RAMAN SPECTROSCOPY: A QUANTITATIVE TOOL FOR
THE STUDY OF DOPED ZIRCONIAS' PHASE
TRANSFORMATION CAUSED BY MOLTEN FLUORIDES

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ABSTRACT

Fully stabilized zirconias (FSZ) were prepared by using CaO, MgO, Y₂O₃, Yb₂O₃, Gd₂O₃ and Nd₂O₃ as dopants. The sintered ceramics were immersed in molten fluorides. Raman spectroscopy was used successfully in order to probe quantitatively the cubic-to-monoclinic transformation (corrosion) caused in the crystal structure of FSZ from the molten fluorides. For this purpose spectra of mixtures of known quantities of FSZ with monoclinic phase were obtained and a calibration curve was established. The curve was found to be a straight line in a plot of the Raman intensity ratio of the 177 versus the 617 cm⁻¹ band against the inverse monoclinic molar fraction. The ceramic with the best performance against corrosion was zirconia with 8 mol % Yb₂O₃ fired at 1600 °C for 2 hours.

INTRODUCTION

The crystal structure of zirconia, one of the best corrosion resistant and refractory materials, is known to change from monoclinic to tetragonal and then to cubic at 1150 and 2200 °C respectively. Small additions of oxides such as MgO, CaO, Y₂O₃ e.t.c. have been used to lower the two transition temperatures and thus act as stabilizers for the tetragonal and the cubic phase (fully stabilized, FSZ). Stabilized zirconia systems have improved mechanical properties with respect to fracture strength and resistance to thermal shock. They are known also to exhibit high ionic conductivity and are used as oxygen/oxide sensors.

Raman spectroscopy has been used in order to study the transformations of pure zirconia and of tetragonal and cubic phase (1,2) during heating and cooling cycle. The transitions from stabilized zirconia's phase to monoclinic after the exposure of the ceramics in the environment of corrosive media have been also investigated (3,4). No quantitative determination for the cubic-to-monoclinic
transformation by Raman spectroscopy is known. The reason is that the spectra of the disordered cubic phase exhibit only a broad continuum decreasing in intensity with increasing frequency and contain few bands with poorly defined maxima.

In the present work Raman spectroscopy was used successfully for determining the percentage of the cubic and monoclinic phase in a zirconia ceramic. For this purpose a calibration curve was obtained by mixing known quantities of doped zirconia powders having cubic crystal structure and pure monoclinic zirconia. The derived calibration curve was then used in order to establish in a quantitative way the resistance ability, regarding the phase transformation, of sintered FSZ after their immersion in molten fluorides. For this purpose different sintering conditions were applied and the CaO, MgO, Y2O3, Yb2O3, Gd2O3 and Nd2O3 were used as dopants in order to find the best conditions and materials for FSZ to be used in molten fluorides bath.

EXPERIMENTAL PROCEDURE

1. **Preparation of Pellets for the Calibration Curve**

   Monoclinic zirconia powder from "Tosoh" and ZrO2 powder fully stabilized with 8 mol % Y2O3 from "Tosoh" and "Zirconia Sales" were used. Mixtures in the correct stoichiometric ratios were prepared, by mixing the powders in a marble mortar, so that the complete range from 0 to 100 mole % of cubic phase could be obtained. In order to avoid the occurrence of a fluorescence signal in the as received material, arising from the presence of some organic impurities, the mixed powders were fired at 1000 °C in the presence of oxygen for two hours. Pellets were prepared from the mixtures by applying a 70 kN pressure. The homogeneity of the pellets was verified by obtaining several spectra for each pellet from different points on the surface.

2. **Identification of Phases (Raman Spectroscopy)**

   Raman spectra were excited with the 488-nm line of a 4 W Spectra Physics argon laser. The plasma lines were removed from the laser beam by using a small monochromator as filter. A cylindrical lens, with 5" focal length, was used to focus the laser line on the sample giving a probed area of approximately 1 mm². The scattered light was collected at an angle of 90° and analyzed with a SPEX 1403, 0.85-m double monochromator equipped with a -20 °C cooled RCA photomultiplier and EG&G/ORTEC photon-counting and amplifier electronics. The power of the incident laser beam was about 100 mW at sample's surface. Typical spectral width and time constant were 1 cm⁻¹ and 0.3 s respectively. The system was also interfaced with computer and the spectra were recorded on X-T recorder's paper and simultaneously were digitized and stored in diskettes. For the necessary
calculations a home-made Fortran program was used. The spectra were excited at room temperature

3. Sintered Fully Stabilized Zirconias Preparation

The zirconia fully stabilized powders used were either purchased from the Zirconia Sales and Tosoh or were prepared by using the co-precipitation method. The powders were uniaxially pressed at 300 MPa. The compacts were sintered in open air for 2-5 h at temperatures ranging from 1200 to 1700 °C. The sintered specimens were in the form of cubes (1 x 1 x 1 cm). The samples exhibiting the presence of the monoclinic phase after the sintering were rejected. The percentage of the stabilizer used was the minimum required for a FSZ. All ceramics samples were prepared by CERECO SA (P.O. Box 146, GR 34100 Chalkis, Greece). The sintered ceramics as well as the stabilizer's percentage, the firing conditions and the physical characteristics (density and pore size) are in Table I.

Table I. Method of Preparation and Physical Properties of Stabilized Zirconias

| MOL % OF STABILIZER | FIRING CONDITION | POROSITY (%) | DENSITY (g/cm³) |
|----------------------|------------------|--------------|-----------------|
| 15 CaO               | 1600 °C, 2h      | 0.70         | 5.03            |
| 8 Gd₂O₃              | 1650 °C, 5h      | 0.15         | 5.88            |
| 15 MgO               | 1700 °C, 2h      | 0.11         | 5.42            |
| 15 Nd₂O₃             | 1600 °C, 2h      | 0.18         | 5.48            |
| 8 Y₂O₃               | 1550 °C, 5h      | 0.15         | 5.99            |
| 8 Yb₂O₃              | 1600 °C, 2h      | 0.14         | 5.78            |

4. Corrosion Tests

Fluoride salts were purchased from Merck (p.a. grade) and were purified further by melt crystallization. A LiF, NaF, KF eutectic (FLINAK) was prepared by mixing the recrystallized compounds in a glove-box. A home-made oven with three heating zones and programmable heating controller and two programmable "Scandiaoven" furnaces were used. All furnaces were equipped with a Ni tube core and were modified in order to accommodate the need for vacuum and/or inert atmosphere. Each of the ceramics was immersed into 50 g of molten FLINAK for a maximum of 15 hours at 700 °C under argon atmosphere. Vitreous carbon crucibles (Le Carbone - Lorraine) were chosen as containers for the FLINAK. The solidified FLINAK was removed mechanically after submerging the samples into water for 48 hours.
RESULTS AND DISCUSSION

1. Deriving the Calibration Curve

The spectrum of the pure monoclinic zirconia powder (Fig. 1.E) exhibits 16 out of the 18 theoretical predicted bands (5,6). Assuming a fluorite structure for ZrO₂ in the cubic phase one should expect only one Raman active frequency but the spectra for doped zirconia's cubic structure are characterized with a broad band in the area of 617 cm⁻¹ together with a high "background" profile (Figure 1.A). The absence of sharp well defined peak has been attributed to the structural disorder associated with the oxygen sublattice (7). In contrast, the bands of the well ordered monoclinic phase are sharp and intense.

In order to correlate the appearance of a zirconia ceramic spectrum with the percentage of the cubic and the monoclinic phase present, a number of pellets were prepared from powder mixtures with known phase percentage. Two sets of pellets were used with cubic phase powder from different manufacturer ("Zirconia Sales" and "Tosoh") in order to test if the calibration curve is "universal" or depends on powders' characteristics.

Our objective was to find an easy and reliable method for calculating each phase's percentage, and thus we used the peak and not the integrated intensities of the bands. The differences in the measured intensities of the different spectra made apparent that only relative factors within each spectrum e.g. ratio of intensities, could be used.

The 177 cm⁻¹ band of the monoclinic phase was chosen for the quantitative study since it exhibits very strong intensity even in the spectra excited from pellets having small percentage of the monoclinic phase (Fig. 1.B). On the other hand the spectra of Fig. 1 suggest that the only criteria in the estimation of the cubic's phase percentage was the cubic's broad band, which unfortunately overlaps with a monoclinic peak, at 617 cm⁻¹.

The intensity of a Raman line depends on a number of factors including incident laser power, frequency of the scattered radiation, absorptivity of the materials involved in the scattering, and the response of the detection system. Thus, the measured Raman intensity, I(ν), can be represented (8) as:

$$I(ν) = I_0 K(ν) C$$

where I₀ is the intensity of the excitation laser line, ν is the Raman shift, K(ν) is a factor which includes the frequency dependent terms: the overall spectrophotometer response, the self-absorption of the medium and the molecular scattering properties. C is the concentration of the Raman active species.
As it was mentioned previously, in the pellet's spectra an overlap of a monoclinic and the cubic peak exists at 617 cm\(^{-1}\). Therefore, the intensity at this wavenumber is the sum of the intensities of the monoclinic, \(I_0 K_m^{617} \chi_m\), and the cubic phase, \(I_0 K_c^{617} (1-\chi)\). Where \(\chi\) is the monoclinic's phase molar fraction in a pellet. The superscript of the \(K\) is the Raman shift of the peak while the subscript represents the phase, \(m\) for monoclinic and \(c\) for cubic. A ratio of the intensity of the 617 cm\(^{-1}\) band to the intensity of the 177 cm\(^{-1}\) peak will yield:

\[
\frac{I_{617}^{m}}{I_{177}^{m}} = \frac{K_c^{617}}{K_m^{177}} \frac{1}{\chi_m} + \frac{K_m^{617} - K_c^{617}}{K_m^{177}}
\]

Where \(I_{617}^{m}\) and \(I_{177}^{m}\) represent the measured intensity of the 617 cm\(^{-1}\) band and the intensity of the monoclinic's phase peak at 177 cm\(^{-1}\) respectively. \(K_m^{177}\) is the frequency dependent constant for the 177 cm\(^{-1}\) monoclinic phase peak.

The plot of the intensity ratio of \(I_{617}^{m}\) to \(I_{177}^{m}\) versus the \(\chi_m\) is in Fig. 2. For convenience the scale for x-axis is logarithmic. The value of the \(I_{617}^{m}\) was obtained by subtracting from the total measured intensity at 617 cm\(^{-1}\) the "background" intensity of the 800 cm\(^{-1}\). The exact wavenumber corresponding to the maximum intensity of the peak was determined by a computer-aided (c.a) search of the digitized spectra, between the 610 and 620 cm\(^{-1}\). The 800 cm\(^{-1}\) was arbitrary chosen as the spectral point where the "background" level is zero since at this wavenumber the intensity of all the pellet's spectra reaches a constant value.

The wavenumber of the monoclinic peak (177 cm\(^{-1}\)) was c.a searched between the 170 and 182 cm\(^{-1}\) and its intensity, \(I_{177}^{m}\), was calculated by subtracting the "background" for the 177 cm\(^{-1}\). The "background" was defined as the line passing through the two data points, one on each side of the peak, with the lowest intensity value. The data points specifying the monoclinic's peak "background" line were located by searching for the lowest intensity data point between the 145 to 170 cm\(^{-1}\) and 182 to 210 cm\(^{-1}\) respectively.

In order to avoid problems arising from random spectral noise, the intensity values used were averaged with the intensities of the neighboring data points. Several Raman spectra were recorded for each composition and the data in the plot (Fig. 2) are the mean values of the real data. No difference was observed between the data obtained from pellets made from "Tosoh's" and "Zirconia Sales" cubic powder. Therefore the method is independent of powders' origin and can be applied to any doped zirconia ceramic undergoing a cubic to monoclinic transformation. A linear regression on all data yields the following equation:

\[
\frac{I_{617}^{m}}{I_{177}^{m}} = \frac{1}{0.11 + 0.26 \chi_m}
\]
The correlation coefficient was 0.9995 while the standard errors for the slope and the intercept were ± 6.4 \times 10^{-3} and ± 2.1 \times 10^{-2} respectively.

2. Dependence of FSZ Endurance in Fluorides Melts on Stabilizer's Cation

The FSZ ceramics of the Table I were immersed in FLINAK for 15 h and at 700 °C. Raman spectroscopy was applied in order to measure the extent of crystal's structure transformation which was caused by FLINAK and the spectra were obtained, at room temperature, from samples' surface before and after the treatment. The use of Raman spectroscopy as an analytical tool for the cubic-to-monoclinic transformation was based on the intensities of the 617 and 177 cm\(^{-1}\) bands which were measured as was described previously. The monoclinic’s phase molar fraction was obtained by using the calibration curve given by equation [3].

There is a profound dependence of ceramics’ endurance in fluoride melts on on stabilizer’s cation size and charge. As a measure of size's and charge's influence the value of Q'\(r^+\) was determined, where Q' represents the ion's charge and r' the ionic radius. In Fig. 3 the Q'\(r^+\) for the different dopant cations are plotted against their respective monoclinic molar fraction values which were calculated from equation [3]. A linear relationship between Q'\(r^+\) values and corrosion exists. Thus the Yb\(^{3+}\) having the largest Q'\(r^+\) value, 5.60 \times 10^{-9} \text{Cb m}^{-1}, is also the more resistant stabilizer. Zr\(^{4+}\) is not expected to react with fluorides since its Q'\(r^+\) value, 8.1 \times 10^{-9} \text{Cb m}^{-1}, is by far the largest among those presented in Fig. 3.

CONCLUSIONS

A calibration curve for calculating the percentage of zirconia’s cubic and monoclinic phase when both are present in a ceramic, by Raman spectroscopy, was developed. A plot of the Raman intensity ratio of the 617 cm\(^{-1}\) band to the 177 cm\(^{-1}\) monoclinic peak against the inverse monoclinic’s phase molar fraction found to yield a straight line. The intensity of the monoclinic peak was calculated by subtracting the "background". In contrast, the intensity for the 617 cm\(^{-1}\) which is attributed to both phases was determined including the "background".

The calibration curve was applied on Raman spectra obtained from zirconias which were stabilized with either CaO, MgO, Y\(_2\)O\(_3\), Yb\(_2\)O\(_3\), Gd\(_2\)O\(_3\) or Nd\(_2\)O\(_3\), after their immersion in molten FLINAK. The quantitative results revealed a dependence between the stabilizer's cation size and charge and the resistance of the FSZ to the phase transformation caused from molten fluorides. Thus the zirconia having as dopant Yb\(_2\)O\(_3\) (largest cation size to charge ratio) is also the more resistant.
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Figure 1: Raman spectra of pellets prepared from A: ZrO$_2$- 8 mol % Y$_2$O$_3$ (cubic phase); B: mixture of 10 % pure ZrO$_2$ (monoclinic phase) with 90 % cubic phase; C: mixture of 25 % monoclinic phase with 75 % cubic phase; D: mixture of 70 % monoclinic phase with 30 % cubic phase; E: pure ZrO$_2$ (monoclinic phase) Spectra were excited at 20 °C; $\lambda_0$=488.0 nm; spectral slit width, 1 cm$^{-1}$.

![Raman spectra](image)

Figure 2: $I^{177}/I_{m}^{177}$ vs. $\chi_{m}^{-1}$.

Figure 3: $Q^{+}/r^{+}$ vs. $\chi_{m}$. 

ZIRCONIA SALES' powder
TOSOH'S powder

Yb$^{3+}$
Y$^{3+}$
Gd$^{3+}$
Mg$^{2+}$
Nd$^{3+}$
Ca$^{2+}$