Low-Frequency Raman Spectroscopy of Pure and La-Doped TiO\textsubscript{2} Nanopowders Synthesized by Sol-Gel Method

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Pure and La-doped titania (TiO\textsubscript{2}) 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 La\textsuperscript{3+} 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 TiO\textsubscript{2}. 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 TiO\textsubscript{2} nanopowders was estimated from the low frequency Raman spectra, using the fact that the phonon modes in nanosized TiO\textsubscript{2} 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 TiO\textsubscript{2} 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 TiO\textsubscript{2} 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 (TiO\textsubscript{2}) has three polymorphic modifications: rutile (tetragonal, $P4_2/mnm$), anatase (tetragonal, $I4_1/amd$), and brookite (orthorhombic, $Pbca$). All of them have numerous applications as important industrial materials. In recent years, nanosized TiO\textsubscript{2}, especially anatase TiO\textsubscript{2}, has attracted much attention as a key material for photocatalysts [1], dye-sensitized solar cells [2], gas sensors [3] and electrochromic devices [4]. The applications of nanosized anatase TiO\textsubscript{2} 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 TiO\textsubscript{2} 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

TiCl\textsubscript{4} was used as the precursor in the synthesis. The Ti(OH)\textsubscript{4} hydrogel was obtained by hydrolysis of TiCl\textsubscript{4} at 0°C with controlled addition of 2.5 wt.% aqueous ammonia into the aqueous solution of TiCl\textsubscript{4} (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)\textsubscript{4} hydrogel was converted to its ethanol-gel by repeated exchange with anhydrous ethanol for several times. The obtained alco gel 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 TiO\textsubscript{2}, LaCl\textsubscript{3}·7H\textsubscript{2}O 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 Phillips diffractometer (PW1710) employing Cu $K_{\alpha 1}$ radiation.

Raman measurements were performed using 514 nm laser line of an Ar\textsuperscript{+}/Kr\textsuperscript{+} 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
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 2θ ≈ 30.8° 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 (≈ 20 × 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.
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 \( \beta \) 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 (\( v_L = 9017 \text{ m/s} \), \( v_T = 5394 \text{ m/s} \), respectively) in calculations, due to the lack of this data for anatase. Calculated \( \beta \) 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 \( w_l \) 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 (\( L_0 = L_C \approx 11.6 \text{ nm} \)). However, in nanopowders with asymmetrical Gaussian distributions, the values of \( L_C \) and \( L_0 \) are different, as in pure TiO2 where \( L_0 \approx 13 \text{ nm} \) while \( L_C \approx 11.3 \text{ nm} \).

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 (La\(^{3+}\)) 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.

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References


