In situ Raman Spectroscopy as a Tool for Discerning Subtle Structural Differences Between Commercial (Ce,Zr)O_2-Based OSC Materials of Identical Composition

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Supplementary Information

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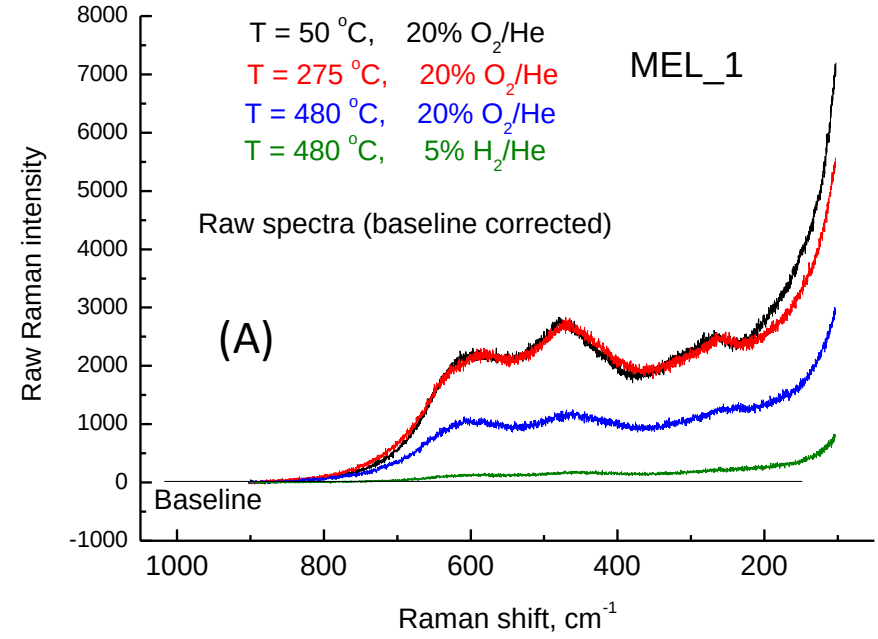
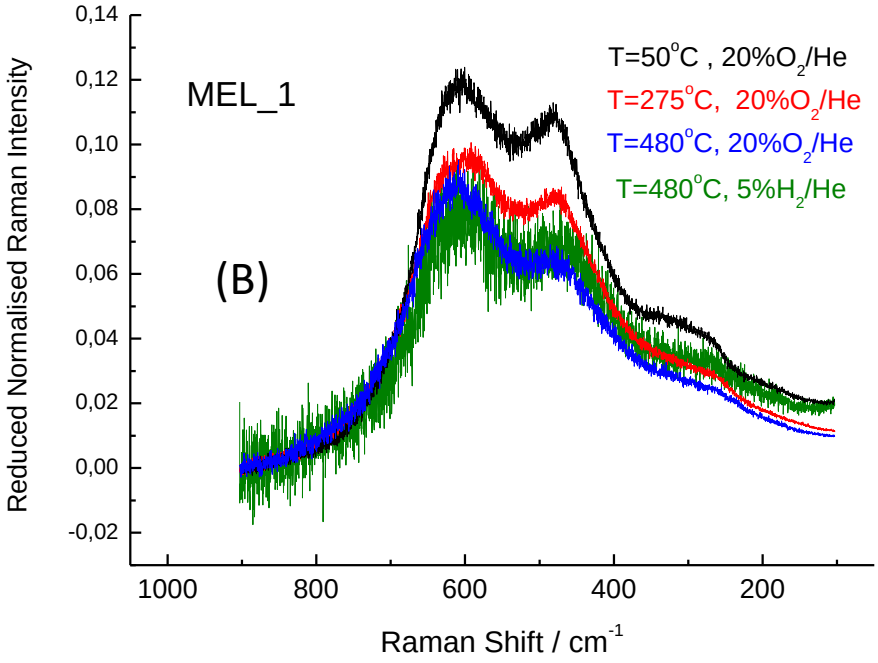
Figure S1 (14 panels)

A detailed outline of raw Raman data handling procedures. The spectrum normalization and "reduction" procedures are demonstrated for the contents of Figure 1

Figure S1 demonstrates in full detail the great advantage of the normalization procedure that eliminates the so-called "path length" effect among colored samples and the great benefit of the "reduction" procedure that disentangles the Raman spectra from thermal effects, thereby offering the advantage of comparing purely vibrational effects even at different temperatures. Panel (A), below, shows selected raw *in situ* Raman spectra obtained for compiling Figure 1. Panel (B) shows the normalized and "reduced" Raman spectra that constitute contents of Figure 1

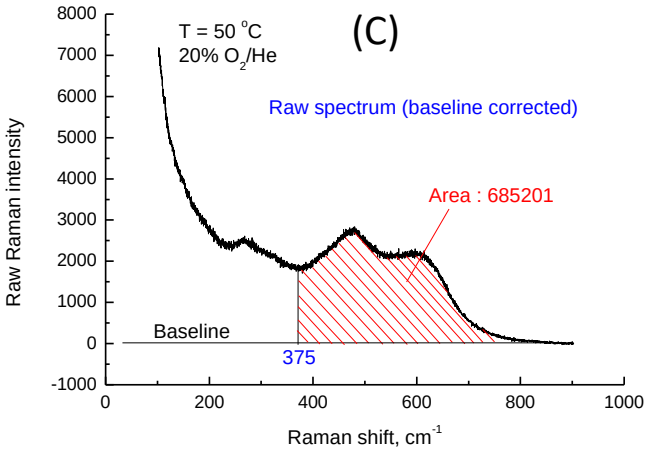


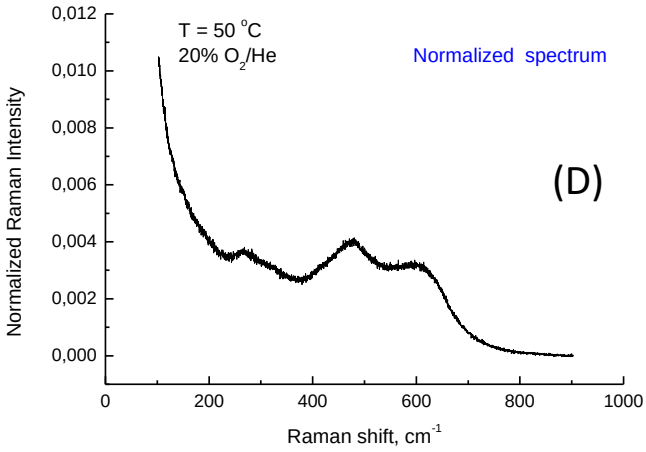


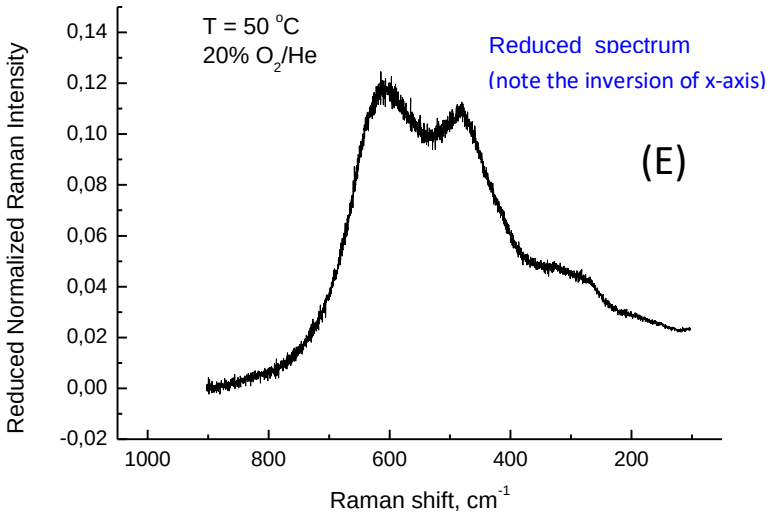
The raw intensity scale (Panel (A)) is entirely arbitrary, subject to instrumental factors, laser power used, spectroscopist's skills etc. Panel (B) is compiled at the inherent reduced intensity scale, which is *universal*. In Panel (B), only the signal-to-noise ratio can be varied between different laboratories.

Below, we demonstrate the above procedure as performed in order to convert each raw spectrum to its universal reduced and normalized form.

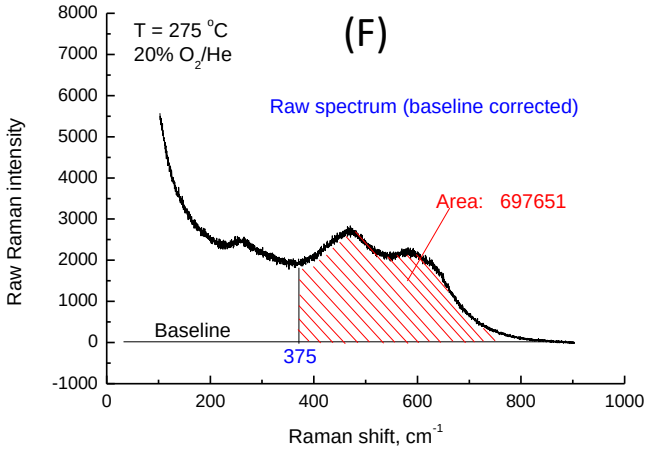
Panels (C), (D) and (E) pertain to the *in situ* Raman spectrum obtained for MEL_1 Sample under 20% O_2/He at 50 ^oC. The raw spectrum (panel (C)) is divided by the area under the 375-900 cm^{-1} range and the normalized spectrum is obtained in panel (D) that exhibits the same features but in universal inherent intensity scale. Finally, the normalized spectrum is subjected to the reduction procedure (see experimental part), the x-axis scale reversed to comply with IUPAC and the reduced spectrum is derived in panel (E), where the exhibited features are disentangled from thermal effects

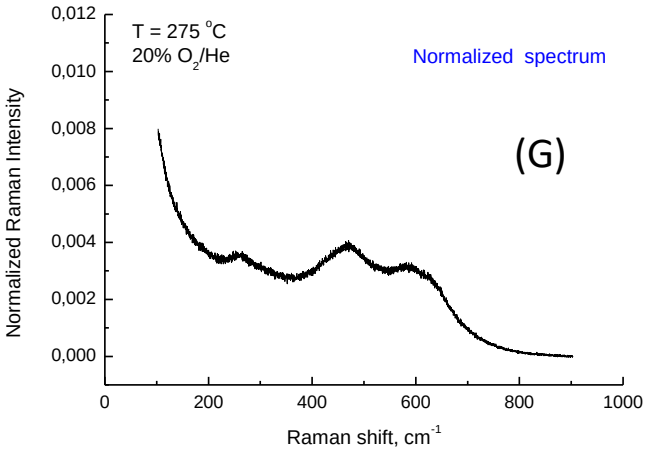


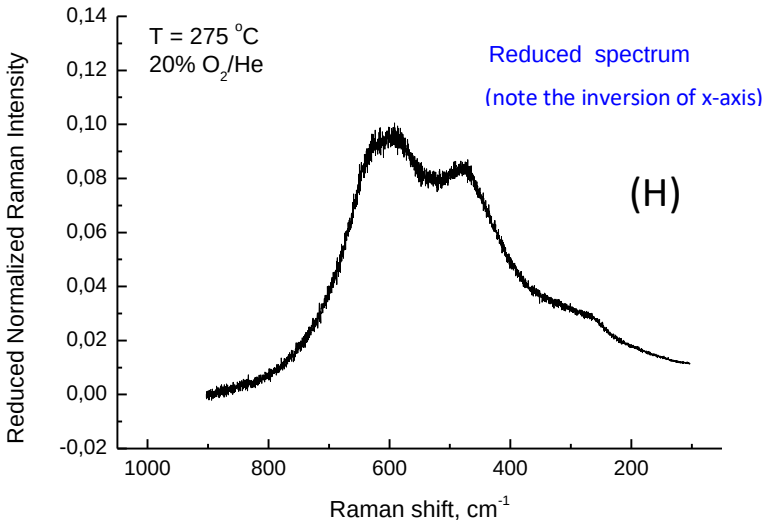




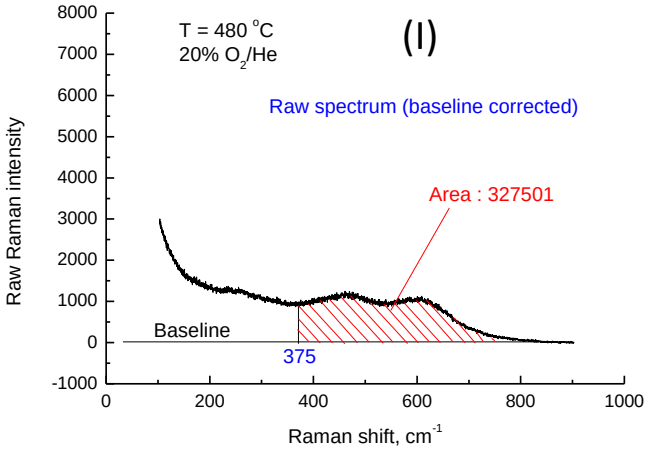
Panels (F), (G) and (H) pertain to the *in situ* Raman spectrum obtained for MEL_1 Sample under 20% O_2/He at 275 ^oC. The procedure followed is identical to the one described above for panels (C), (D) and (E).

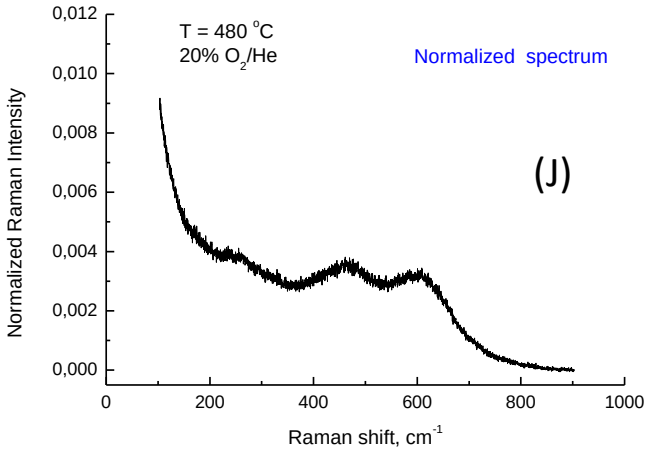


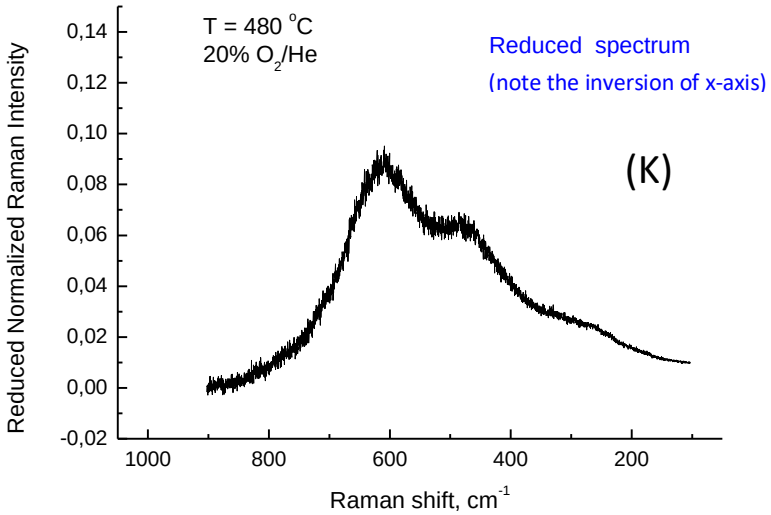




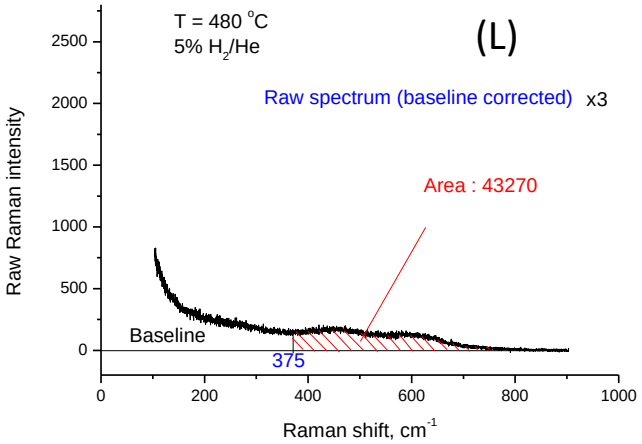
Panels (I), (J) and (K) pertain to the *in situ* Raman spectrum obtained for MEL_1 Sample under 20% O_2/He at 480 ^oC. The procedure followed is identical to the one described above for panels (C), (D) and (E).

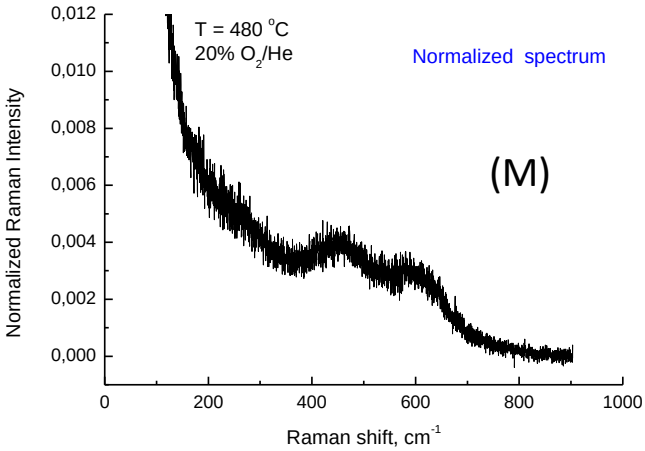


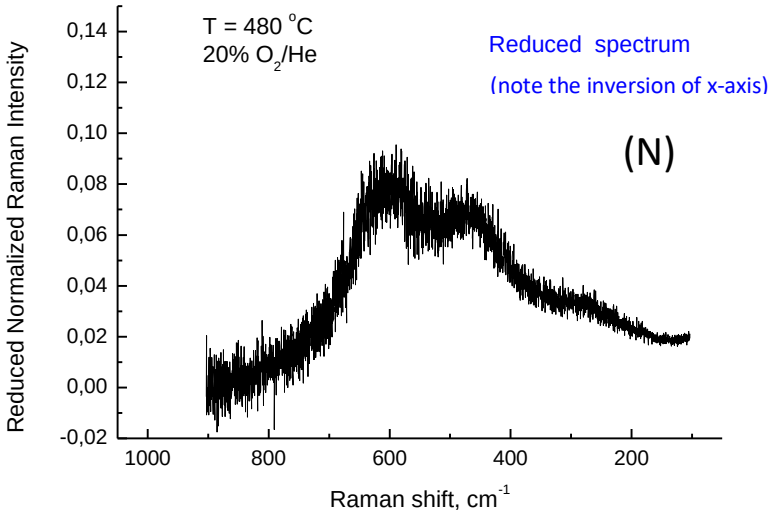




Panels (L), (M) and (N) pertain to the *in situ* Raman spectrum obtained for MEL_1 Sample under 5% H_2/He at 480 °C. The procedure followed is identical to the one described above for panels (C), (D) and (E).







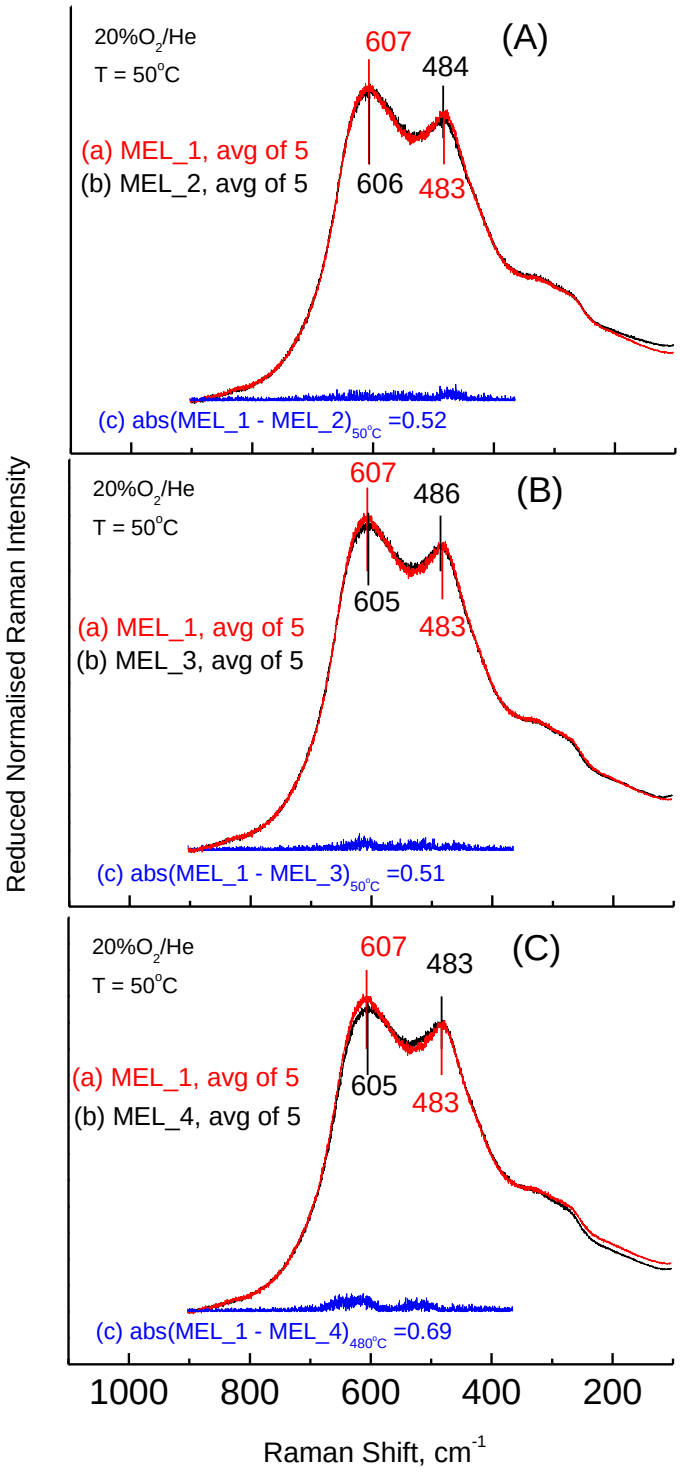


Figure S2. Comparative plots of reduced and normalized *in situ* Raman spectra obtained under 20% O_2/He at 50 °C. (A) MEL_2 vs MEL_1; (B) MEL_3 vs MEL_1; (C) MEL_4 vs MEL_1. Traces (a) pertain to MEL_1; traces (b) pertain to MEL_*i* (*i* = 2, 3, 4) as indicated in each panel. Traces (a) and (b) are averages of five recordings. Traces (c) with blue color in panels (A), (B) and (C) show the absolute difference of traces (a) and (b) under comparison in each case.

Recording parameters, see Fig. 1 caption.