

A RAMAN SPECTROSCOPY INVESTIGATION OF Cd^{2+} AND Ca^{2+} INCORPORATED ZrO_2 MATERIALS

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Abstract: Calcium-containing zirconium oxide samples, prepared at 1123 K and cadmium-containing zirconium oxide samples, prepared at 1073 K in air, were studied by combined macro- and micro-Raman spectroscopy and X-ray diffraction. The phases evolution with the cations concentration is described.

Zirconium oxide solid solutions containing oxide of divalent or trivalent metal cations are important technological materials. In fact the incorporation of lower-valent cations in ZrO_2 causes the formation of anionic vacancies and the solid acquires interesting properties such as electrical (ionic conductivity) [1-2] and structural features (stabilization of crystalline modifications) [3]. Identifying the structures existing or coexisting at RT in these systems is an important problem to which Raman Spectroscopy is increasingly applied. In this communication the results of a Raman spectroscopy study are compared with those of XRD analysis concerning several zirconia samples prepared at relatively low temperature (< 1273 K) with different content of Ca^{2+} or Cd^{2+} impurities. These new materials are of interest for several applications, including heterogeneous catalysis.

The Raman measurements confirm the evolution, observed by XRD, of the ZrO_2 material by increasing the doping level from monoclinic to tetragonal and finally to cubic phase. However some discrepancy appears. In Fig.1 (A), spectrum (b) of a sample with 8.80 mol% Ca content, is typical of the stabilized tetragonal ZrO_2 phase, whereas spectrum (e), of a sample with 13.95 mol% Ca content, can be considered characteristic of the cubic phase. Raman spectra of samples in the intermediate compositional range show the features of both the tetragonal and cubic phases whereas, according to XRD measurements, those sample appear already cubic. The existence of ZrO_2 materials with an axial ratio c/a of unity (cubic structure), but characterized by a Raman spectrum presenting also features of the tetragonal phase, has already been reported [4]. It has been attributed to a new “metastable tetragonal form without tetragonality”, indicated as $t''\text{-ZrO}_2$, intermediate between the tetragonal and the cubic phases [5].

To investigate this intermediate phase, we prepared some new samples by mixing, at RT, fractions of pure tetragonal and cubic materials with various weight ratios. Their Raman spectra and XRD patterns were then measured. Comparison of a representative example, the spectrum of the sample with 13.89 mol% Ca content (Fig.1 (A), spectrum (d)) with the spectrum obtained by mixing 85 wt% of a cubic sample (18.80 mol% Ca) and 15 wt% of a tetragonal sample (8.80 mol% Ca), shows two almost identical spectra, as illustrated in Fig. 1(B). An analogous spectrum can also be obtained by summing spectra of the tetragonal and cubic phases. According to the X-ray diffraction analysis, the mixture samples appeared cubic ($c/a = 1$) like the sample with Ca content in the transition range from tetragonal to cubic. The different indications on the sample phase composition given by the two techniques could arise from their different sensitivity to the modification of the oxygen sublattice, being much higher for Raman spectroscopy than for XRD [6]. These results suggest that under our experimental conditions (samples heated at 1123 K) the Raman spectra of samples in the transition range of Ca content (8.8 – 13.89 mol%) might be attributed to a heterogeneous material (two phases) rather than to the homogeneous new phase t'' . The heterogeneity of the materials in the transition range was confirmed by a micro-Raman survey

Indeed, the signals from different material grains showed the contribution of different phases (tetragonal and cubic).

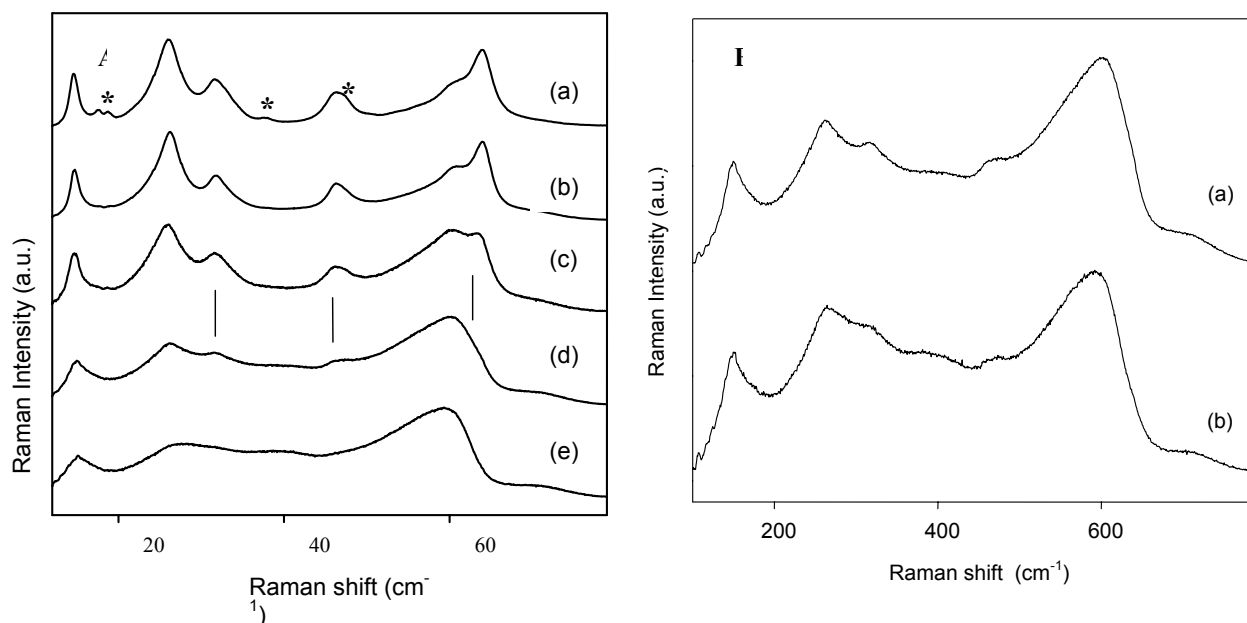


Fig. 1. A: Raman spectra of zirconia samples with different content of calcium (mol%): (a) 6.19; (b) 8.80; (c) 9.49; (d) 13.89; (e) 13.95. The asterisks indicate the components of the monoclinic phase (spectrum (a)) and the vertical bars the position of some tetragonal bands.

B: Curve (a): spectrum (d) in A (Ca content 13.89 mol%); (b): spectrum of a mixture of 85% in weight of a cubic sample (ZrO_2 with Ca content 18.80 mol%) and 15% in weight of a tetragonal sample (ZrO_2 with Ca content 8.80 mol%).

The stabilization process achieved through the diffusion of impurities inside the material should depend on the amount of dopant, grain size and grain size distribution. Because our materials consist of grains with various sizes, the tetragonal-cubic transition could develop incompletely in the large grains. The micro-Raman analysis confirms this hypothesis, since it shows that the tetragonal contribution to the Raman signal is preferentially originated from zirconia grains of larger size. Similar results have been found for the Cd^{2+} incorporated zirconia materials. In this case the compositional transition range was from 11.88 to 17.23 mol% Cd.

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