JOURNAL OF MATERIALS SCIENCE **40** (2005) 1593– 1597

Piezo-spectroscopic behavior of the emission bands of α-alumina in the 13900–14250 cm^{-1} spectral range

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The emission spectrum of α-alumina in the spectral range between 13900 and 14250 cm^{-1} is characterized by several bands which are much weaker than the two intense and sharp R1 and R2 bands appearing at 14400 and 14430 cm^{-1}, respectively; these latter are known as Ruby lines and they are the emission bands used in the Ruby laser. Furthermore these bands shift in frequency with stress (Piezo-Spectroscopic effect). In this paper, for the first time, the stress-dependent peak frequency of the weaker bands in the 13900–14250 cm^{-1} range is calibrated, and the results are presented as Piezo-Spectroscopic coefficients. The calibration is performed by reporting the frequency shift of each investigated band as function of varying stresses. The stresses, residual in nature, are obtained by fabricating composite materials where α-alumina is mixed in various amounts with (i) Ceria-Stabilized Tetragonal Zirconia Polycrystals (Ce-TZP) and (ii) silicon carbide, SiC. The composite materials are prepared at high temperature (1500°–1800°C); due to the difference in thermal expansion, upon cooling to room temperature α-alumina develops compressive and tensile stresses, when mixed with Ce-TZP and SiC, respectively. The stress values necessary for the calibration are obtained from the frequency shift of the R2 band, using its well-established Piezo-Spectroscopic coefficient (7.6 cm^{-1}/GPa). Then the newly obtained Piezo-Spectroscopic coefficients of the bands in the 13900–14250 cm^{-1} range are tested to retrieve the stresses in two sets of composites; finally the stress values are compared with those obtained in the same samples from the frequency shift of the R2 band. The comparison shows a very good agreement, thus providing evidence that the bands in the 13900–14250 cm^{-1} range can be used to monitor stresses in α-alumina-based materials.

1. Introduction

Strain can induce a shift of the characteristic frequencies of spectral bands, be they Raman, Infra-Red or luminescence bands. This is known as Piezo-Spectroscopic (PS) effect and it has been used to determine the stress in a variety of ceramics, since this class of materials operates mostly in the elastic regime. The initial work concerning a PS analysis of polycrystalline ceramics is due to Grabner [1], but the complete, correct frame of the method, has been provided in a seminal paper by Ma and Clarke [2]. It is not by chance that in both Refs. [1] and [2] the material investigated is alumina, Al_2O_3. Besides being for ceramists what steel is for the metallurgists, alumina has the peculiarity of having two intense, sharp luminescence bands (R1 and R2, at about 14400 and 14430 cm^{-1}, respectively), which have a long known [3], and well-defined stress dependence [4]. The mathematical equation, which empirically represents the PS effect, is given by:

$$\Delta\nu = \Pi_{ij}\sigma_{ij} \qquad (1)$$

where $\Delta\nu$ represents the frequency shift of a given spectral band calculated with respect to an assumed stress-free reference state (usually single crystal, free powder or pure sintered material), Π_{ij} is the tensor of the derivatives of the frequency shifts with respect to stresses, σ_{ij}, applied along the axis of the crystallographic system;

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Π_{ij} is called the tensor of the PS coefficients, which is defined for the specific spectral band under consideration. In Equation 1 the Repeated Index Notation is used [5].

Very often ceramic materials of practical interest are constituted by randomly distributed ensemble of grains, so the stress information along specific crystallographic directions is lost; in this case Equation 1 is substituted by the following:

$$\Delta\nu = \Pi\langle\sigma\rangle \tag{2}$$

where now Π represents an effective average PS coefficient, and $\langle\sigma\rangle$ is the spatial average of the trace of the stress tensor. An important implication of Equations 1 and 2 is that the frequency shift of a certain spectroscopic band gives information on the stress in the material/phase to which that particular band belongs. It is also evident that retrieving the stress information from the experimentally observed frequency shift $\Delta\nu$ is based upon the knowledge of the PS coefficients.

Alumina present several polymorphs, of which α-alumina is the most important. α-alumina has the crystallographic structure of sapphire/corundum, with the oxygen ions ordered in a hexagonal close packed arrangement and the aluminium ions occupying two thirds of the octahedral sites. Chromium ions, Cr^{3+}, are a ubiquitous, natural substitutional impurity in alumina. More specifically Cr^{3+} substitutes for $Al^{+3}$and in this case the octahedron of oxygen ions surrounding a single Cr^{3+} ion is not perfectly symmetrical because of a trigonal distortion along one of the Cartesian axis. The emission (luminescence) spectrum due to Cr^{3+} in the sapphire/corundum structure is characterized by the two intense and sharp lines already mentioned, but there are also some weaker bands, already noted by Schawlow [3], which could in principle exhibit a PS effect, as originally suggested by Molis and Clarke [6].

In this work we have determined the average PS coefficients of 6 emission bands of α-alumina in the 13900–14250 cm^{-1} spectral range. Since it is quite established that the bands in this region are due (i) to Cr^{3+} pairs constituting single chromophoric, luminescent sites and (ii) to vibronic transitions (i.e., transitions simultaneously involving electronic an vibrational states) [1, 7, 8], the focus of this contribution is the evaluation of PS coefficients of these bands, so that they can be used as *in-situ* strain gages, analogously to the R1-R2 bands [2, 9, 10].

The evaluation of the PS coefficients is accomplished through a so-called PS calibration that is usually performed in either of the two following methods. In the first method, a sample of the material under investigation is increasingly stressed to a known extent and each stress is then plotted against the observed frequency shift of the spectral band(s) under examination in that material. The slope of the best fitting line provides then the PS coefficient(s) [4, 10]. In the second method, the material presenting the spectral lines to be calibrated is used to prepare a composite by mixing it with a second material presenting immiscibility with the first one [11]. If the preparation of the composite requires a high temperature step (as it is typical of ceramic-based materials like alumina), upon cooling the sign of the residual stress in first material is dictated by the difference between its Coefficient of Thermal Expansion (CTE) and the CTE of the other material in the composites: in this study we have used two different type of composites, one obtained mixing alumina with silicon carbide, SiC, and another type mixing alumina with Tetragonal Zirconia Polycrystals (TZP). The CTE of alumina (about 8 $\cdot 10^{-6}$ K^{-1}) is larger than SiC (about $4 \cdot 10^{-6}$ K^{-1}) and smaller than TZP (about $11 \cdot 10^{-6}$ K^{-1}). As a result, upon cooling, alumina will try to shrink more than SiC and less than TZP; displacement compatibility along the Al_2O_3/SiC and TZP/ Al_2O_3 interfaces will then originate in alumina a tensile and compressive residual stress, respectively. Thus, with this second method, the sign of the residual stress in alumina can be changed by using a second material with lower or higher CTE; the magnitude of the residual stress can be modified by varying the relative amount of the two materials; this is so because the stresses in the two materials constituting the composite are connected via the static equilibrium condition:

$$f_1\langle\sigma\rangle_1 + f_2\langle\sigma\rangle_2 = 0$$

where f is the volume fraction, $\langle\sigma\rangle$ is the average hydrostatic stress and the indexes 1 and 2 refer to the two materials constituting the composites. (The average residual stress and stress distribution in ceramic composites have been extensively investigated, both experimentally [9, 10] and theoretically [12]). In this work we have made use of the approach based on the difference of CTE's and varying volume fraction [12] just to span a larger set of stress values for the PS calibration.

2. Experimental procedure

Two sets of TZP/alumina composite samples having 0–100 vol% (with increment of 10 vol%) of alumina were prepared following a standard ceramic preparation procedure. In the first set the starting powders were ZrO_2 containing 12 mol% of CeO_2 (Ce-TZP, Tosoh Inc., Japan) and alumina (AKP-53, Sumitomo, Japan); this set will be referred to as Ce-TZP/Al_2O_3. The second set was prepared using ZrO_2 containing 3 mol% of Y_2O_3 (Y-TZP, Tosoh Inc., Japan) and alumina (Taimei Chemicals, Japan); this set will be referred to as Y-TZP/Al_2O_3. For both sets the starting powders were weighted in the desired ratios and homogenised by ball-milling for 24 h in isopropanol. Then the mixed powders were dried, uniaxially and then isostatically pressed and sintered at 1500°C for 2 h. After sintering the density was higher then 99% of the theoretical density for all samples. A third set of composites was prepared mixing alumina powder with 5, 17 and 33 vol% of SiC nanoparticles (the details of the preparation of these samples are reported in Ref. [13]); this set will be referred to as Al_2O_3/SiC. As stress-free reference state, pure polycrystalline alumina was used. In order to study the influence of the grain size on the emission spectrum of pure alumina, some pellets were sintered for 2 h at varying temperatures, namely from 1400°C to 1650° with increments of 50°C.

The luminescence spectra were acquired using a micro-focused Raman set-up (System 1000, Renishaw, Wotton-under-Edge, UK). The laser power was about 0.5 mW. The micro-focused configuration allows focusing the exciting laser radiation onto the sample through the objective of an optical microscope; the scattered radiation carrying the spectral information is then collected by the same objective and transmitted to the frequency analyzer. The dispersed radiation was captured with a Charge-Coupled Device (CCD). A 20× objective with 0.9 numerical aperture was used in both sessions and the lateral resolution was about 10 μm. 5 spectra from each sample were collected at random points. The peak frequencies were obtained from a fitting algorithm included in a commercial software (Grams 32, Galactic Co., Salem NH, USA); the fitting is based on the Levenberg/Marquardt procedure for non-linear least square fit [14]. Instrumental fluctuations were compensated for, by monitoring the peak frequency of an electronic transition from a neon discharge lamp. The frequency shifts mentioned throughout the communication have been obtained by subtracting from the peak frequency of the sample under investigation the peak frequency of the stress-free reference sample (pure polycrystalline alumina).

3. Results

A typical luminescence spectrum of the samples under investigation is reported in Fig. 1: The R1-R2 bands are roughly two orders of magnitude more intense than the weaker emission bands in the 13900–14250 cm^{-1} region. In the same figure the result of the mathematical deconvolution of the total, experimental spectrum with 6 single bands in the 13900–14250 cm^{-1} range is presented. During the fitting of the spectra all parameters of the fitting bands were completely relaxed, in order not to bias the outcome of the fitting procedure. In this spectral region the spectra have been found to be independent from the grain size, which has been interpreted as evidence of the fact that the spectra are originating from the bulk and not from the disordered structure at the grain boundaries. Fig. 2 presents two spectra collected from alumina subject to residual compression and tension; as for the R1-R2 bands, compressive stress shifts the peak frequencies of the bands in the 13900–14250 cm^{-1}range to lower wave numbers, and the opposite for tensile stress.

Ce-TZP/Al$_2$O$_3$ samples with 10, 30, 50, 70 and 90 vol% and Al$_2$O$_3$/SiC samples with 5, 33 vol% were used for the PS calibration; the remaining samples of the same sets (20, 40, 60 and 80 and 17 vol%, respectively) were used for a first test. In Fig. 3 the frequency shift, $\Delta\nu$, of two bands (at 13985 and 14206 cm^{-1} in Fig. 1) with respect to pure polycrystalline alumina has been plotted against the stress determined according to Equation 2 applied to the R2 luminescence band (the PS coefficient of the R2 band is 7.6 cm^{-1}/GPa [4]). Since the relevant length scale of the samples, i.e. the grain size, GS, is much smaller than the region probed, the assumption of hydrostatic behavior of stress is applicable (in all samples GS is of the order of 1–2 μm at the most, whereas the region probed is several hundreds μm^3). The slope of the best fitting lines of Fig. 3 represents the PS coefficients of the two bands. Table I reports the PS coefficients for all six bands deconvoluted from the experimental spectra (Fig. 1). Fig. 4 reports the correlation graph for the samples used for the first test (20, 40, 60 and 80 vol% of Ce-TZP/Al$_2$O$_3$ and 17 vol% SiC/Al$_2$O$_3$): the x-axis reports the stress determined from the R2 band and the y-axis reports the stress determined converting the frequency shifts of the 13985 and 14206 cm^{-1} bands with the PS coefficients determined from Fig. 3 (all conversion from frequency shifts to stress have been obtained from Equation 2).

Finally the spectra collected from the Y-TZP/Al$_2$O$_3$ set were used as a second independent test of the goodness of the PS coefficients presented in Table I: the correlation plots (analogous to Fig. 4) are reported in Fig. 5. It can be seen that the correlation in Fig. 5 is

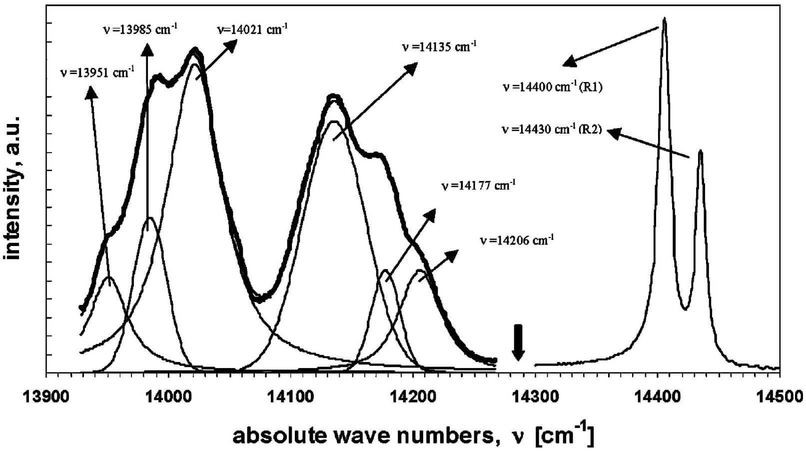

Figure 1 Typical luminescence spectrum of the alumina-containing composites under investigation. The thin line at the right of the thick arrow reports the spectral region with the intense R$_1$-R$_2$ doublet. The thick line at the left of the thick arrow reports the spectrum with the weaker emission bands that have been object of the PS calibration. Under the same conditions of acquisition (laser power and integration time) the R$_1$-R$_2$ doublet is about two orders of magnitude more intense than the weaker spectral features below 14250 cm^{-1}. The result of the mathematical fitting of the experimental spectrum with six bands is also displayed. The label of each band represents the peak frequencies and they have been used to designate that specific band throughout the paper.

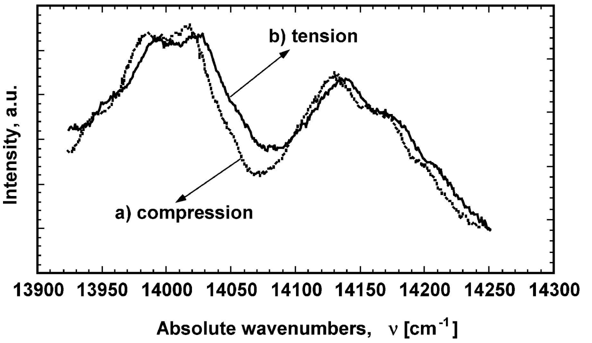

Figure 2 Luminescence spectrum of alumina in the 13900–14250 cm^{-1} range. The spectra belong to sample 10 vol% Al_2O_3/Ce-TZP (a) and 33 vol% SiC/Al_2O_3 (b). In the former case alumina is in compression and in the latter it is in tension. The spectral shift induced by stress can be clearly distinguished.

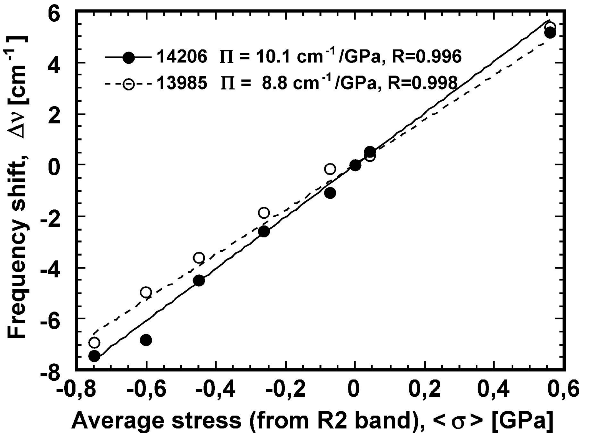

Figure 3 Result of the PS calibration for the bands at 13985 and 14206 cm^{-1}. The PS coefficients, Π, are the slope of the best fitting lines. Since the frequency shifts are calculated with respect to pure polycrystalline alumina, it is assumed that $\Delta\nu = 0$ when $\langle\sigma\rangle = 0$; accordingly the best fitting line has the form $y = mx$. R represents the correlation parameter. Table I reports the PS coefficients for all bands indicated in Fig. 1.

worse than in Fig. 4, but the linear correlation is undisputable, as expressed from the R parameter.

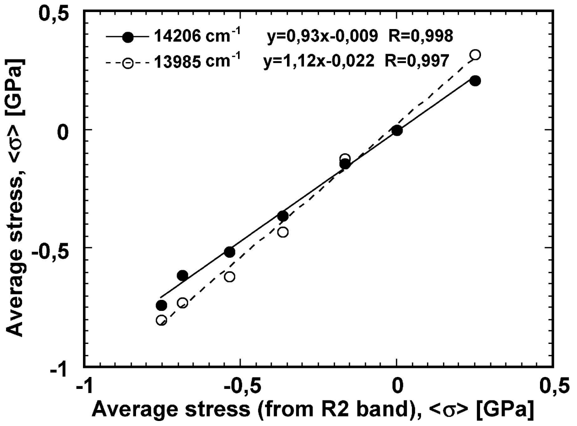

Figure 4 Correlation graph for the first test set of samples (20, 40, 60 and 80 vol% of Ce-TZP/Al_2O_3 and 17 vol% SiC/Al_2O_3), reporting the stress obtained from the frequency shift of the R2 band (x-axis) versus the stress obtained from the frequency shift of the bands at 13985 and 14206 cm^{-1}. The conversion from frequency shift to stress has been performed using Equation 2; the PS coefficient of the R_2 band is 7.6 cm^{-1}/GPa [4], whereas the PS coefficients of the bands at 13985 and 14206 cm^{-1} have been determined in Fig. 3. Since this is a correlation graph, the best fitting lines reported in the legend have the more general form $y = mx + q$.

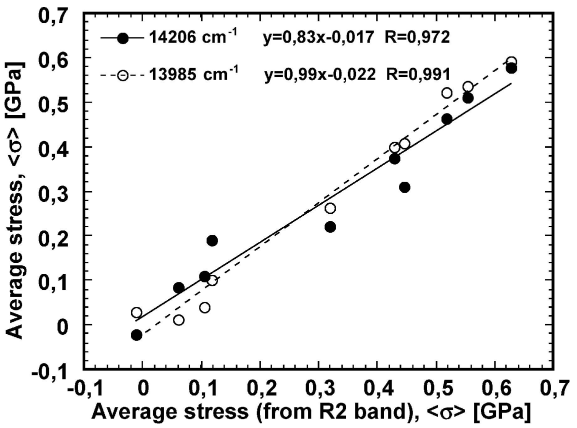

Figure 5 Correlation graph for the second test set of samples (10–100 vol% of Y-TZP/Al_2O_3). Possible explanations for the higher uncertainty of the stress data obtained from the frequency shift of the band at 14206 cm^{-1} are discussed in the text.

4. Discussion

The spectral bands of alumina in the region 12900–14250 cm^{-1} have not been unequivocally assigned: with reference to Fig. 1, it is generally accepted that the bands in the region 14050–14250 cm^{-1} are originated by pair interaction of Cr^{3+} ions (nearest neighbor, NN and next nearest neighbor, NNN) [3, 8], whereas the features in the region 13900–14050 cm^{-1} are vibronic in nature (i.e. transitions involving simultaneously an electronic and a vibrational change of state). An indirect proof of this statement is given by the frequency difference between this region and the R1-R2 bands (14400–14430 cm^{-1}), which is roughly 400 cm^{-1}; this value falls between the peak frequencies of the two most intense Raman bands of alumina (389 and 417 Rcm^{-1}). So, it seems reasonable to consider the broad, red light of the R1-R2 emissions as an excitation source and the spectral features around 14000 cm^{-1} as the Raman response due to that excitation. Irrespective of the nature of the bands in the 13900–14050 cm^{-1} range, Figs 3–5 and Table I clearly demonstrate that they are suitable for a PS analysis. Whilst it is true that the R1-R2 bands are more intense and more precise for a stress determination, the PS coefficients determined in this work can be useful for a stress analysis if (i) the R1-R2 bands are masked by some other bands (which can be present if alumina is used in a composite with a second

TABLE I PS coefficients for all bands indicated in Fig. 1. For each band the pertinent PS coefficient, the standard error and the correlation parameter R are reported

Peak frequency (cm^{-1})	PS coefficient (cm^{-1}/GPa)	Std. error (cm^{-1}/GPa)	Correlation parameter R
13951	11.3	1.0	0.967
13985	8.8	0.3	0.995
14021	8.3	0.6	0.980
14135	8.1	0.1	0.998
14177	9.3	0.7	0.971
14206	10.1	0.3	0.996

material whose bands fall in the R1-R2 region) and/or (ii) if the luminescence spectrum of alumina is excited with a source having frequency below the R1-R2 bands, so that these become inaccessible.

The worse correlation of Fig. 5 with respect to Fig. 4 suggests that, if the stresses need to be determined with high accuracy, it is advisable to perform a PS calibration on the specific α-alumina under examination. Should this not be possible, the expected error, derived from Table I, is about 50 to 100 MPa, depending on the band used. The possible explanation of the larger scatter of the stress values derived from the 14206 cm^{-1} band with respect to the 13985 cm^{-1} band in the second test set (Fig. 5) is possibly due to some weak bands peculiar of the Y-TZP/Al_2O_3 samples overlapping with the former, α-alumina band: these weak bands might not be intense enough to show up independently in the experimental spectrum, but they might influence the fitting procedure, giving origin to unaccountable error in the frequency shift of the 14206 cm^{-1} band.

Finally we observe that the PS coefficients presented in Table I are virtually all larger than the PS coefficients of the R1-R2 bands (7.56 and 7.61 cm^{-1}, respectively [4]) and also larger than the PS coefficients of the two most intense Raman bands of alumina (2.2 cm^{-1}/GPa and 1.1 cm^{-1}/GPa, for the bands at 379 and 417 Rcm^{-1}, respectively [15]). We believe that the explanation for this fact is different for the bands originating from pair interactions (14050–14300 cm^{-1} range) and from vibronic transition (13900–14050 cm^{-1} range): in the former case the electrons responsible for the emission are less tightly bound than R1-R2 and, in fact, the bands appear at lower frequencies. In the latter case the observed PS coefficients are due to the superposition of stress dependence of the electronic and vibrational states, thus resulting in larger PS values.

5. Conclusions

The stress dependence of the peak position of several emission bands of α-alumina in the spectral range 13900–14250 cm^{-1} have been determined for the first time. The dependence, expressed as PS coefficients, has been tested to derive stress values from frequency shifts in two sets of composites containing α-alumina. Albeit less precise than the more used R1-R2 bands, these bands appear suitable for a PS determination of stress. The PS coefficients determined in this work are larger, i.e. the bands examined are more stress-sensitive, than all previously reported PS coefficients both of luminescence and Raman bands of α-alumina.

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Received 18 May
and accepted 8 November 2004