

Low-Frequency Raman Spectroscopy of Pure and La-Doped TiO₂ Nanopowders Synthesized by Sol-Gel Method

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Pure and La-doped titania (TiO₂) nanopowders are synthesized by sol-gel technology. The crystallite sizes determined by X-ray diffraction measurements range from 10 to 15 nm. Dependence of structural and morphological characteristics of nanopowders on synthesis conditions and La³⁺ content is investigated by the Raman spectroscopy. Very intensive modes observed in the Raman spectra of all nanopowder samples are assigned to anatase phase of TiO₂. Additional Raman modes of extremely low intensity can be related to the presence of a small amount of brookite amorphous phase in nanopowders, which is in accordance with the results of X-ray diffraction analysis. The particle size distribution in TiO₂ nanopowders was estimated from the low frequency Raman spectra, using the fact that the phonon modes in nanosized TiO₂ observed in the low frequency region ($\omega < 40 \text{ cm}^{-1}$) can be well described by the elastic continuum model, assuming that nanoparticles are of perfect spherical shape and isotropic. The nanosized particle distribution obtained by this method is used for the calculation of the frequency and shape of the most intensive E_g Raman mode in anatase TiO₂ by the phonon confinement model. The calculated broadening of this mode, associated with the particle size distribution, coincides well with the characteristics of E_g mode observed in measured Raman spectra of TiO₂ nanopowders. This confirms the Raman spectroscopy method as a powerful tool for determination of particle size distribution in nanosized materials.

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1. Introduction

Titanium dioxide (TiO₂) has three polymorphic modifications: rutile (tetragonal, $P42/mnm$), anatase (tetragonal, $I41/amd$), and brookite (orthorhombic, $Pbca$). All of them have numerous applications as important industrial materials. In recent years, nanosized TiO₂, especially anatase TiO₂, has attracted much attention as key material for photocatalysts [1], dye-sensitized solar cells [2], gas sensors [3] and electrochromic devices [4]. The applications of nanosized anatase TiO₂ are primarily determined by its physicochemical properties such as crystalline structure, particle size, surface area, porosity and thermal stability. The aim of this study is to investigate the variations in anatase structure induced by doping of nanopowders with lanthanum. In our previous paper [5] it was shown that La-doping improves thermal stability of sol-gel synthesized TiO₂ nanopowders. The Raman spectroscopy method is primarily used here to correlate the amount of brookite phase, as well as the particle size and particle size distribution in anatase phase, with the content of La-dopant.

2. Experimental details

TiCl₄ was used as the precursor in the synthesis. The Ti(OH)₄ hydrogel was obtained by hydrolysis of TiCl₄ at 0°C with controlled addition of 2.5 wt.% aqueous ammonia into the aqueous solution of TiCl₄ (0.3 mol/l) and careful control of the pH value of the solution. After aging in the mother liquor for 5 h, filtering and washing out with deionized water, obtained Ti(OH)₄ hydrogel was converted to its ethanol-gel by repeated exchange with anhydrous ethanol for several times. The obtained alcogel was placed in a vessel, dried at 280°C and calcined at temperature of 550°C, and after that converted to the nanoparticles. In the case of La-doped TiO₂, LaCl₃·7H₂O was used.

Powder X-ray diffraction (XRD) was used for the identification of crystalline phases, quantitative phase analysis and estimation of crystallite size and strain. The XRD patterns were collected on a Philips diffractometer (PW1710) employing Cu $K_{\alpha 1,2}$ radiation.

Raman measurements were performed using 514 nm laser line of an Ar⁺/Kr⁺ laser and Jobin Yvon T64000 triple spectrometer system, equipped with confocal microscope and a nitrogen-cooled CCD detector. Low-frequency Raman measurements were performed in the backscattering geometry using the 442 nm line of a He-Cd laser as an excitation source, a Jobin Yvon U1000

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monochromator and a photomultiplier as a detector. All Raman scattering measurements were performed at room temperature in air.

3. Results and discussion

Relevant and the most intensive diffraction peaks in the XRD patterns of all samples belong to anatase crystal structure of TiO_2 (JCPDS card 78-2486). The presence of low-intensity diffraction peak at $2\theta \approx 30.8^\circ$ that can be ascribed to the brookite phase of TiO_2 was observed in all XRD patterns (JCPDS card 29-1360). Structure refinements were performed by the Rietveld method [6]. The obtained average anatase (brookite) crystallite size was 12 nm (35 nm) and 10 nm (26 nm) for pure TiO_2 and TiO_2 doped with 1 wt.% of La, respectively. The average strain in anatase was 4.2×10^{-3} in pure TiO_2 , whereas its value was 5.7×10^{-3} in La-doped TiO_2 . The percent of brookite phase obtained by quantitative phase analysis is 16% and 24% in pure and La-doped TiO_2 , respectively. These results show that doping with 1 wt.% of La induced crystallite size decrease, whereas strain value and brookite content increased. The large values of the average strain in brookite crystallites ($\approx 20 \times 10^{-3}$) indicate that this phase is highly disordered both in pure and La-doped samples.

In the Raman spectra of both pure and La-doped TiO_2 samples the dominant modes (Fig. 1a) can be assigned to the Raman active modes of the anatase crystal [7]: ≈ 143 ($E_{g(1)}$), 197 ($E_{g(2)}$), 399 ($B_{1g(1)}$), 519 (A_{1g} , $B_{1g(2)}$) and 639 cm^{-1} ($E_{g(3)}$). The additional Raman modes at about 243, 294, 323 and 362 cm^{-1} (Fig. 1b), can be ascribed to the brookite phase of titania [8]. Low intensities and large widths of these modes confirm great disorder and partial amorphization of brookite in all the samples. The content of brookite for TiO_2 doped with La up to 4 wt.% [5] is higher or close to the amount in pure TiO_2 , whereas for greater La wt.% brookite content decreases.

The position of anatase $E_{g(1)}$ Raman mode for different TiO_2 samples ranges between 143 and 144 cm^{-1} , whereas its line width varies from 12.1 to 13.7 cm^{-1} . Several factors can contribute to the changes in the peak position, line width and shape of this mode in TiO_2 nanopowders ([9] and references therein). Dominance of one or more of these factors, observable in Raman spectra, is determined by the structural characteristics of a TiO_2 nanopowder: particle size distribution [9–11], existence of mixed phases (anatase in combination with considerable amount of rutile or brookite phase) [5], value and type of the strain (compressed or tensile) [9, 11], discrepancy from stoichiometry [12] as well as type of defects [5, 9], etc. We assumed that the main factors that influenced the behavior of $E_{g(1)}$ mode in our samples were the confinement effect due to anatase nanoparticle size distribution, disorder induced by existence of considerable amount of brookite phase and the strain effects caused by introducing of La^{3+} ions into the TiO_2 lattice.

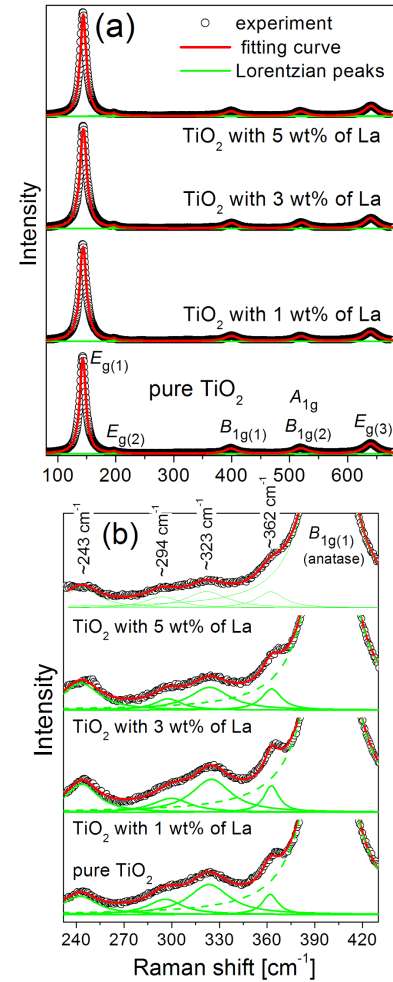


Fig. 1. Raman spectra of pure and La-doped TiO_2 samples. Lorentzian fits of anatase (a) and brookite (b) modes in the experimental Raman spectra (\circ).

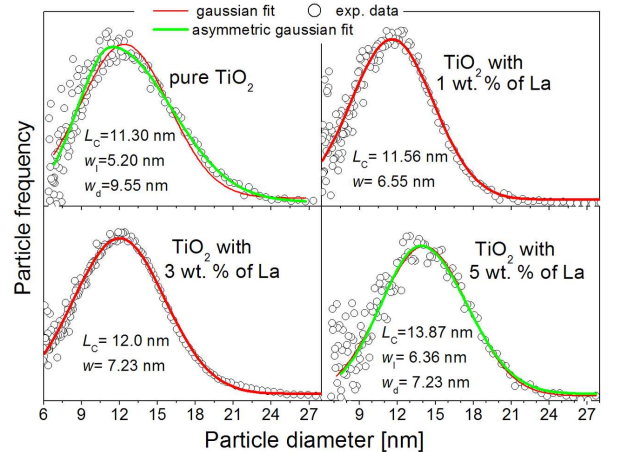


Fig. 2. Particle size distributions in pure and La-doped TiO_2 nanopowders estimated from low-frequency Raman spectra.

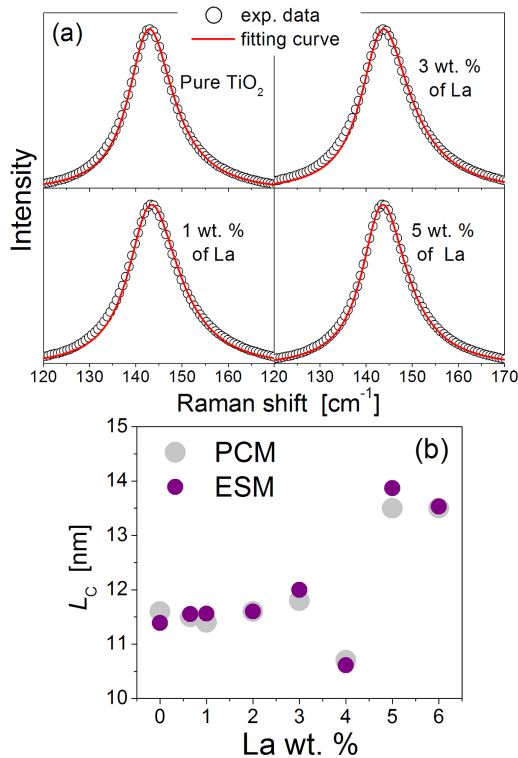


Fig. 3. PCM fits of $E_{g(1)}$ Raman mode for pure and La-doped anatase samples (a). Most frequent particle size L_C obtained by ESM (black circles) and PCM (gray circles) in dependence of wt.% of La in TiO₂ nanopowders (b).

Raman scattering from confined acoustic vibrations in nanoparticles was observed in low frequency part of spectra of various materials. The elastic sphere model (ESM) was generally used to analyze the acoustic phonon confinement. This model describes the oscillations of homogeneous elastic sphere and was successfully applied to explain the experimental spectra of nanoparticles [13–15]. According to ESM, the frequency of an acoustic Raman mode is scaled as the inverse of the dimension of a vibrating particle: $\omega = \beta_L/D$, where β_L is a coefficient calculated from ESM [14, 15]. In this paper we used procedure proposed by Ivanda et al. [15] for the extraction of information on nanoparticle size distribution from the low-frequency Raman spectra of TiO₂ nanoparticles. Values of longitudinal and transversal sound velocities for rutile TiO₂ were used ($v_L = 9017$ m/s, $v_T = 5394$ m/s, respectively) in calculations, due to the lack of this data for anatase. Calculated β_L was 239.6. Inhomogeneous broadening of the spectrum as a consequence of the non-uniform particle size distribution of the sample was incorporated. The evaluated particle size distributions in pure and La-doped TiO₂ are presented in Fig. 2 together with the best fits of these distributions obtained by Gaussian and asymmetric Gaussian functions. The parameters L_C — most frequent particle size, w — symmetric Gaussian halfwidth, and w_1 and w_d — left and right

halfwidths of asymmetric Gaussian, are shown in Fig. 2. Let us note that the value L_C is equal to average particle size L_0 in symmetric Gaussian distribution, as in TiO₂ with 1 wt.% of La ($L_0 = L_C \approx 11.6$ nm). However, in nanopowders with asymmetrical Gaussian distributions, the values of L_C and L_0 are different, as in pure TiO₂ where $L_0 \approx 13$ nm while $L_C \approx 11.3$ nm.

The intensities of $E_{g(1)}$ mode for pure and La-doped TiO₂ nanopowders were calculated by phonon confinement model (PCM), described in detail in our previous papers [5, 9, 10]. The particle size distributions obtained by ESM were used as initial distributions for the best-fit calculations of the $E_{g(1)}$ mode by PCM (Fig. 3a). The dependence of the most frequent particle size L_C on La content in TiO₂ nanopowders is shown in Fig. 3b. The values of L_C in the distributions used finally in PCM (gray circle) are very close to the corresponding values of L_C in the distributions obtained by ESM (black circle). The values of the average particle size estimated from the Raman spectra is a little bit greater than the average anatase crystallite size obtained by XRD, which can be a consequence of presence of brookite crystallites in the powders. Finally, we had to include the effects of compressive strain in PCM of Raman $E_{g(1)}$ mode in nanopowders with higher La content.

4. Conclusion

A detailed Raman study of sol-gel synthesized anatase TiO₂ nanopowders doped with lanthanum ions (La³⁺) in the range from 0 to 6 wt.% was presented. Very intensive modes observed in the Raman spectra of all nanopowders were assigned to anatase phase of TiO₂, whereas the additional modes of extremely low intensity can be related to the presence of small amount of brookite phase. The particle size distributions in TiO₂ nanopowders estimated from the low frequency Raman spectra by ESM coincide with the distributions used for the best-fit calculation of the anatase E_g Raman mode by the PCM. Obtained results show that the particle size in TiO₂ nanopowders doped with La up to 4 wt.%, is close to or smaller than in the pure TiO₂, whereas nanoparticles are larger for higher La content. Also, PCM analysis implies existence of compressive strain in nanopowders with more than 3 wt.% of La.

Acknowledgments

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References

- [1] S. Sakka, *J. Sol-Gel Sci. Techn.* **37**, 135 (2006).
- [2] J.N. Hart, D. Menzies, Y-B. Cheng, G. P. Simon, L. Spiccia, *J. Sol-Gel Sci. Techn.* **40**, 45 (2006).

- [3] D. Kim, A. Rothschild, D.-J. Yang, H. L. Tuller, *Sensor Actuat. B, Chem.* **130**, 9 (2008).
- [4] C.G. Granqvist, A. Azens, J. Isidorsson, M. Kharrazi, L. Kullman, T. Lindström, G.A. Niklasson, C.-G. Ribbing, D. Rönnow, M. Stromme Mattsson, M. Veszelei, *J. Non-Cryst. Solids* **218**, 273 (1997).
- [5] M. Šćepanović, S. Akrabić, V. Berec, A. Golubović, Z. Dohčević-Mitrović, A. Kremenović, Z.V. Popović, *Acta Phys. Pol. A* **115**, 771 (2009).
- [6] A. Kremenovic, J. Blanusa, B. Antic, P. Colombar, V. Kahlenberg, C. Jovalekic, J. Dukic, *Nanotechnology* **18**, 145616 (2007).
- [7] T. Ohsaka, F. Izumi, Y. Fujiki, *J. Raman Spectrosc.* **7**, 321 (1978).
- [8] S. Yin, K. Ihara, B. Liu, Y. Wang, R. Li, T. Sato, *Phys. Scr. T* **129**, 268 (2007).
- [9] M.J. Šćepanović, M. Grujić-Brojćin, Z. Dohčević-Mitrović, Z.V. Popović, *Mater. Sci. Forum* **518**, 101 (2006).
- [10] M.J. Šćepanović, M. Grujić-Brojćin, Z.D. Dohčević-Mitrović, Z.V. Popović, *Appl. Phys. A* **86**, 365 (2007).
- [11] J.E. Spanier, R.D. Robinson, F. Zhang, S-W. Chan, I.P. Herman, *Phys. Rev. B* **64**, 245407 (2001).
- [12] J.C. Parker, R.W. Siegel, *Appl. Phys. Lett.* **57**, 943 (1990).
- [13] L. Saviot, B. Champagnon, E. Duval, I.A. Kudriavtsev, A.I. Ekimov, *J. Noncryst. Solids* **197**, 238 (1996).
- [14] R. Kostić, S. Aškrabić, Z. Dohčević-Mitrović, Z.V. Popović, *Appl. Phys. A* **90**, 679 (2008).
- [15] M. Ivanda, K. Furi, S. Musi, M. Risti, M. Goti, D. Risti, A.M. Tonejc, I. Djerdj, M. Mattarelli, M. Montagna, F. Rossi, M. Ferrari, A. Chiasera, Y. Jestin, G.C. Righini, W. Kiefer, R.R. Gonçalves, *J. Raman Spectrosc.* **38**, 647 (2007).