ZrO_2 PHASE IDENTIFICATION WITH RAMAN SPECTROSCOPY

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APPLICATION NOTE RAMAN-020 (US)

Author: A.J.R.Bauer, Ph.D.

Abstract

This application note documents the use of a TSI ChemLogix™ ProRaman-L instrument to differentiate between monoclinic and tetragonal zirconia.

Motivation

Zirconia is an engineered ceramic with a myriad of uses, including orthopedic and dental prosthetics, as protective coatings, refractory materials in industry, thermal insulation, abrasives and enamels. Oxygen ions can move freely through the crystal structure at high temperature, leading to its use in oxygen sensors. Toughened zirconia is used to make ceramic cutlery. It is known as a catalyst for many reactions, and a catalyst support for many others.

ZrO_2 is useful for all these applications chiefly because of its remarkable physical properties. It exhibits high mechanical strength, excellent wear resistance, holds a smooth surface and has high fracture toughness. Additionally, it has low thermal conductivity, making it an excellent heat insulator, and high dielectric strength.

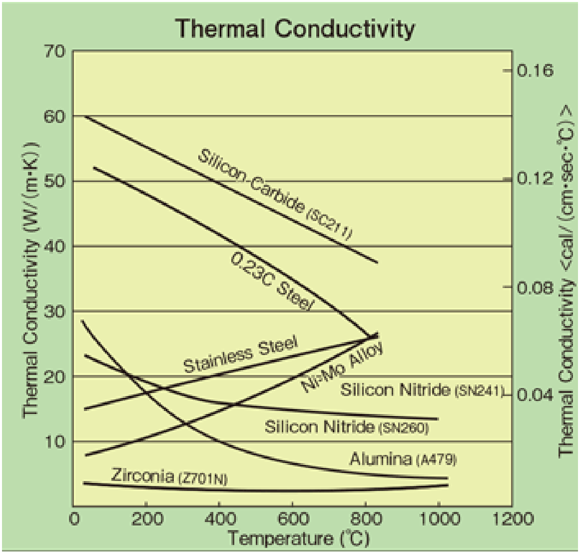

Figure 1. Thermal conductivity of a variety of materials, including ZrO_2.[1]

Three phases of zirconia are known—monoclinic, tetragonal and cubic. A tendency toward higher symmetry at higher temperatures is observed in the Raman spectra, as in other oxides. ZrO_2 is one of the most well-studied ceramics because of the martensitic transistion between tetragonal and monoclinic zirconia. A martensitic transition is one that takes place in a diffusionless and military (coordinated) manner; the composition does not change, but only the crystal structure. This transition is one of the most interesting things about zirconia – as tetragonal ZrO_2 changes to the monoclinic form, there is an increase in the volume of the material (about 4%). This volume increase causes the material to crack upon cooling from high temperatures. For this reason, pure polymorphs of zirconium oxide are not commonly used in engineering applications.[1,2]

In order to contain the problem of cracking upon cooling, zirconia is often blended with other oxides to stabilize one phase or the other. A small addition of yttria, for example, eliminates these destructive phase changes by lowering the phase transition temperatures, resulting in superior physical properties. Most often, the tetragonal form is stabilized to a high toughness by inhibiting the tetragonal-monoclinic transition. The resulting material will put any crack tip into compression and stop the crack formation. This type of toughening is common in material for dental prostheses and industrial grinding applications.[2]

Zirconium oxide can also be used to stabilize other materials, like alumina. Zirconia Toughened Alumina (ZTA) has a toughening mechanism due to transformation of the crystal structure under stress. ZTAs have 2 to 20% volume percent of ZrO_2 particles in an alumina matrix. When under stress, the zirconia particle perform the transition described earlier, increasing in volume from 3 to 5%, compressing the surrounding crack and restricting its rate of propagation. This material is appreciably stronger than the native alumina.[3]

Measurements and Results

A TSI ChemLogix ProRaman-L with 785 nm excitation was used to analyze monoclinic and tetragonal ZrO_2. Laser power was maximized (300 mW), and the standard lens tube assembly used. Acquisitions were 1 s long, the data presented averaged 60x. These spectra match those found in the literature well. Figure 2 shows the acquired spectrum of monoclinic ZrO_2. This spectra matches those found in the literature very well. The symmetries of the Raman-active phonon modes seen here have been assigned in Zhao, et.al. The 177-189 cm^{-1} pair are B_g and A_g, 222 cm^{-1} is B_g, 330 cm^{-1} is B_g, 376 cm^{-1} is A_g+B_g. 473 cm^{-1} is A_g, 633 cm^{-1} is A_g.[4]

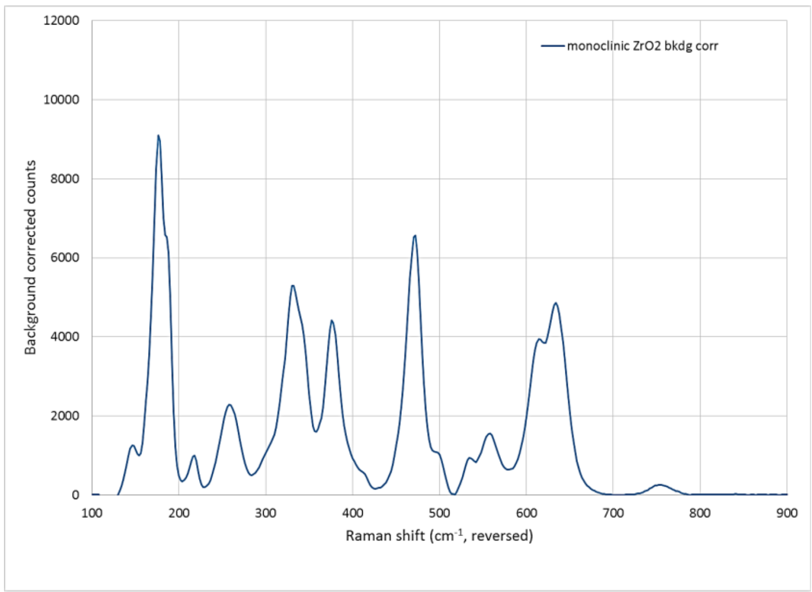

Figure 2. Monoclinic ZrO_2 spectrum, acquired with ProRaman-L instrument.

Tetragonal zirconia has a less complex geometry than does the monoclinic form, yielding a simpler Raman spectrum. In the tetragonal case, 155 cm^{-1} is assigned as B_{1g}, 260 cm^{-1} as E_g, 320 cm^{-1} as B_{1g}, 460 cm^{-1} as E_g, 606 cm^{-1} as B_{1g} and 641 cm^{-1} as E_g.[5]

It is clear that Raman spectroscopy can be used to differentiate these two important engineering materials, as well as differentiating the two of them from the perhaps better-known cubic zirconium, used as a diamond surrogate in jewelry.

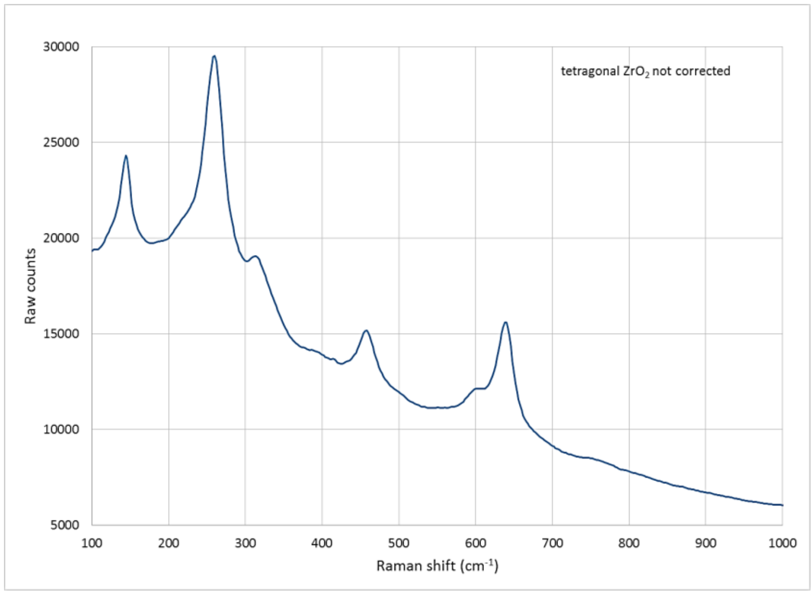

Figure 3. Tetragonal ZrO_2 spectrum acquired with ProRaman-L instrument.

Summary

Monoclinic and tetragonal zirconia have distinct Raman spectra. Besides merely differentiating the phases, Raman spectroscopy has also been used to measure residual stress after wear in these materials and to measure the transformation rates.[7]

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