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Raman study of phase transitions in pure and alloyed zirconia induced by ball-milling and a laser beam

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Abstract

High-temperature phases of ZrO_2 were obtained at room temperature by incorporating a few mole fractions of other oxides (MgO, Y_2O_3 or CoO) in a zirconia crystal lattice using high-energy ball-milling. Raman spectra obtained after an adequate period of ball-milling show the formation of ZrO_2–MgO and ZrO_2–Y_2O_3 cubic solid solutions and a ZrO_2–CoO tetragonal solid solution. However, in the case of pure monoclinic zirconia, the transformation from a monoclinic to a tetragonal structure could not be completed by the use of ball-milling only. The spectra of fully stabilized solid solutions did not change essentially with laser power, while insufficiently milled samples underwent phase changes when the laser power increased. In pure milled zirconia, annealing effects were observed. © 1997 Elsevier Science B.V.

Keywords: Raman spectroscopy; ZrO_2-based solid solutions; Ball-milling; Laser–material interaction

1. Introduction

Because of its properties (high melting point, low thermal conduction, high strength, high ionic conductivity, etc.), ZrO_2 is an important material in industry and technology. Zirconia has three temperature-dependent polymorphs: monoclinic (below 1170°C), tetragonal (between 1170 and 2370°C) and cubic (above 2370°C). The high-temperature phases, which have much better mechanical properties, can be quenched at room temperature by incorporating other oxides in the crystal lattice [1–3]. Alloying can be achieved by high-energy ball-milling of mixtures of ZrO_2 and other oxides for appropriate milling times [4–6] in order to avoid the high temperatures needed for sintering or the calcination process [3,7]. The stability and structure of the polymorph produced depend on the type and amount of added oxide [2,3,8]. The milling of pure ZrO_2 did not entirely transform monoclinic ZrO_2 (m-ZrO_2) into tetragonal ZrO_2 (t-ZrO_2) [4,9,10].

In the present work, Raman spectroscopy was used to study the synthesis of zirconia with the appropriate amount of Y_2O_3, MgO and CoO and the formation of cubic or tetragonal solid solutions at room temperature using high-energy ball-milling. The stability of the structures achieved was investigated by changing the power of the excitation laser.

2. Experimental

Syntheses were performed in air at room temperature in the 14*g* acceleration, Fritsch planetary

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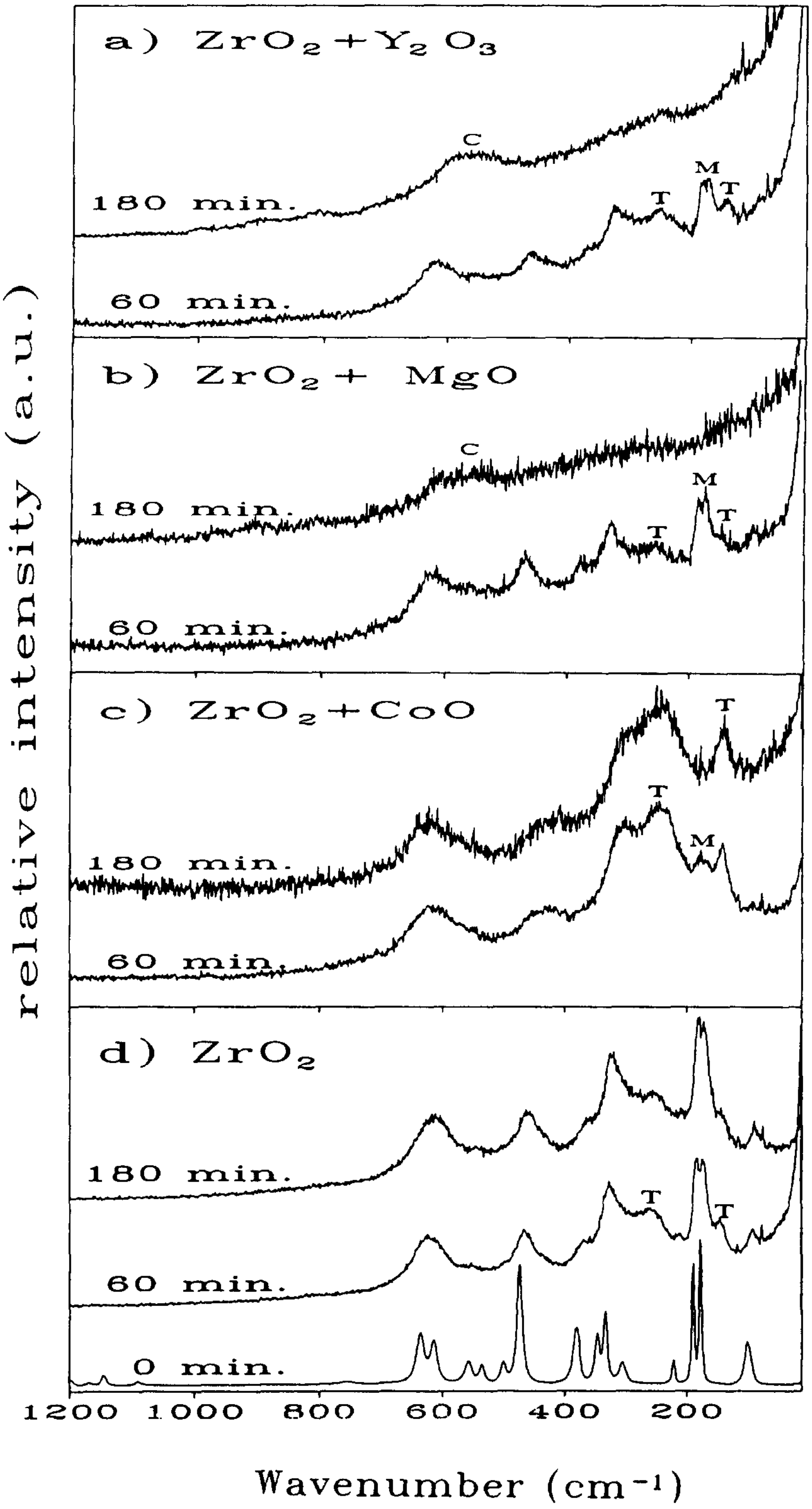

a) $ZrO_2+Y_2O_3$
C
M
T
T
180 min.
60 min.
b) ZrO_2+ MgO
C
M
T
T
180 min.
60 min.
c) ZrO_2+CoO
T
T
M
180 min.
60 min.
d) ZrO_2
T
T
180 min.
60 min.
0 min.
1200
1000
800
600
400
200
relative intensity (a.u.)
Wavenumber (cm^{-1})

microball mill Pulverisette 7, with a vial and balls made of tungsten carbide (WC). The materials used were commercial ZrO_2, Y_2O_3, MgO and CoO with a purity of better than 99.9%. Four types of powder charges were used: three were ZrO_2 plus another oxide with mass ratio 5:1, and the fourth was ZrO_2 alone. The ball to powder mass ratio was approximately 40:1. No sample was milled for longer than 180 min. A coherent INNOVA 100-15 argon-ion laser operating at the 514.5 nm line was used for excitation, and Raman spectra were recorded using a computerized DILOR Z24 triple monochromator. In the first stage of the experiment, the laser power was 50 mW since a stronger beam affected the samples. In the second stage of the experiment, this influence was studied, keeping the laser power between 25 and 200 mW.

3. Results and conclusions

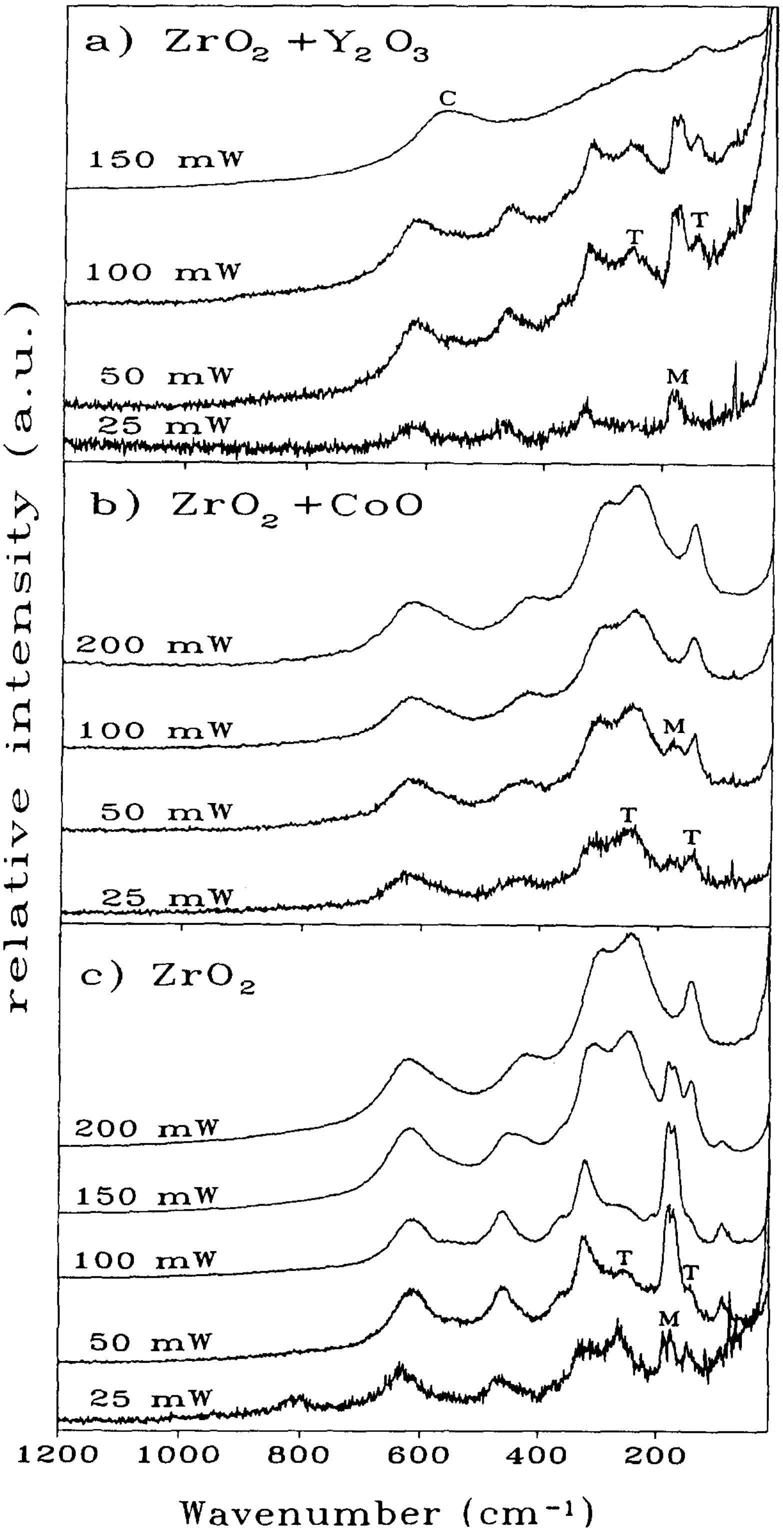
Factor group analysis predicts a different number of Raman bands for the three zirconia polymorphs. In monoclinic $P2_1/b$ (C_{2h}^5) ZrO_2 (four molecules per unit cell) 18 Raman vibrational modes are active: $9A_g + 9B_g$ symmetry; in tetragonal $P4_2/nmc$ (D_{4h}^{15}) ZrO_2 (two molecules per unit cell) 6 vibrational modes are Raman active: $A_{1g} + 2B_{1g} + 3E_g$. Only one F_{2g} mode is Raman active for the cubic fluorite structure $Fm3m$ (O_h^5) — one molecule per unit cell.

In pure ZrO_2 (Fig. 1, spectrum d; 0 min) we observed 14 bands whose positions were in accordance with results of other authors [8,11], confirming that the stucture of zirconia was monoclinic. The most intensive bands were observed at 178 and 190 cm^{-1} and were used as an indication of monoclinic structure in a particular sample. The most prominent bands relating to tetragonal structure are found at around 150 and 260 cm^{-1} [4] and only one F_{2g} mode for the cubic fluorite structure is observed at approximately 600 cm^{-1}. This enables good differentiation of these two structures (in contrast to XRD analysis [11]). All these facts make it possible to monitor the changes during the alloying of ZrO_2 by ball-milling.

Fig. 1 shows the Raman spectra of different ZrO_2-based mixtures milled for 60 and 180 min (shorter periods of ball-milling did not produce any phase changes). The spectra of ZrO_2 milled with 10 mol.% of Y_2O_3 (Fig. 1, spectrum a) for 60 min showed that ZrO_2 underwent only a partial phase transition from the monoclinic to the tetragonal structure because there was not enough Y_2O_3 to incorporate in the ZrO_2 crystal lattice. However, after 180 min of milling ZrO_2 plus 10 mol.% Y_2O_3, a cubic solid solution was achieved. The spectrum associated with this phase possesses only one asymmetric broad band in the vicinity of 600 cm^{-1} assigned to the F_{2g} mode of the cubic (fluorite) lattice. The disorder within the oxygen sublattice and the appearance of oxygen vacancies cause Raman scattering from points of the Brillouin zone with $q \neq 0$ [1,12]; therefore, Raman bands of this sample are broad and asymmetric. This consideration corroborates the statement of Chen et al. [6] that continued fragmentation and aggregation which increase the number of lattice defects during milling caused "alloying" between oxides. A similar evolution of the stabilization process was observed in ZrO_2 milled with 38 mol.% MgO, and disorder in the cubic (fluorite) structure is, moreover, evident (Fig. 1, spectrum b)). The milling of ZrO_2 with 25 mol.% CoO for 60 min (Fig. 1, spectrum c)) did not allow a complete phase transition to the tetragonal structure, but the milling of the powder mixture for 180 min resulted in the tetragonal solid solution structure with the character of a well-ordered lattice [4]. In contrast to the behaviour of zirconia in the oxide mixtures, the milling of pure m-ZrO_2 did not result in a complete phase transition to the other polymorph (Fig. 1, spectrum d) even after 180 min (in agreement with Refs. [9,10]).

A change of laser power has a strong influence on the samples (Fig. 2), and represents a good method for obtaining the stability of prepared ZrO_2-based milling samples. Thus, a mixture of 2.5 g of ZrO_2 and 0.5 g of Y_2O_3 milled for 60 min was transformed into the

Fig. 1. Raman spectra of (spectrum a) ZrO_2 milled with Y_2O_3, (spectrum b) ZrO_2 milled with MgO, (spectrum c) ZrO_2 milled with CoO, (spectrum d) pure ZrO_2 before and after milling for different milling times. (Laser power, 50 mW; M, monoclinic structure bands; T, tetragonal structure bands; C, cubic structure bands.)


a) ZrO2 +Y2 O3
C
150 mW
100 mW
T
T
50 mW
M
25 mW
b) ZrO2 +CoO
200 mW
100 mW
M
50 mW
T
T
25 mW
c) ZrO2
200 mW
150 mW
100 mW
T
T
50 mW
M
25 mW
relative intensity (a.u.)
1200
1000
800
600
400
200
Wavenumber (cm-1)

cubic structure after it had been illuminated with a 150 mW laser beam (Fig. 2, spectrum a). In the case of a ZrO_2–CoO mixture milled for 60 min, the treatment with the laser beam allowed the completion of the phase transformation into the tetragonal polymorph (Fig. 2, spectrum b). Pure m-ZrO_2 that contained some tetragonal structure after 60 min of milling was transformed back into the monoclinic structure with a laser power of only 100 mW as a consequence of the annealing effect. This occurred because tetragonal zirconia appeared in a sample with crystallite sizes below 30 nm, which, on being heated, grew and was transformed to the stable monoclinic phase. On the other hand, pure ZrO_2 milled for 180 min transformed into the tetragonal phase after being irradiated with a 200 mW laser beam (Fig. 2, spectrum c). The reason for such behaviour was the presence of wear-produced WC [13] (“invisible” to Raman spectroscopy), which was incorporated in the crystal lattice due to the temperature achieved by the laser beam.

In conclusion, we point out that the ball-milling method of sample preparation causes phase transformations in mixtures of ZrO_2 with metal oxides that would otherwise have to be heated to more than 1500°C. Raman spectroscopy is an excellent tool for monitoring the structural changes in such materials. In particular, the effect of a power change of the incident laser beam showed it to be of great importance because the power change caused a change in the structure of ZrO_2-based mixtures.

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Fig. 2. Raman spectra of (spectrum a) ZrO_2 milled with Y_2O_3 for 60 min, (spectrum b) ZrO_2 milled with CoO for 60 min, (spectrum c) pure ZrO_2 milled for 180 min with different laser excitation powers. (M, monoclinic bands; T, tetragonal bands; C, cubic bands.)