

Raman spectroscopic investigation of the effects of heat-treatment and Al, Ce or Eu doping concentration on TiO₂ powder crystallization

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Abstract

In this paper, we study the effects of various doping elements (Aluminum, Cerium or Europium) with different contents and of heat-treatment on the structural properties of TiO₂ nano-crystalline powders. The sol-gel technique was used to prepare the doped and undoped TiO₂ powders. The structures of the obtained samples were investigated using Raman spectroscopy, which allowed to monitor the formation of anatase and rutile crystalline phases as a function of the annealing temperature. We have shown that all the doping elements contribute to stabilize anatase phase at high calcination temperature. Furthermore, doping with Europium was found to be the most efficient anatase phase stabilizer.

Key words:

Doped TiO₂ powder, Aluminum, Cerium, Europium, Raman spectroscopy, sol-gel, anatase, rutile.

1. Introduction

Recently, TiO₂ powders doped with diverse elements have been investigated for many applications, among which photocatalytic activity is the most important [1-6]. For instance, TiO₂ powders doped with cerium were analysed for photocatalytic activity [7-9]. As another example, nano-powders of Aluminum-doped TiO₂ were used to make thick films-based gas sensors exhibiting a good selectivity and sensitivity to CO and O₂ gases. These Al-doped TiO₂ powders showed stable anatase phase up to 800°C [10]. Besides, the properties of TiO₂ nanoparticles doped with Europium have been studied for optical applications [11-14]. Hence, the impact of such dopants on the structural properties of titanium dioxide is of crucial importance for these various applications.

In this paper, we report on the crystallization of sol-gel-derived TiO₂ powders as a function of heat-treatment temperature and of doping contents ranging between 1 and 7 (mol.%), with different elements (Al, Ce or Eu). The crystal phase was studied using micro-Raman spectroscopy.

2. Materials and methods

2.1. Synthesis of TiO₂ powders

All chemical products have been purchased from Aldrich and used as-received. A TiO₂ sol was prepared using titanium isopropoxide (Ti(OⁱPr)₄), isopropanol (PrOH) and acetic acid (AcOH) with a molar ratio

AcOH/Ti = 6. The obtained mixture was diluted with methanol. The solution was slowly evaporated at room temperature to yield a powder. Then, the residual solvents (isopropanol, acetic acid and methanol) were eliminated by heating the obtained product at 120°C for 48 h. The resulting powder was ground using an automatic crusher.

Furthermore, for the preparation of doped powders with 1%, 2%, 5% and 7% of Europium, Cerium or Aluminum, the as-synthesized sol of TiO₂ was doped with europium (III) nitrate pentahydrate Eu(NO₃)₃·5H₂O, Cerium(III) nitrate hexahydrate Ce(NO₃)₃·6H₂O and Aluminum nitrate nonahydrate Al(NO₃)₃·9H₂O respectively.

To investigate the effect of the calcination temperature on the structural properties of the obtained powders, they have been heat-treated for 1 hour in air at a temperature ranging from 400°C to 1100°C.

2.2. Characterisation

The Raman spectra were obtained in a confocal configuration using a triple-grating spectrometer (Jobin-Yvon T64000) and the 514.5 nm line of an Ar⁺ laser as the excitation source with a power of 0.2 W on the sample. The absence of any phase change under the continuous laser irradiation has been carefully checked prior to the data acquisitions. All Raman spectra were recorded at room temperature in the wavenumber range 50-700 cm⁻¹.

3. Results and discussion

In the corresponding Raman spectra of the pure TiO_2 sample annealed at different temperatures ranging between 400 and 1100°C (Fig. 1), the formation of anatase phase appears at from the lower temperature 400°C, while the rutile phase begins to be observed at 700°C. Considering that the Raman scattering cross-section is constant for the anatase phase and that the spectra acquisitions have been performed in almost the same conditions, the increasing intensity of each peak in Fig. 1 may be attributed to the increasing crystallinity of the powder, due to the heat-treatment. Moreover, Fig. 1 shows the complete and rapid phase conversion from anatase to rutile for heat-treatment temperatures between 600 and 800°C. The observed Raman frequencies for TiO_2 products at different calcination temperatures are listed in Table 1.

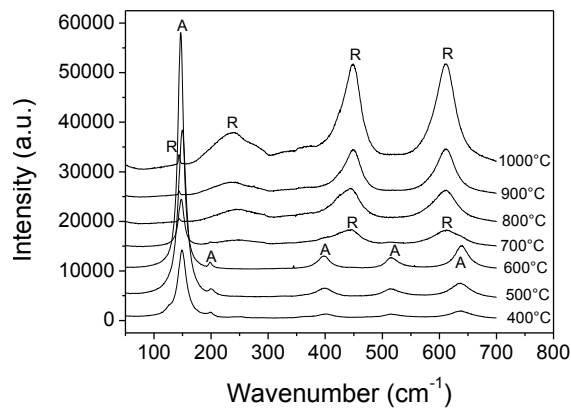


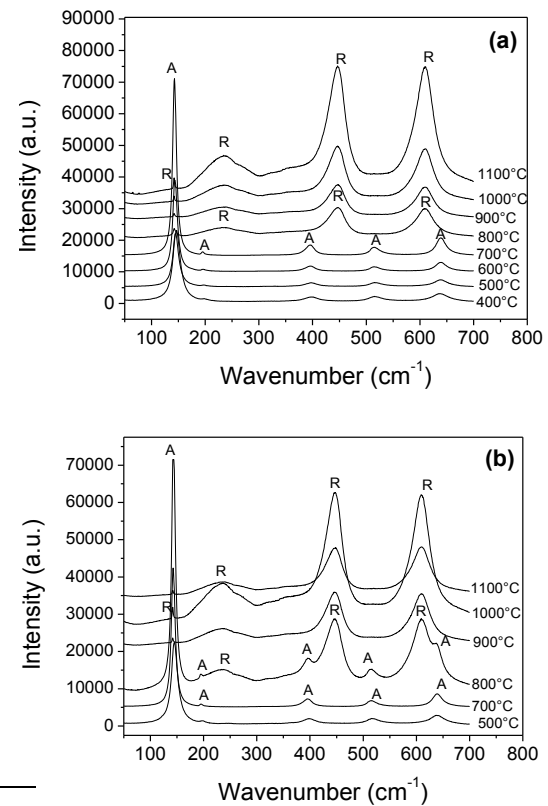
Fig. 1. Raman spectra of a pure TiO_2 powder annealed at different temperatures for 1 hour.

Table 1

Observed Raman frequencies (cm^{-1}) and their assignments in pure and doped TiO_2 powders annealed at different temperature.

	TiO_2 (600°C)	TiO_2 - 1%Eu (900°C)	TiO_2 - 5%Al (800°C)	TiO_2 - 1%Ce (800°C)	Assignment
Anatase					
ν_1	147	144	143	145	E_{g1}
ν_2	197	195	196	197	E_{g2}
ν_3	397	395	395	395	B_{1g}
ν_4	515	512	513	512	A_{1g}
ν_5	515	512	513	512	B_{1g}
ν_6	640	636	638	637	E_{g3}
Rutile					
	(700°C)	(1000°C)	(900°C)	(900°C)	
	144	142	142	143	B_{1g}
	237	238	237	239	Multi- phonon process
	449	447	446	444	E_g
	612	609	610	610	A_{1g}

Fig. 2 shows the Raman spectra of TiO_2 powders doped by Aluminum with 1%, 2%, 5% and 7% contents. For sample doped with 1% Al and heat-treated from 400°C to 700°C, the vibration bands have been clearly attributed to the anatase phase while the rutile phase bands were observed from 800°C to 1100°C. For 2% Al-doped sample, at 800°C the characteristic vibration bands of both phases were observed and the complete polymorph conversion from anatase to rutile was achieved at 900°C. For the higher Aluminum contents (5% and 7%), only the anatase phase is obtained for temperatures up to 800°C. For all contents in Al, the rutile phase was completed at 900°C and above.



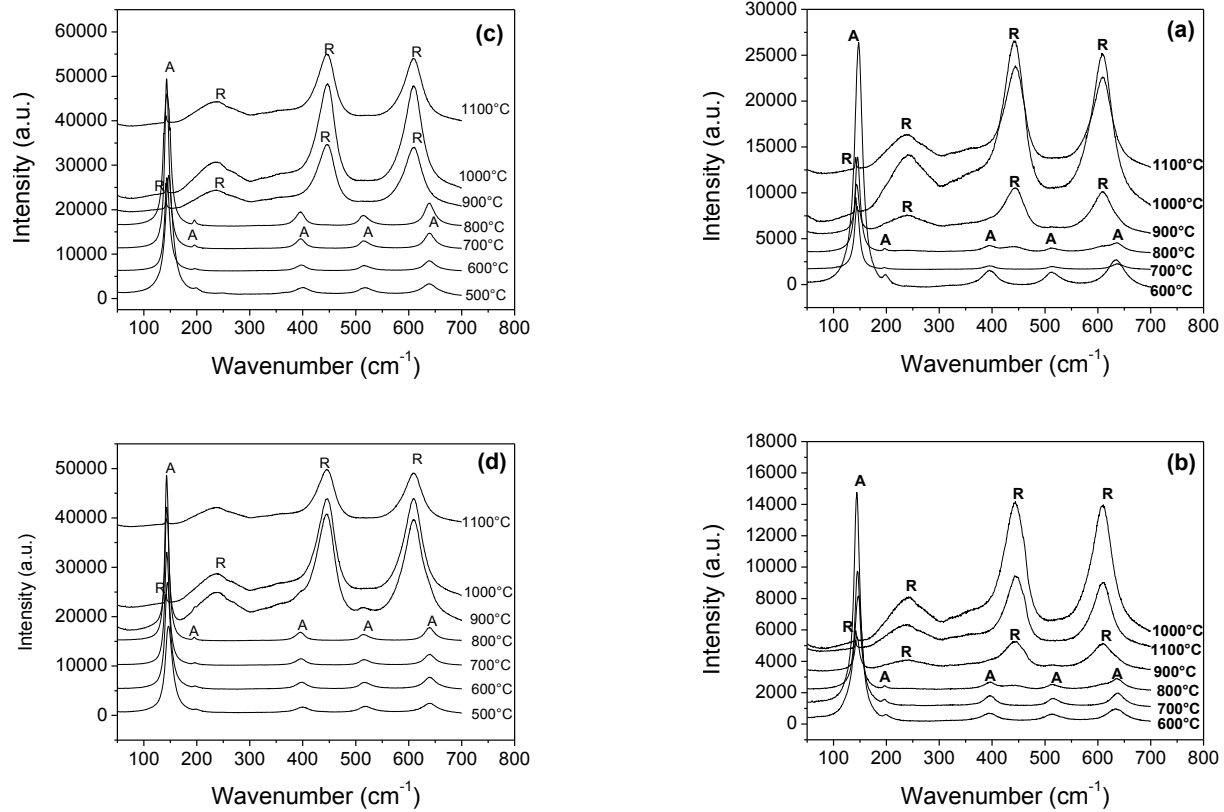


Fig. 2. Raman spectra of TiO₂ powders doped with different Al contents
(a) 1%, (b) 2%, (c) 5% and (d) 7%.

Fig. 3 shows the Raman spectra of TiO₂ powders doped with 1%, 2%, 5% and 7% Cerium contents. At all Cerium contents, the anatase phase was observed for temperatures up to 800°C. Furthermore, when the calcination temperature became higher than 800°C, the rutile phase was the only observed phase. One can also note, for high Ce concentrations (5 and 7 %), the presence of Raman band around 460 cm⁻¹. This band could be attributed to the triply degenerate Raman-active mode of cubic fluorite-type crystallizing CeO₂. This mode, assigned to F_{2g} symmetry, can be viewed as a symmetric breathing mode of the oxygen atoms around cerium ions [15, 16].

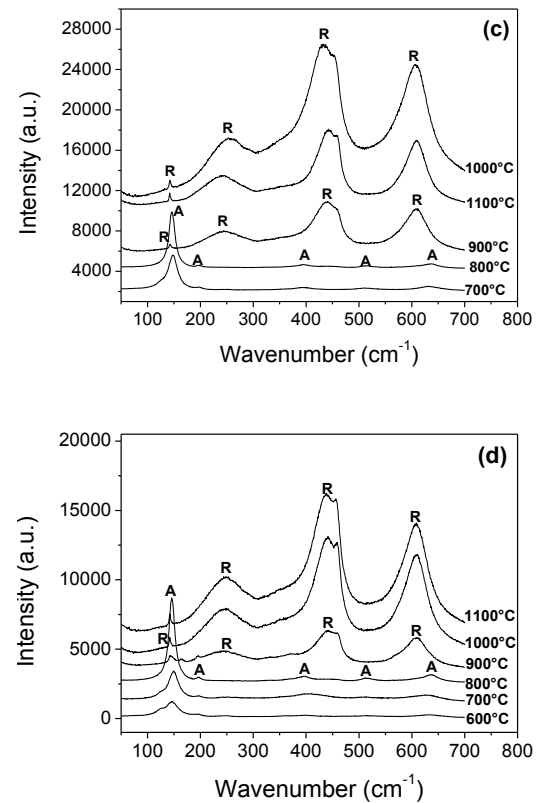


Fig. 3. Raman spectra of TiO₂ powders doped with different Ce contents
(a) 1%, (b) 2%, (c) 5% and (d) 7%.

Fig. (4) presents Raman spectra of 1%, 2%, 5% and 7% Eu-doped TiO_2 powders annealed at different temperatures for 1 hour. As it can be seen, anatase phase appears at 400°C for all samples, while the rutile is observed at 1000°C. This result corresponds to tremendous influence of Europium on the crystallization of TiO_2 . Indeed, rutile phase was observed at 700°C for pure TiO_2 powders and at 800°C or 900°C for TiO_2 powder doped with Cerium or Aluminum, depending on their concentration, while in the case of Eu-doped TiO_2 powders, rutile phase appeared at 1000°C and the phase transition was even not completed at this temperature for the highest Eu concentration. This result demonstrates that Eu^{3+} plays the role of anatase phase stabilizer, much better than other doping elements. It can be noted that only a few amount of europium (1%) is sufficient to stabilize the anatase phase up to 900°C.

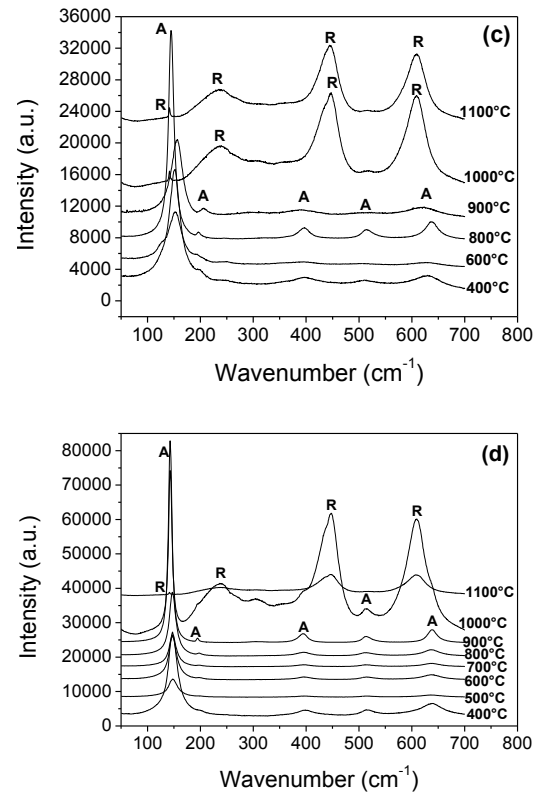
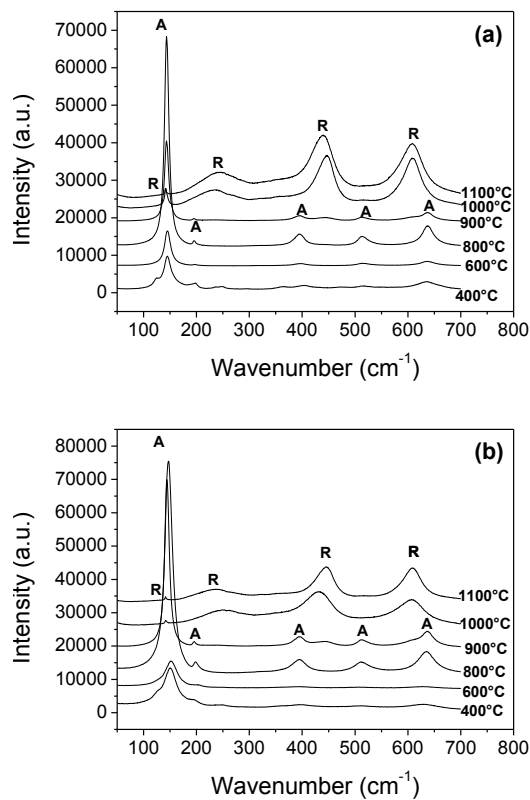


Fig. 4. Raman spectra of TiO_2 powders doped with different Eu contents (a) 1%, (b) 2%, (c) 5% and (d) 7%.

Raman spectra can also be used to evaluate the crystallite size. Indeed, a phonon confinement model has been reported [17], expressing the relation between the size of TiO_2 anatase nanocrystals and the full-width at half-maximum (FWHM) of the E_g Raman mode around 147 cm^{-1} . Fig. 5 shows that the mean crystallite size, derived using this phonon confinement model, remained between 4 and 8 nm for the non-doped TiO_2 powder, increasing with the calcination temperature. Furthermore, it increased from 3 nm to 10 nm for the samples doped with Cerium and from 5 nm to 13 nm for those doped with Aluminum. For the Eu-doped samples, it increased from 4 nm to 14 nm. Furthermore, for a given temperature, the mean crystallite size of samples doped with Aluminum was found to be the largest. Hence, it is shown that a relative control of the mean crystallite size (between 3 and 14 nm) can be performed by acting either on the doping or on the heat-treatment temperature.

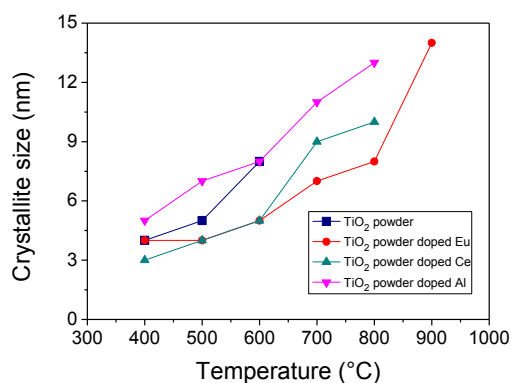


Fig. 5. TiO₂ anatase crystallite size, determined using the FWHM of E_{g(1)} Raman mode and the phonon confinement model [17] and reported as a function of the heat-treatment temperature.

4. Conclusion

Nanocrystalline TiO₂ powders doped with Aluminum, Cerium and Europium at several concentrations were prepared by the sol-method. These powders were heat-treated at different temperatures ranging from 400°C to 1100°C and their structure was studied by Raman spectroscopy. Raman analysis of pure and doped TiO₂ powders demonstrated that doping the TiO₂ matrix with aluminum, cerium or europium improves anatase phase stability at high temperature. It was shown that the Europium is the most efficient dopant for anatase phase stabilization up to 900 °C (instead of 600°C for the undoped sample). Moreover, the mean crystallite size increased with the annealing temperature and could be controlled between 3 and 14 nm, depending on the doping species.

Acknowledgements

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