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Characterization of Anatase TiO_2 Nanopowder by Variable-Temperature Raman Spectroscopy

M. J. Šćepanović, M. Grujić-Brojčin, Z. D. Dohčević-Mitrović, Z. V. Popović
Center for Solid State Physics and New Materials, Institute of Physics, Pregrevica 118,11080 Belgrade, Serbia

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Abstract:

Raman spectroscopy has been used for characterization of commercial nanosized TiO_2 powder with declared grain size of 5 nm. The Raman spectra measured in Stokes and anti-Stokes regime confirm the anatase phase of TiO_2 powder in temperature range 25-1173 K. It is shown that phonon-confinement (due to small grain size) and nonstoichiometry (caused by laser irradiation in vacuum) have a great influence on blueshift and broadening of the main E_g Raman mode at low temperatures, while the influence of the strong anharmonic effect becomes dominant at higher temperatures. The phonon confinement effect decreases due to the crystallite growth at temperatures above 673 K.

Keywords: *Anatase TiO_2 nanopowder, Raman spectroscopy*

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1. Introduction

Recent interest in nanocrystalline anatase TiO_2 has been driven by its potential in a variety of technological applications, as well as in fundamental studies of size-induced modifications of the physical properties and phase stability of nanoscale inorganic systems [1, 2]. Raman spectroscopy is a powerful tool in the study of microstructure of nanosized materials, and therefore a promising technique for characterization of TiO2 nanopowders [3]. The changes in the Raman spectrum of nanocrystalline anatase, the phase most commonly synthesized at ambient conditions, have been variously interpreted as originating from the phonon confinement [4-6], non-stoichiometry [7] or internal stress/surface tension effects [8]. Although the majority of published studies point out phonon confinement as the main factor responsible for the changes observed in the Raman spectrum of nanocrystalline anatase [4-6], some researchers have interpreted their results favoring other factors, depending on structural characteristics of nanopowders.

In the present work we investigate the temperature dependence of Raman spectra of commercial anatase TiO_2 nanocrystals with a declared average crystallite size of about 5 nm using variable-temperature Raman scattering. The Stokes and anti-Stokes Raman spectra at different temperatures in the range from about 23 to 1173 K are shown. We demonstrated that, depending on temperature, phonon confinement, anharmonic and nonstoichiometric effects have different influence on the frequency shift and the broadening of the lowest frequency E_g Raman mode. A Comparison between experimental spectra of anatase TiO_2

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*) Corresponding author: maja.scepanovic@phz.bg.ac.rs

nanopowder and spectra calculated by the phonon confinement model with anisotropic dispersion relations and temperature dependant parameters reveals information about the structure, stoichiometry and crystallite size at all given temperatures.

2. Experimental details

In this study TiO_2 nanopowder (Aldrich 637254-50G, 99.7%) with a declared average crystallite size of about 5 nm was investigated.

Low frequency Raman measurements were performed at room temperature in the backscattering geometry using the 514.5-nm line of an Ar^+ laser, Jobin–Yvon U1000 monochromator and a photomultiplier as the detector. Raman measurements at low temperatures were performed by the same equipment in vacuum in the cryostat system.

High temperature Raman measurements were taken with same Ar^+ laser line using a Jobin Yvon T64000 spectrometer equipped with a Linkam TS 1500 microscope heating stage and nitrogen cooled charge-coupled-device detector (CCD). Overheating of the samples was avoided using a minimal laser power when no changes of the Raman spectra were noticed.

3. Results and discussion

Fig. 1 shows nanosize particle distribution estimated by the procedure for the evaluation of the particle size from the low frequency Raman (LFR) spectrum proposed by Ivanda et al. [9]. A room temperature LFR spectrum is presented in the inset of the same figure. The existence of two modes in LFR spectrum resulted in the distribution with two maxima. As the particle frequency corresponding to the second maximum is very low, only the distribution from the first maximum was fitted by log-normal function with the parameters 7.28 nm and 0.20.

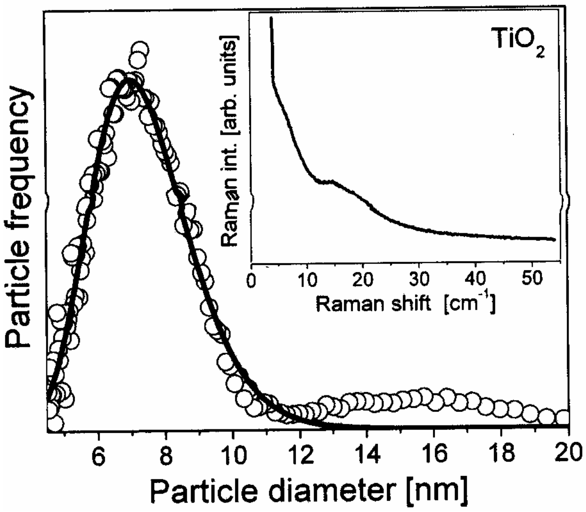


Fig. 1. Size distribution (open circles) of TiO_2 nanopowder obtained from room temperature LFR spectrum (inset) and its fit by a log-normal function (full line).

All Raman spectra measured at temperatures between 23 and 1173 K confirm the anatase phase of this TiO_2 nanopowder (some of them are shown in Fig. 2). Raman modes can be assigned to the Raman spectra of the anatase single crystal [10]: ~144 (E_g), 197 (E_g), 399

(B_{1g}), 513 (A_{1g}), 519 (B_{1g}) and 639 cm^{-1} (E_g). With temperature increasing above room temperature, the linewidth of all noted modes increases, while the frequencies of three modes (two E_g and one B_{1g} mode) exhibit different temperature dependence. The frequencies of B_{1g} mode at 396 cm^{-1} and E_g mode at 637 cm^{-1} at room temperature shift to lower frequencies with the increasing temperature, in accordance to literature [11]. The blueshift and broadening of the lowest frequency anatase E_g Raman mode at different temperatures will be particularly analyzed. Note that the increase of temperature above 1173 K is followed by a partial transformation of anatase to rutile TiO_2, as expected [12].

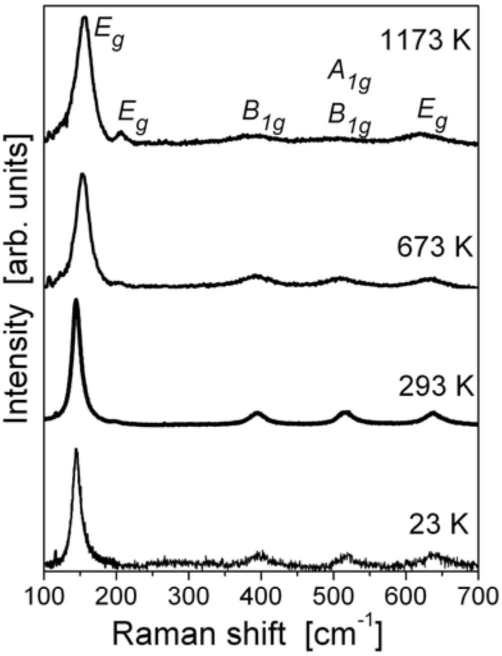


Fig. 2 Raman spectra of anatase TiO_2 taken at 23, 293, 673 and 1173 K.

The Stokes and anti-Stokes Raman spectra of the lowest frequency E_g mode at different temperatures in TiO_2 nanopowder are shown in Fig. 3(a) and (b). Lower temperatures (T < 300 K) were obtained by the cryostat system in vacuum. Higher temperatures were achieved by the microscope heating stage in air.

Several factors like phonon confinement [2-5, 8, 13, 14], strain [8, 15], non–homogeneity of the size distribution [8], defects and nonstoichiometry [7, 8], as well as anharmonic effects due to temperature increase [16] can contribute to changes in the peak position, linewidth and shape of the E_g Raman mode in anatase TiO_2 nanopowder.

The asymmetric shape of the E_g modes at room and lower temperatures points to a pronounced phonon confinement effect, while at higher temperatures its more symmetric broadening indicates that a strong anharmonic effect is dominant.

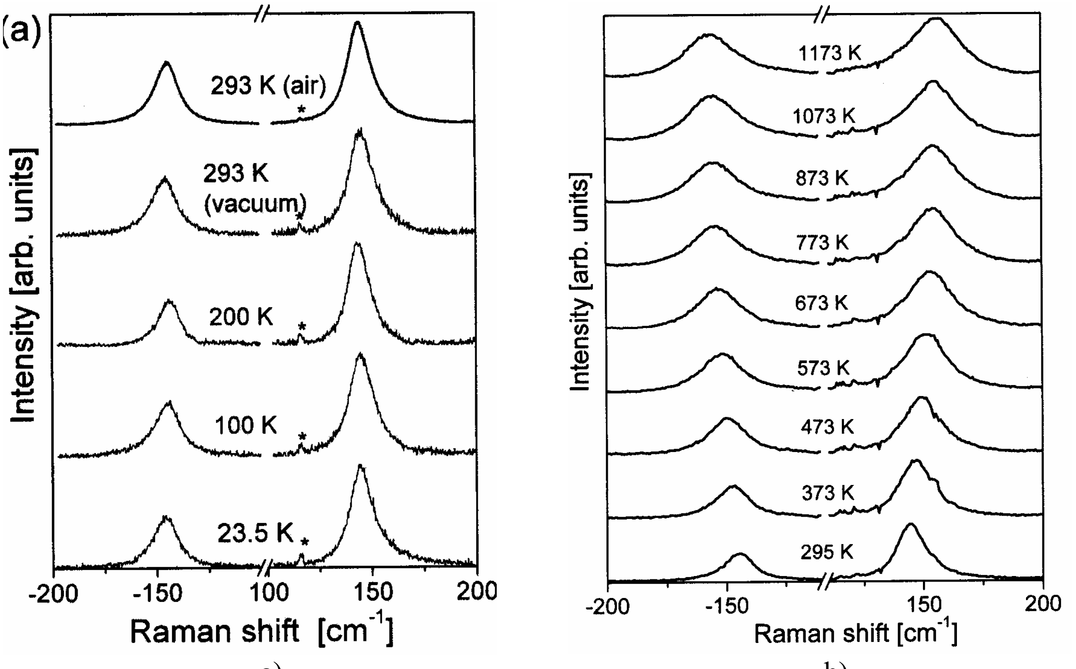
The redshift and narrowing of the Raman E_g mode in anatase TiO_2 nanopowder, in comparison to the room temperature position and linewidth, are expected at low temperatures [17]. The absence of this effect here can be ascribed to discrepancy from the stoichiometry and the presence of a specific kind of nonstoichiometric defects, due to laser irradiation in vacuum, which usually cause blueshift and broadening of the Raman E_g mode [7, 8]. That effect compensates the expected redshift and narrowing at low temperatures.

According to the phenomenological work of Richter et al. [13] and Campbell et al. [14] for spherical particles of diameter L and Gaussian confinement function, the resulting

Raman intensity $I(\omega)$ can be presented as a superposition of weighted Lorentzian contributions over the whole Brillouin zone [14, 15]:

$$I(\omega) = \sum_{i=1}^{m} \int_{0}^{\infty} \rho(L)\, dL \int_{BZ} \frac{\exp\left(\frac{-q^2L^2}{8\beta}\right) d^3q}{[\omega - \omega_i(q,T)]^2 + \left(\frac{\Gamma(T)}{2}\right)^2}\,, \quad (1)$$

where $\rho(L)$ is the particle size distribution, q is wave vector expressed in units of π divided by value of unit cell parameter, and $\Gamma(T)$ is the mode line width at temperature T. The sum is carried over m dispersion curves $\omega_i(q, T)$, depending on mode degeneration [15]. Then, according to theoretical curves of anatase calculated by Mikami et al. [18], the dispersion relations were approximated in cosine form [17], $\omega_i(q,T) = \omega_0(T) + B_i(1 - \cos(2\pi \cdot q))$, where $\omega_0(T)$ is frequency in the center of Brillouin zone at temperature T, and B_i are fitting parameters. The angular integral in a wave vector space in the Brillouin zone was performed by integrating along the Γ-X, Γ-N, and G-Z symmetry directions, weighting each by the number of equivalent symmetry directions [17]. Confinement factor is assumed to be $\beta \approx 7$. The values of $\omega_0(T)$, as well as those of $\Gamma(T)$, at a specified temperature were treated as adjusting parameters in the fitting procedure. We supposed a log-normal particle size distribution with the average crystallite size of L_0=7.3 nm and standard deviation σ=0.20 obtained from LFR measurements.



a) b)

Fig. 3 Stokes and anti-Stokes Raman shift of E_g mode anatase TiO_2 measured at different temperature ranges: 23 to 293 K (a) and 295 to 1173 K (b).

The comparison of the normalized experimental and calculated spectra according to described procedure at several temperatures (23, 295, 673, and 1073 K) is shown in Fig. 4. A good agreement between these results confirms the proper choice of particle size distribution taken according to LFR measurements.

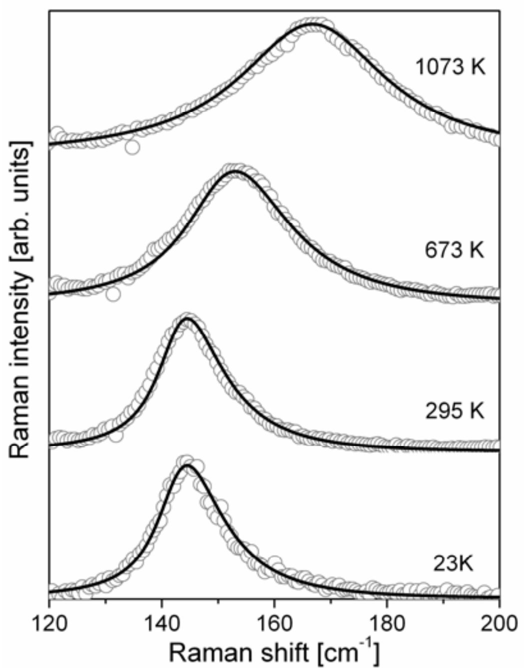
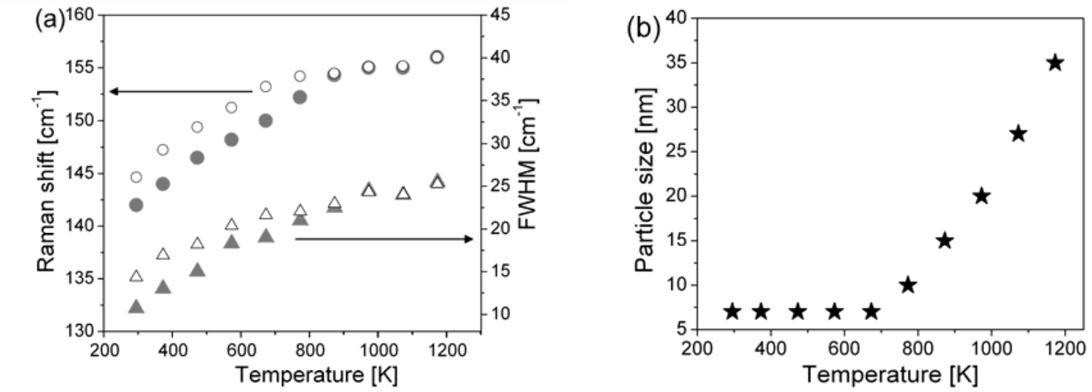


Fig. 4 Normalized experimental (*open circles*) and calculated (*solid lines*) spectra of anatase TiO_2 nanopowder measured at different temperatures.

It is evident that frequency and linewidth increases by heating above room temperature, while the lineshape of E_g mode becomes more symmetric. As-read experimental (open symbols) and fitted (full symbols) positions $\omega_0(T)$ and linewidths $\Gamma(T)$ of Raman E_g mode are compared in Fig. 5(a). The influence of phonon confinement effect can be estimated through the difference between measured and calculated values, which decreases with temperature increases above 673 K (500°C). It is related to the crystallite size increase shown in Fig. 5(b), obtained by the fitting procedure described above, where it is changed from 7.3 to 35 nm, when the temperature grows from 673 to 1173 K. This coincides with the results of Balaji et al. [12], where upon annealing at temperatures at and below 400°C the crystallite size does not change significantly, while this size grows continuously as the annealing temperature is raised to 900°C.



a) b)

Fig. 5 As-read experimental (open symbols) and fitted (full symbols) positions and halfwidths of Raman E_g mode (a) and the temperature dependence of particle size obtained from fitting procedure (b).

The Raman spectrum of TiO_2 nanopowder measured at room temperature after heating at 900°C (1173 K), shown in Fig. 6, confirms crystallite growth due to heating. Namely, the position (143.5 cm^{-1}) and linewidth (8.8 cm^{-1}) of the lowest frequency E_g Raman mode in this spectrum are close to their values characterstic for the Raman spectrum of polycrystalline anatase TiO_2 [16].

4. Conclusion

Commercial TiO_2 nanopowder in the anatase phase was temperature treated in order to investigate the phonon behavior and stability of this nanocrystalline material. The temperature dependence of the Raman spectra of anatase TiO_2 nanocrystals was measured in the temperature range 23-1073 K. Variations of the frequency and linewidth of Raman modes with temperature were demonstrated. The blueshift and broadening of the lowest frequency E_g Raman mode are particularly analyzed by the phonon confinement model, including anisotropic dispersion relations with temperature dependant parameters.

The study shows the utilisation of Raman spectroscopy for determination of structure and crystallite size of nanocrystalline TiO_2. These results have shown that the contributions of confinement effect and nonstoichiometry due to laser irradiation in vacuum are pronounced at low temperatures. However, at high temperatures the contribution due to anharmonic effect is dominant. Decreasing of phonon confinement effect with temperature increase above 673 K is ascribed to crystallite growth at higher temperatures.

Acknowledgement

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Садржај: *Метода Рамановe спектроскопије употребљена је за карактеризацију комерцијалног* TiO_2 *нанопраха, декларисане величине зрна од 5 nm. Раманови спектри, мерени у Стоксовом и анти-Стоксовом режиму, потврдили су анатас фазу* TiO_2 *праха у температурном опсегу 25-1173 K. Показано је да фононско ограничење (услед мале величине зрна) и нестехиометрија (изазвана ласерским озрачивањем у вакууму) имају велики утицај на плави помак и ширење најинтензивнијег* E_g *Раман мода на ниским температурама, док утицај јаког анхармонијског ефекта постаје доминантан на вишим температурама. Ефекат фононског ограничења смањује се услед повећања кристалита на температурама вишим од 673 K.*

Кључне речи*: Анатас* TiO_2 *нанопрах, Раманова спектроскопија*