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Quantitative determination of the cubic, tetragonal and monoclinic phases in partially stabilized zirconias by Raman spectroscopy

C. G. KONTOYANNIS*, M. ORKOULA
Institute of Chemical Engineering and High Temperature Chemical Processes, and Department of Pharmacy, University of Patras, P.O. Box 1414, GR 26500 Patras, Greece

Vibrational Raman spectroscopy was employed successfully for the simultaneous quantitative determination of the cubic, tetragonal and monoclinic phases of partially stabilized zirconia. Pressed pellets with known composition were prepared and used as standard mixtures. From the standard pellets, a calibration curve was obtained which was found to be a straight line if $(I^{640} - 0.47\ I^{260})/I^{177}$ is plotted against the inverse monoclinic molar fraction. I^{260}, I^{177} are the Raman intensities for the tetragonal and monoclinic peaks at 260 and 177 cm^{-1}, respectively, and were calculated by subtracting the "background". In contrast, I^{640} represents the intensity for the 640 cm^{-1} band, which is attributed to all three phases, and was measured including the "background".

1. 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 [1, 2]. Small additions of oxides such as MgO, CaO, and Y_2O_3, have been used to lower the two transition temperatures. When the dopant concentration is equal to or more than that needed for complete stabilization (i.e. for the formation of the cubic, fluorite-type zirconia phase) then the fully stabilized zirconia (FSZ) is formed [3, 4]. When the stabilizer percentage is less than that required for FSZ, then a mixture of cubic and tetragonal phase (partially stabilized zirconia, PSZ) occurs. Stabilized zirconia systems have improved mechanical properties with respect to fracture strength and resistance to thermal shock [5]. However, the application of these ceramics is not without problems, especially in the abrasive environment of molten fluoride baths. A destabilization process occurs leading to a crystal structure transformation and consequently to the alteration of the properties associated with the cubic or the tetragonal phase.

Raman spectroscopy has been used in order to study the transformations of pure zirconia and of PSZ and FSZ [6–14] during the heating and cooling cycle, as well as for the study of the transitions of cubic and/or tetragonal phase(s) of stabilized zirconia to monoclinic after the exposure of the ceramics in an environment of corrosive media [15–17]. Quantitative studies of the phase transitions have been performed for the case of the tetragonal to monoclinic transformation [8, 11–14]. Unfortunately, none of the quantitative determinations has taken into consideration the existence of the cubic phase in PSZ ceramics and thus the molar fraction of the monoclinic phase was miscalculated [8, 11, 13, 14]. The reason for this is the difficulty the cubic spectrum presents for such an investigation because 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 [7].

In the present work, Raman spectroscopy was used successfully for determining the percentage of the cubic, tetragonal and monoclinic phase in a PSZ ceramic. For this purpose, a calibration curve was obtained by mixing known quantities of PSZ powders having cubic and tetragonal crystal structure with pure monoclinic zirconia.

2. Experimental procedure

Monoclinic zirconia powder ("Tosoh") ZrO_2 powder partially stabilized with 3 mol % Y_2O_3 ("Martinswerk"), and ZrO_2 with 8 mol % Y_2O_3 ("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 0–100 mol % monoclinic 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 powders were fired at 1000 °C in the presence of oxygen for 2 h. 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.

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

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* Author to whom correspondence should be addressed.

monochromator as filter. A cylindrical lens, with 5 in focal length, was used to focus the laser line on the sample giving a probed area of approximately 1 mm^2. The scattered light was collected at an angle of 90° and analysed 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 surface. The 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.

The phase content of the ZrO_2–3 mol % Y_2O_3 from "Martinswerk" was determined with X-ray diffractometry. A θ–θ Philips PW 1840/00/10 diffractometer system and CuK_α (50 kV and 40 mA) was used. Scanning speed was 0.3° min^{-1}.

3. Results and discussion

3.1. Theory

The spectrum of the pure monoclinic zirconia powder (Fig. 1a) exhibits 16 out of the 18 theoretically predicted bands [9]. Assuming a fluorite structure for ZrO_2 in the cubic phase, one should expect only one Raman active frequency but the spectra for the cubic structure of doped zirconia are characterized with a broad band from 530–670 cm^{-1} together with a high "background" profile (Fig. 1e). The absence of a sharp well-defined peak has been attributed to the structural disorder associated with the oxygen sublattice [10]. In contrast, the bands of the well-ordered monoclinic phase are sharp and intense. In the spectrum of the PSZ (Fig. 1d), where the tetragonal phase co-exists with the cubic structure, all six Raman modes predicted by group theory for the tetragonal structure are displayed [9].

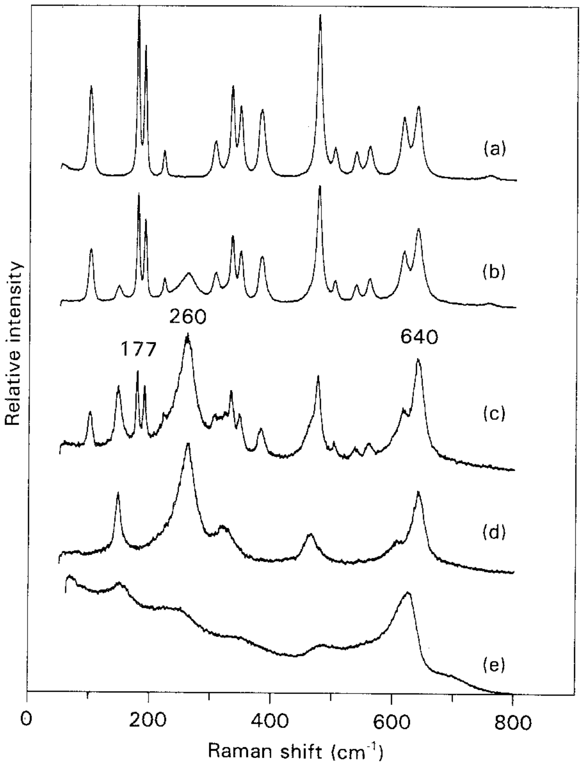

Figure 1 Raman spectra of pellets prepared from (a) pure ZrO_2 (monoclinic phase), (b) a mixture of 75% monoclinic phase with 25% ZrO_2–3 mol % Y_2O_3 (PSZ), (c) a mixture of 30% monoclinic phase with 70% ZrO_2–3 mol % Y_2O_3 (PSZ), (d) ZrO_2–3 mol % Y_2O_3 (cubic and tetragonal phase), (e) ZrO_2–8 mol % Y_2O_3 (cubic phase); spectra were excited at 20 °C, $\lambda_0 = 488.0$ nm, spectral slit width 1 cm^{-1}.

3.2. Determination of the tetragonal molar fraction in the PSZ powder

In order to correlate the appearance of a zirconia ceramic spectrum with the percentage of the cubic, tetragonal and the monoclinic phase present, a number of pellets was prepared. Because no pure tetragonal powder was available, PSZ powder was mixed with a known percentage of the monoclinic phase. Therefore, it was also necessary to estimate the percentage of the tetragonal and cubic phase in the as-received PSZ. The tetragonal fraction was determined, according to [11], from the integrated X-ray intensities ratios of the tetragonal and cubic peaks of a PSZ powder by applying the equation

$$x_t = \frac{1.14[I_t(400) + I_t(004)]}{1.14[I_t(400) + I_t(004)] + I_c(400)} \qquad (1)$$

where x_t is the tetragonal molar fraction and $I_t(400)$, $I_t(004)$, $I_c(400)$ are the integrated intensities, excluding the "background", of the tetragonal crystal structure for (400), (004) and cubic phase for (400), respectively. The 2θ region was scanned from 72.5°–76.0° (Fig. 2). The tetragonal molar fraction of the PSZ was found to be 0.49.

3.3. Method

Our objective was to find an easy and reliable method for calculating the percentage of each phase 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 with each spectrum, i.e. ratio of intensities, could be used (Fig. 1).

The 177 and 260 cm^{-1} bands of the monoclinic and the tetragonal phase, respectively, were chosen for the quantitative study. Both peaks exhibit very strong intensities even in the spectra excited from pellets having a small percentage of the respective phase. The intensity of the 177 and 260 cm^{-1} peaks was measured without their "background", as described in Section 3.6. On the other hand, the only criteria in the estimation of the cubic phase percentage were (a) the high "background" profile, which decreases with the percentage of cubic phase, and (b) the broad band from 610–640 cm^{-1} which unfortunately overlaps with a monoclinic and a tetragonal peak (Fig. 1). Because of the difficulty in assessing the quantitative contribution of the former, especially for mixtures with low cubic concentration, efforts were concentrated on the exploitation of the broad band. The intensity of the

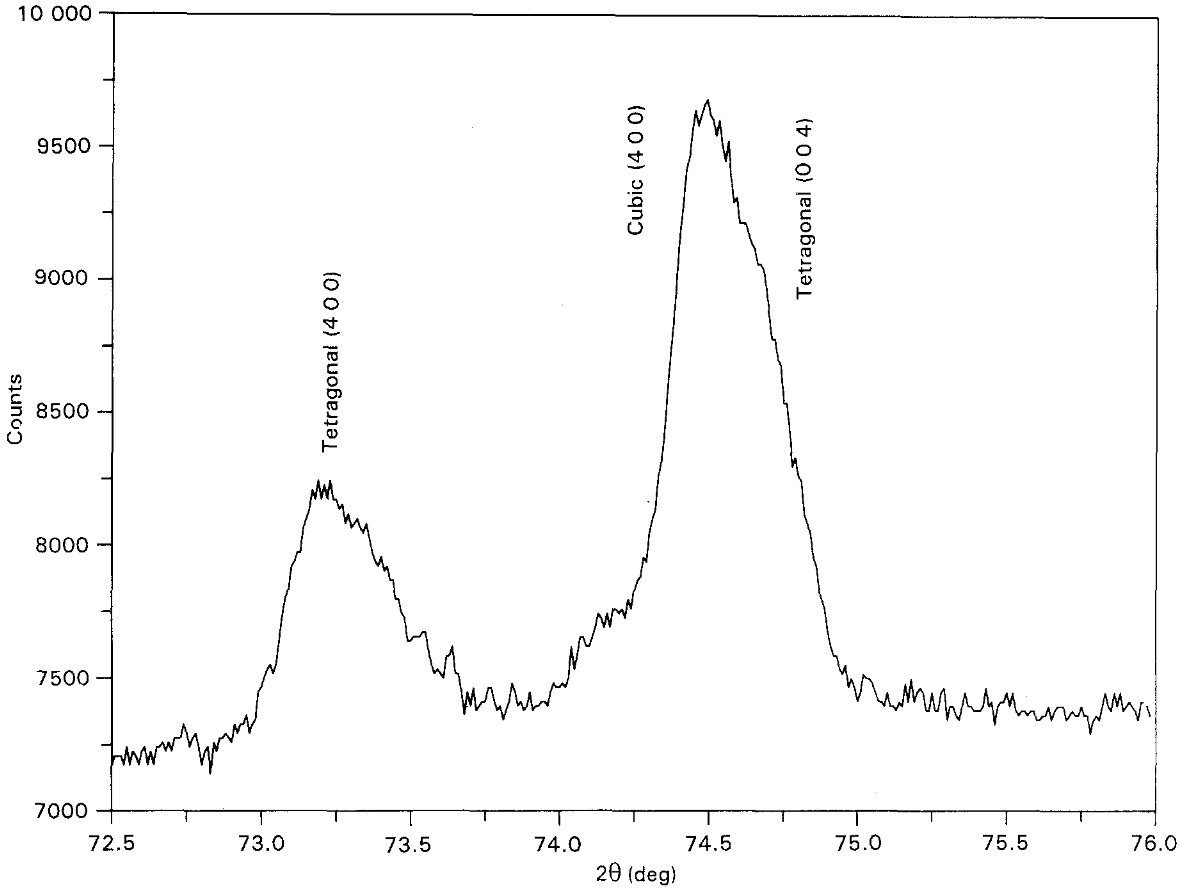

Figure 2 XRD pattern of ZrO_2–3 mol % Y_2O_3 powder for the scanning angle with $2\theta = 72.0°–76.0°$.

cubic band was measured at $640\,cm^{-1}$, and the "background's" intensity, which is due to the presence of the cubic phase, was included.

3.4. Theoretical derivation of the calibration curve for the determination of the monoclinic phase

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, $I(\nu)$, can be represented [18] as

$$I(\nu) = I_0 K(\nu) C \qquad (2)$$

where I_0 is the intensity of the excitation laser line, ν is the Raman shift, $K(\nu)$ 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. In the frequency range of the spectra measurements of zirconia, the overall spectrometer response can be considered constant and thus the ratios of the K factors are dependent only on the scattering parameter associated with each band. Therefore, the values which were obtained for the K ratios can be used for quantitative calculations in every zirconia spectrum which was excited at room temperature and measured with any conventional Raman spectrometric system.

As mentioned previously, in the pellet's spectra the broad band of the cubic phase overlaps with a monoclinic and a tetragonal peak. Therefore, the intensity of the 640 wave number is the sum of the intensities of the monoclinic, $I_0\,K_m^{640}\,\chi_m$, the tetragonal, $I_0\,K_t^{640}\,\chi_t$ and the cubic phase, $I_0\,K_c^{640}\,\chi_c$. Where χ_m, χ_t and χ_c are the molar fractions of the monoclinic, tetragonal and cubic phases, respectively. The superscript to the K is the Raman shift of the peak, while the subscript represents the phase, m for monoclinic, t for tetragonal and c for cubic. A ratio of the intensity of the $640\,cm^{-1}$ band to the intensity of the $177\,cm^{-1}$ peak will yield

$$\frac{I^{640}}{I^{177}} = \frac{x_m K_m^{640} + x_t K_t^{640} + x_c K_c^{640}}{x_m K_m^{177}} \qquad (3)$$

where I^{640} and I^{177} represent the measured intensity of the $640\,cm^{-1}$ band and the intensity of the monoclinic phase peak at $177\,cm^{-1}$, respectively. K_m^{177} is the frequency dependent constant for the $177\,cm^{-1}$ monoclinic phase peak. In addition, the Raman intensity ratio of the tetragonal $260\,cm^{-1}$ peak to the intensity of the $177\,cm^{-1}$ monoclinic peak can be written as

$$\frac{I^{260}}{I^{177}} = \frac{x_t K_t^{260}}{x_m K_m^{177}} \qquad (4)$$

Using Equation 4 and the relationship

$$x_m + x_t + x_c = 1 \qquad (5)$$

Equation 3 can be rearranged as:

$$\frac{I^{640} - FI^{260}}{I^{177}} = \frac{K_{\mathrm{m}}^{640} - K_{\mathrm{c}}^{640}}{K_{\mathrm{m}}^{177}} + \frac{K_{\mathrm{c}}^{640}}{K_{\mathrm{m}}^{177}} \frac{1}{x_{\mathrm{m}}} \qquad (6)$$

where F is a constant and is equal to $(K_{\mathrm{t}}^{640} - K_{\mathrm{c}}^{640})/K_{\mathrm{t}}^{260}$. Then a plot of the $(I^{640} - FI^{260})/I^{177}$ versus x_{m}^{-1} is expected to yield a straight line.

3.5. Determination of *F*

The constant F can be calculated by determining the values of $K_{\mathrm{t}}^{260}/K_{\mathrm{m}}^{177}$, $K_{\mathrm{c}}^{640}/K_{\mathrm{m}}^{177}$ and $K_{\mathrm{t}}^{640}/K_{\mathrm{m}}^{177}$.

(a) $K_{\mathrm{t}}^{260}/K_{\mathrm{m}}^{177} = 1.8$, was determined from Equation 4. The mean value of I^{260}/I^{177} was calculated from the intensity ratios of spectra excited from pellets with known molar fractions of the monoclinic, tetragonal and cubic phases.

(b) $K_{\mathrm{c}}^{640}/K_{\mathrm{m}}^{177} = 0.16$, was calculated from Equation 7.

$$\frac{I^{640}}{I^{177}} = \frac{K_{\mathrm{c}}^{640} x_{\mathrm{c}}}{K_{\mathrm{m}}^{177} x_{\mathrm{m}}} + \frac{K_{\mathrm{m}}^{640}}{K_{\mathrm{m}}^{177}} \qquad (7)$$

The mean value of I^{640}/I^{177} was determined from the intensity ratios of spectra excited from pellets prepared by mixing powders of pure monoclinic and cubic phase only and thus the relationship is valid only for pellets with no tetragonal crystal structure. The only other unknown parameter in Equation 7, $K_{\mathrm{m}}^{640}/K_{\mathrm{m}}^{177}$, was determined from spectra of pure monoclinic powder where the Raman intensity ratio is equal to the ratio of the K factors.

(c) $K_{\mathrm{t}}^{640}/K_{\mathrm{m}}^{177} = 1.0$, was estimated from Equation 3. The mean value of I^{640}/I^{177} was calculated from the intensity ratios of spectra excited from pellets with known molar fractions of the monoclinic, tetragonal and cubic phases. Therefore, $F = (K_{\mathrm{t}}^{640}/K_{\mathrm{m}}^{177} - K_{\mathrm{c}}^{640}/K_{\mathrm{m}}^{177})/K_{\mathrm{t}}^{260}/K_{\mathrm{m}}^{177} = 0.47$.

3.6. Calibration curve

The plot of $(I^{640} - FI^{260})/I^{177}$ against the inverse monoclinic molar fraction is shown in Fig. 3. In order to avoid problems arising from random spectral noise, the intensity values used were averaged with the intensities of the neighbouring data points.

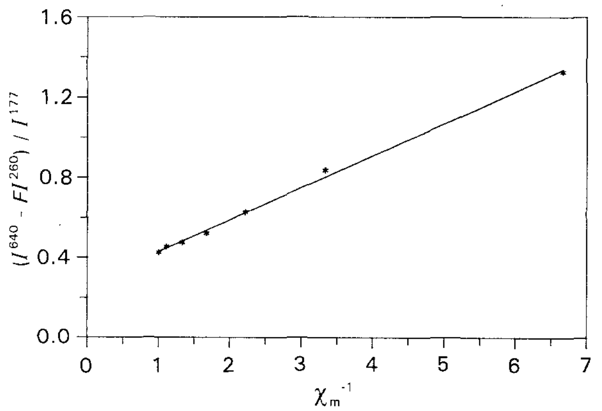

Figure 3 Plot of the $(I^{640} - FI^{260})/I^{177}$ against the inverse monoclinic molar fraction, x_{m}, where I^{640}, I^{260}, I^{177} are the Raman intensities at 640, 260 and 177 cm^{-1}, respectively.

The value of I^{640} was obtained by subtracting from the total measured intensity at 640 cm^{-1}, the "background" intensity of the 800 cm^{-1}, as demonstrated in Fig. 4a. The exact wave number corresponding to the maximum intensity of the peak was determined by a computer-aided (c.a.) search, of the digitized spectra, between the 625 and 650 cm^{-1}. 800 cm^{-1} was arbitrarily chosen as the spectral point where the "background" level is zero, because at this wave number the intensity of all the spectra of the pellet reaches a constant value.

The wave number of the tetragonal peak (260 cm^{-1}) was c.a. searched between the 245 and 275 cm^{-1} and its intensity, I_{m}^{260}, was calculated by subtracting the "background" for the 260 cm^{-1}, as shown in Fig. 4b. 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 "background" line were located by searching for the lowest intensity data point between 190–210 cm^{-1} and 380–450 cm^{-1}, respectively. The "background" intensity corresponding to the peak was calculated from the mathematical expression of the "background" line.

The intensity of the 177 cm^{-1} monoclinic peak was calculated using the same procedures as for the 260 cm^{-1} band. For the maximum intensity of the 177 cm^{-1} peak, the limits were 170 and 190 cm^{-1}, while the search for the data points with the lowest intensities was conducted between the 145 and

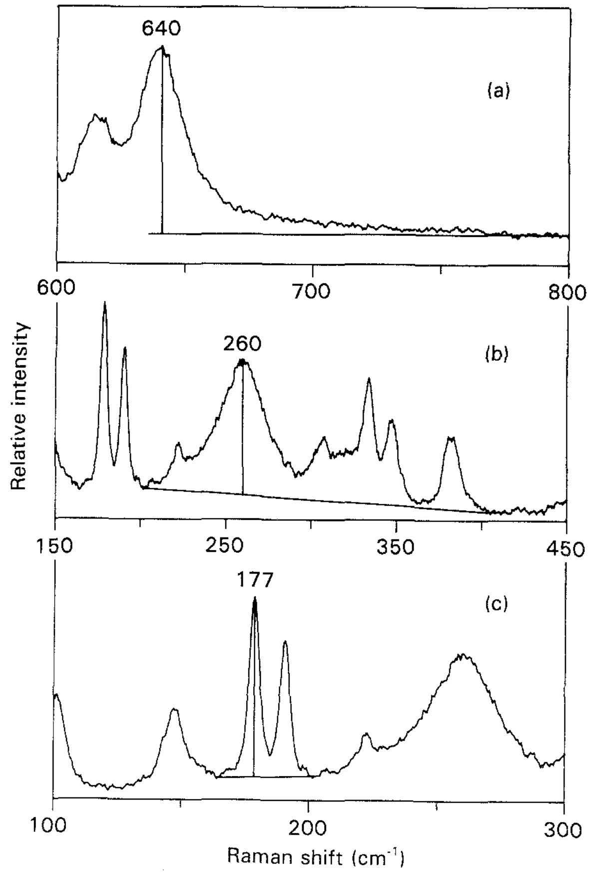

Figure 4 Regions of the Raman spectrum of a pellet with 45 mol % pure ZrO_2 (monoclinic phase) and 55 mol % ZrO_2–8 mol % Y_2O_3 (cubic phase). The intensities for the (a) 640, (b) 260 and (c) 177 cm^{-1} bands, were calculated as shown.

TABLE I Mean values of the $(I^{640} - 0.47 I^{260})/I_m^{177}$ and the coefficient of variation for zirconia pellets

Molar fraction of monoclinic phase	$(I^{640} - 0.47 I^{260})/I_m^{177}$	Coefficient of variation
0.15	1.325	5.9
0.30	0.835	3.0
0.45	0.627	5.0
0.60	0.522	4.1
0.75	0.476	4.3
0.90	0.455	5.7
1.0	0.425	6.2

170 cm^{-1}, and 190 and 210 cm^{-1}, respectively (Fig. 4c).

Several Raman spectra were recorded for each composition and the data in the plot (Fig. 3) are the mean values (Table I) of the real data. A linear regression on all the data yields the following equation

$$\frac{I^{640} - FI^{260}}{I^{177}} = \frac{1}{x_m}0.16 + 0.27 \qquad (8)$$

The correlation coefficient was 0.9987, while the standard errors for the slope and the intercept were $\pm 3.7 \times 10^{-3}$ and $\pm 9.0 \times 10^{-3}$, respectively.

As a rough estimate, the standard error in the calculation of the molar fraction of the monoclinic phase can be considered to be approximately equal to $\pm 1 \times 10^{-2}$, which represents the largest standard error among those determined for the slope and the intercept of Equation 7. Because several Raman spectra were recorded, the coefficients of variation (CV), which represent the percentage of the relative standard deviation, were also calculated and are presented in Table I.

3.7. Calculation of the molar fraction of the tetragonal and cubic phases

For the determination of the molar fractions of the tetragonal and cubic phases in a zirconia ceramic where all crystal structures are present, the following relationship can be used

$$\frac{I^{640}}{I^{260}} = \frac{x_m K_m^{640} + x_t K_t^{640} + x_c K_c^{640}}{x_t K_t^{260}} \qquad (9)$$

The percentage of molar fraction of the monoclinic phase can be determined from the calibration curve (Equation 8). Combination of Equations 5, 8 and 9 will yield the unknown x_c and x_t.

4. Conclusions

A method for calculating the percentage of the monoclinic, tetragonal and cubic phase in a zirconia ceramic, by Raman spectroscopy, has been developed. The relationship describing the calibration curve for the determination of the monoclinic phase is given by $(I^{640} - 0.47 I^{260})/I^{177} = x_m^{-1} 0.16 + 0.27$ where I^{640}, I^{260}, I^{177} are the Raman intensities at 640, 260 and 177 cm^{-1}, respectively, and x_m is the monoclinic molar fraction. The intensities of the monoclinic and the tetragonal peaks were calculated by subtracting the "background". In contrast, the intensity for the 640 cm^{-1}, which is attributed to all three phases, was determined including the "background". Raman spectroscopy clearly demonstrates its potential as a non-destructive quantitative analytical technique for studying doped zirconia.

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