup> for gels treated at 500 and 700°C can be generated by cubic zirconia-type ZrO<sub>8</sub> units in the zirconia-rich glass phase. Tetragonal zirconia can be detected by infrared and Raman spectra for gels devitrified at lower temperatures. Crystalline phases such as monoclinic zirconia, zircon and  $\alpha$ -cristobalite can be detected for gels treated at higher temperatures, depending upon the heat-treatment temperature, the period and schedule of treatment, and the glass composition.

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Received 11 September  
and accepted 10 December 1987