PACS: 78.30.-j; 78.67.-n

V. S. Grinevich, L. M. Filevska

Odesa Mechnikov National University, ul. Dvoryanska 2, Odesa, 65082 Ukraine, E-mail: grinevich@onu.edu.ua, tel. +38-048-7317403

RAMAN SCATTERING IN NANOSCALE TIN DIOXIDE

The Raman scattering spectra peculiarities are analyzed for nanosized samples of tin dioxide using the authors' own research and the available literature. The presented results show the series of differences in RS spectra in the nanoobjects in comparison with the bulk material. The principle peculiarities comprise: the broadening of peaks, the spectra 'washing-out' (the notable dispersion presence), the peaks shifting to the short waves part from the basic positions, the new lines appearance which are not specific for the bulk SnO2. The principle reason for the deviations is quantum-size effect of the spatial confinement for phonons. The oxygen vacancies notably influence the shape and intensity of RS spectra for studied materials. New bands in the low-frequency part of the spectrum are conditioned by the nanoparticles' normal vibrations.

INTRODUCTION

Metal oxides are the active components in many modern electronic devices [1,2]. There are enough comprehensive reviews devoted to the properties of tin dioxide [2], and to other transparent conductive oxides [1].

Chemical and electrical properties of tin dioxide in the nanocrystalline state strongly depend on the particle size [2,3]. The defectiveness of the subsurface layers, caused by the decrease of crystallites grains, influences the electronic processes in them. This leads both to the appearance of surface vibration modes in the Raman scattering (RS) and in the infrared absorption (IR). At the same time the temperature of the material's reduction by hydrogen decreases and the intercrystalline barriers also influence the charge transport. The Raman spectroscopy is one of the most sensitive methods for the materials science investigations, therefore the nanosized tin dioxide being studied by this method gives plenty of information, especially in the field of its application in electronics.

The present work comprises the comparison of several sources from the available data together with the authors' results on the RS in nanosize tin dioxide.

GENERAL STATE IN RAMAN STUDIES OF NANOSIZE TIN DIOXIDE

Raman scattering (RS) for bulk SnO_2 rutile structure crystals was studied in detail by the authors [4]. Tin dioxide has six atoms in the unit cell, which resulted in 18 branches of vibration modes: 3 acoustic and 15 optical ones. Authors of [5] mentioned, that Raman active modes for SnO_2 rutile are: E_g 476 cm^{-1}, A_{1g} 638 cm^{-1}, B_{2g} 782 cm^{-1}, and B_{1g} 123 cm^{-1}. The last mode is weakly registered, as it has low scattering intensity.

The authors [5] studied SnO_x nanoparticles produced by gas-phase condensation and by "in-flight" sintering using Raman spectroscopy. They identified different vibration states of the rutile crystal phase of bulk SnO_2 particles and of sub-stoichiometric SnO_x of different sizes (5, 10, 20 nm). Raman spectra for different sizes of particles are shown in Figure 1 [5].

As soon as the oxygen content in $SnO_{1.5}$ particles was significantly lower than in the bulk SnO_2, it was supposed a higher density of oxygen vacancies in the samples. The weak modes A_{1g} and B_{2g} are present only for particles' spectra in comparison with the similar modes in the bulk SnO_2. The E_g mode, can be registered only in a bulk SnO_2 sample, the B_{2g} mode is of very weak intensity exists at 747 cm^{-1} for 10 nm and 5 nm thick samples. Furthermore, the two bands of 275 cm^{-1} and 515 cm^{-1} were observed only in nanocrystalline samples but not in bulk ones. Two possible interpretations are applicable: the band 275 cm^{-1} can be defined as B_{1g} mode and 515 cm^{-1} as A_{2g} mode. Although the both modes are inactive in RS for bulk sample and can't be detected in the rutile lattice, the authors [5] believe that the reduced lattice symmetry caused by the low oxygen stoichiometry make these transitions possible. The band 515 cm^{-1} is most likely connected with surface phonon states, similar to those previously detected by authors [6].

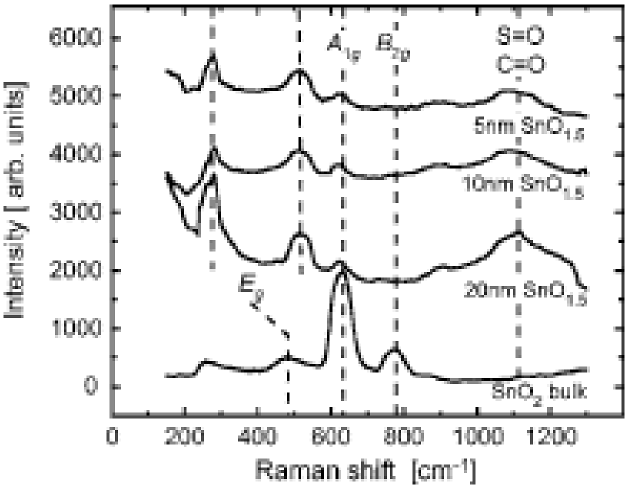


Fig. 1. Raman spectra for $SnO_{1.5}$ nanoparticles of different diameters [6].

Analyzing the entire Raman spectrum for the SnO_2 nanoparticles of 3 to 100 nm [7] they showed that the state of disorder and size of nanoparticles strongly affect the vibration properties of this material. The nanoparticles' sizes decrease is associated with the classical SnO_2 modes shifting and broadening. The correspondence between Raman bands and nanoparticles' sizes are well described by the spatial correlation model, at least for particles bigger than 8-10 nm. The decreasing of grain size leads to the appearance of two bands in the high frequency part of the spectrum. It is suggested that these bands appear due to the contribution of non-stoichiometric surface layer with different symmetry that SnO_2. The measured thickness of this layer is ~ 1.1 nm that is two or three unit cells size. The bands corresponding to the vibration of spherical as a whole nanoparticles appear in the low-frequency part of spectrum.

Raman spectra in the SnO_2- nanorods of different diameters obtained by redox reaction at different growth conditions were measured at room temperature by the authors [8]. The low-frequency Raman peaks were initially registered in the work. It was found that low frequency peaks were shifted to the higher frequency region with nanorods' diameter decreasing. The low frequency peaks' size dependence in SnO_2 nanorods may be caused by surface modes. Raman peaks detected in SnO_2 nanorods differ in depending on wavelengths of the excitation light (514.5 nm and 785 nm), thus, spectral line broadening is observed and the line shape becomes asymmetric. Moreover, some IR- active modes turned into the Raman-active ones, which is caused by such type of order breach as local defects in the crystal lattice and oxygen vacancies in thinner nanorods, which ones are formed as nanorods at the reducing of their diameter to 15 nm or less.

Authors [8], detected 3 categories of peaks: 1st: Low-frequency peaks in the interval of 30 – 100 cm^{-1} were located at 33.8; (34.9); 45.7; (51.9); 57.4; and 73.6 cm^{-1}. 2nd: Classic SnO_2 modes were located at 113.2 (114.6); 472.9 (472.4); 630.4 (630.1); and 768.5 (770.6) cm^{-1}, corresponding to modes B_{1g}, E_g, A_{1g}, and B_{2g} in the bulk SnO_2. 3rd: Abnormal peaks in the range 100-850 cm^{-1} were located at the 157.9; (156.3); 247.4; 392.8; 430.4; 602.1; 711.6 cm^{-1}. Symmetrical and thin Raman peak line in the bulk material broadens and became asymmetrical for the studied SnO_2 nanorods.

Raman peaks for low frequencies interval may be related to the elastic vibrations of nanorods itself, i.e., with existing of confined acoustic- phonon modes in the nanorodes. In [8] it was shown that the wave numbers of the Raman shift for both vibration modes are proportional to the sound velocity and inversely proportional to the nanorods' diameter *d*, i.e., low-frequency peaks are shifted to higher frequencies with nanorods diameter reduction.

As it is shown in [8] the less strictness of the selection rules (k = 0) with increasing disorder or size reduction explains the appearance of anomalous peaks in the range 100-850 cm^{-1} in nanorods samples of a smaller diameter. Infrared modes may turn into weak, but active Raman ones if structural changes are caused by the disorder and size effects. The peak at 247.4 cm^{-1} corresponds to the IR-active E_u(2)TO, a peak at 430.4 cm^{-1} - IR-active E_u(3)LO, and peaks at 392.8 , 602.1 and 711.6 cm^{-1} - silent A_{2g}, IR-active E_u(l)TO A_{2u}LO modes, respectively. These modes are low active in Raman sense and were observed in other works due to structural distortion caused by local disorder in the crystal lattice and oxygen vacancies. Oxygen vacancies stimulate a non-stoichiometric SnO_x increase on the surface and may also be responsible for IR-active modes appearance. In the nanorods of SnO_2 studied in [8], the atomic ratio of tin to oxygen in the samples with IR-active peaks, is 1.44 (compared to 1.86 ratio for bigger size samples without IR-active modes) which indicates the presence of oxygen vacancies on the nanorods surfaces. The peaks of one and the same mode are different in different papers; the authors [8] explained this by specific microstructures of SnO_x nanorods samples. The peaks 601 and 300 cm^{-1} are stimulated by IR-active E_u(l) TO and $E_u(\upsilon_2)$TO, modes respectively. Nature of the peak at 157.9 (156.3) cm^{-1} stays not evident. It may be caused by sircumnuclear modes as the Raman spectrum reflects the single-phonon density of states.

The diameters of the nanorods in samples A and B, studied in [8], averaged at 15 ± 3 and 22 ± 2 nm respectively. The authors registered the Raman line peak's broadening and its shape asymmetry. As the samples A and B have different diameters, then the surface area to volume ratio for A is more. Moreover, the XPS results showed that samples A have more oxygen vacancies on the surface of the nanorods than samples B, which is mainly responsible for the IR- active modes. Thus, samples A have six IR-active modes and the samples B none. The Lamb theory application to the Raman experiments showed that some surface first-order modes can not be detected under these experimental conditions. Perhaps that forbidden phonon mode for the first order Raman scattering can be Raman active in the second-order Raman scattering due to the less strictness of the selection rules k = 0.

The investigation of RS spectra in tin dioxide crystallites with their sizes 4 nm and 25 nm (Figure 2) is presented in [3].

As it can be seen at the figure, the Raman spectra for different crystallites' size differ sharply. This agrees well with the results of previous studies and is a result of the selection rules violations for nanocrystalline objects due to the large number of surface atoms influence, which contribute to the Raman spectra. Nanocrystalline tin dioxide RS with a crystallites size of ~25nm containing vibration modes E_g, A_{1g} and B_{2g}, were registered by [8] in nanorods and are specific for rutile structure SnO_2.

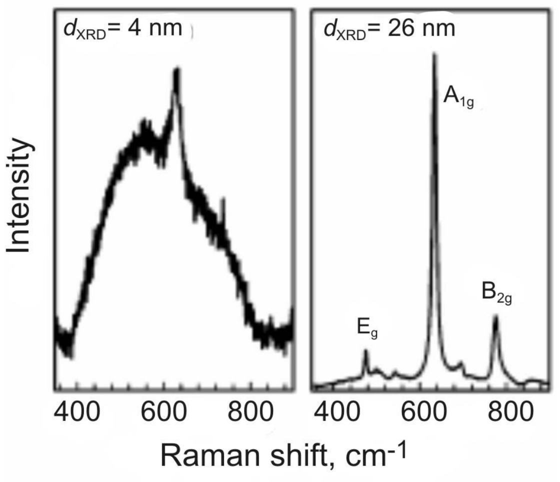


Fig. 2. Raman spectra of tin dioxide with different crystallites size [4].

It was established, that both in TiO_2, and in SnO_2 films with small nanocrystallites sizes the similar quantum size RS effect has place due to violations of phonon momentum conservation principle [9]. Manifestation of the essential role of boundary phonons which contribution increases with nanocrystal size reduction is notable for the first-order Raman scattering due to the whole Brilloin zone phonons involvement in the scattering. Both the dispersion dependence of vibration modes frequencies and half-width intensities for the corresponding peaks in this case leads to a decrease in intensity, to the broadening and the Raman scattering bands shift. For nanocrystalline TiO_2 samples depending on the size of nanocrystallites, the position and the half-width of the Raman lines together with their intensity in the low- and the high-frequency parts of the spectrum seriously varies which is considered by the authors [10] as the spatial restriction of phonons' confinement.

However, as the authors [5, 7, 11] show, the Raman scattering is also influenced both by boundary phonons capture and by deviations from oxygen stoichiometry. When the ratio of O/Ti<2, the short-wave shift of the peaks E_g, the significant broadening of the lines and their intensity change also have place.[9,12]. Moreover, it was found that the most noticeable changes in the Raman spectrum are observed at small deviations from stoichiometry.

The authors [13] also showed a simple link between particle size and the peculiarities of Raman spectra of TiO_2 aerogels by analyzing the evolution of the peaks 142 and 630 cm^{-1}, in dependence on the morphology. Since the regularities of the phonon dispersion for anatase are not known, the authors used a similar dispersion for rutile. At the same time it was shown that there is good agreement between particle size estimated using their model and detected by the X-ray diffraction.

METHODS FOR THE FILMS' PREPARATION AND OF RESEARCH

The films' preparation methods are based on sol-gel technique modified by a polymer (polyvinyl acetate) application and is given in [14]. Bis(acetylacetonato)dichlorotin (BADCT) was used as a tin dioxide precursor [15]. The tin dioxide layers were formed after the 500 – 600 C annealing of the mixed solution of the polymer and precursor in acetone deposited on the glass substrate.

The tin dioxide layer's surface morphology was investigated by the industrial Atom Force microscope (AFM) NT-MDT-206. The measurements were fulfilled by a siliceous probe with a nominal radius ~10 nm (the production firm NT-MDT).

The Raman spectra were excited by He-Ne laser with 632 nm wavelength. Since the samples were thin films on glass substrates the authors enhanced the response by means of directing the laser beam on the film in a sliding mode. The monochromator MDR-23 (LOMO) output was registered by a PC method.

RESULTS AND DISCUSSION

The Raman spectra were studied for the films, obtained from the solution of 5% precursor and 0.1% polymer. Nanosized films structure is confirmed by the surface morphology studies. The AFM image of the sample surface morphology is given at Fig. 3.

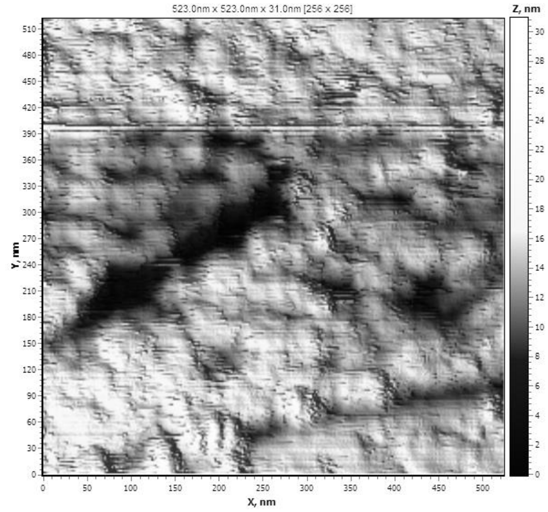
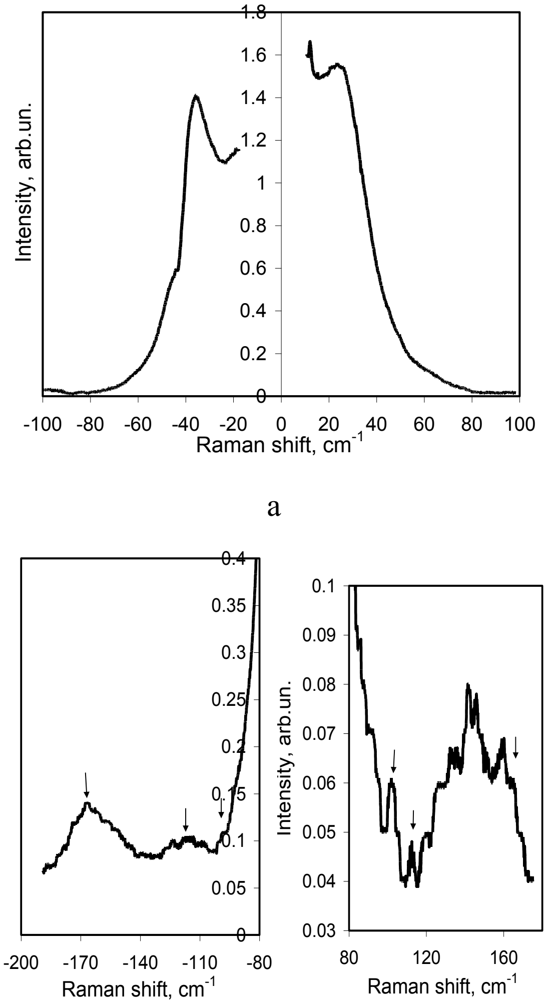


Fig. 3. AFM image of the surface morphology for tin dioxide investigated film.

The resulting RS spectra for the low-frequency region of the nanoscopic tin dioxide layers are not fully legible and asymmetrical. The peaks broadening and their asymmetry may, similar to other researchers, also be the result of selection rules violations for nanocrystalline objects due to the considerable number of surface atoms contribution to the Raman spectra. The surface morphology studies showed the nanoclusters presence in the films. This also allows one to connect the asymmetry in the Raman spectra with size effects and to comment it in the frames of the spatial phonons confinement. Figures 4(a) and 4(b) show the Raman scattering results in tin dioxide films obtained using polymers.

In the range of up to 100 cm^{-1} at least one phonon was registered at 25 cm^{-1} (Stokes region), and in the anti-Stokes region - at 34.9 cm^{-1}. The same peak was registered in [8] and it is connected with the normal vibrations of SnO_2 nanorods. Consequently, also in our case, this peak may contribute as a vibration of nanoparticle as a whole. Stokes peak has a value different from reported in the literature, as nanostructures of our samples differ from the samples of other researchers. The clusters in our films, according to the AFM image (Fig. 3), have a quasi spherical shape.

The interval 100-200 cm^{-1} contains three types of phonons scattering in the left (a) and in the right parts of the spectrum, and at the same time have the noticeable absence of symmetry in the bands' positions: 97.78, 115.5, 166.7 cm^{-1} and in corresponding them 102.3, 112.39, 165.2 cm^{-1}.



a

Anti-Stokes region Stokes region

b

Fig. 4 (a and b). Raman spectra in the tin dioxide films produced using the polymers: a) in the range of 0-100 cm^{-1}; b) in the range of 100-200 cm^{-1} in the anti-Stokes and Stokes regions.

Two of the pointed bands are registered in [8]. The band 115,5 (112,39) cm^{-1}, evidently corresponds to the classical SnO_2 B_{1g}, mode and the band 166,7 (165,2) cm^{-1} is close to the circumnuclear mode 157,9 cm^{-1}, which is also detected in [8]. Such type asymmetry was observed also in [8] where authors studied the Raman scattering in nanoscopic rods of tin dioxide. In the said work the asymmetry of the spectra was influenced by the dimensional limitations in two directions. Basing on the surface morphology investigations at the Fig.3 and in [14], where nanostructured clusters were registered in these films, the Raman spectra asymmetry was also connected with size effects. As it is shown in [8] for nanorods of SnO_2, this asymmetry can be explained by phonons confinement.

However, the Raman shift of the peaks and their broadening in the investigated films can be attributed to another reason. This reason may be the stoichiometric deviation of the film composition, namely, the presence of oxygen vacancies. As it was shown in [11] for titanium dioxide films, the significant changes of this type spectra were observed at small deviations from stoichiometry. The majority researchers of nanostructured tin dioxide reported about oxygen vacancies as the basic defect in the material, defining their optical, electrical and adsorption properties.

CONCLUSION

The RS results presented in the work for the nanoscale tin dioxide showed the similar type of the Raman spectra deviations registered in nanosized material and in bulk crystalline tin dioxide for all studies.

The principal deviations in RS spectra were: the peaks broadening, not full legibility of the spectra (the presence of the noticeable dispersion), and their short waves shift from the basic positions, and the appearance of the new bands which are not specific for the bulk tin dioxide.

One of the main reasons for the said deviations is the effect of the spatial phonons confinement. At the same time the oxygen vacancies essentially influence the shape and intensity of the RS spectra in the investigated material.

The new bands presence in the low frequency part is considered to be due to the nanoparticles vibrations as a whole.

REFERENCES

1. D. S. Ginley, H. Hosono, D. C. Paine, *Handbook of Transparent Conductors*, Springer, New York (2010).
2. M. Batzill, U. Diebold. The surface and materials science of tin oxide // *Prog-*

ress in Surface Science, **79**, pp. 47-154 (2005).

3. M.N. Rumyantseva. *Chemical modification and sensory properties of nanocrystalline tin dioxide*, Authoref. diss ... dokt.him.nauk, Moscow, 46 p (2009) in Russian.
4. R.S. Katiyar, P. Dawson, M.M. Hargreave, G.R. Wilkinson, Dynamics of the rutile structure. III. Lattice dynamics, infrared and the Raman spectra of SnO_2 // *J. Phys. C Solid State Phys.* **4**, pp. 2421-2431(1971). doi: 10.1088/0022-3719/4/15/027.
5. C. Meier, S. Luttjohann, VG Kravets, H. Nienhaus, A. Lorke, P. Ifeacho, H. Wiggers, Ch. Schulz, M. K. Kennedy and F. E. Kruis. Vibrational and defect states in SnOx nanoparticles // *J. of Appl. Phys.* **99** 113108-6 p. (2006).
6. K. N. Yu, Y. Xiong, Y. Liu, and C. Xiong, Microstructural change of nano-SnO_2 grain assemblages with the annealing temperature // *Phys. Rev. B,* **55**, pp. 2666-2671(1997).
7. A. Dıreguez, A. Romano-Rodrıguez , A. Vil`a, and J.R. Morante, The complete Raman spectrum of nanometric SnO_2 particles // *J. of Appl. Phys.* **90**(3) pp. 1550-1557 (2001) DOI: 10.1063/1.1385573.
8. Y.-K. Liu, Y. Dong, G.H. Wang, Low frequency and abnormal Raman spectrum in SnO_2 Nanorods // *Chan.Phis. Lett.*, **21**(1) pp. 156-159 (2004).
9. WF Zhang, Y.L. He, M.S. Zhang, Z. Yin, Q. Chen. Raman scattering study on anatase TiO_2 nanocrystals // *J. Phys. D: Appl.Phys.*, **33,** pp. 912-916 (2000).
10. D. Bersani, P.P. Lottici. Phonon confinement effects in the Raman scattering by TiO_2 nanocrystals. *Appl. Phys. Lett.*, **72**(1), pp. 912-916 (1998).
11. T.S. Busko, O.P. Dimitrenko, N.P. Kulish, N.M. White, N.V. Vityuk, A.M. Eremenko, N.P. Smirnova, V.V. Shlapatskaya, Optical properties of radiation-sensitized TiO_2 films with anatase structure // *Problems of Atomic Science and Technology, Series: Physics of Radiation Damage and Radiation Materials*, **92** (2), pp. 43-47 (2008) in Russian.
12. J.C. Parker, R.W. Siegel. Calibration of the Raman spectrum to the oxygen stoichiometry of nanophase TiO_2 // *Appl. Phys. Lett.*, **57**(9) pp. 943-945(1990).
13. S. Kelly, F.H. Pollak, M. Tomkiewiez, Raman spectroscopy as a morphological probe for TiO_2 aerogels // *J.Phys. Chem. B,* **101,** pp. 2730-2734(1997).
14. L.N. Filevskaya, V.A. Smyntyna, V.S. Grinevich Morphology of nanostructured SnO2 films prepared with polymers employment // *Photoelectronics*, 15, pp. 11-14 (2006).
15. B. Ulug, H.M. Türkdemir, A. Ulug, O. Büyükgüngör, M.B. Yücel, V.A. Smyntyna, V.S. Grinevich, L.N. Filevskaya. Structure, spectroscopic and thermal characterization of bis(acetylacetonato) dichlorotin(IV) synthesized in aqueous solution// Ukrainian chemical journal. – 2010. –76, №7. – P. 12-17.

This article has been received within 2015

PACS: 78.30.-j; 78.67.-n

V. S. Grinevich, L. M. Filevska

RAMAN SCATTERING IN NANOSCALE TIN DIOXIDE

Summary

The Raman scattering spectra peculiarities are analyzed for nanosized samples of tin dioxide using the authors' own research and the available literature. The presented results show the series of differences in RS spectra in the nanoobjects in comparison with the bulk material. The principle peculiarities comprise: the broadening of peaks, the spectra 'washing-out' (the notable dispersion presence), the peaks shifting to the short waves part from the basic positions, the new lines appearance which are not specific for the bulk SnO_2. The principle reason for the deviations is quantum-size effect of the spatial confinement for phonons. The oxygen vacancies notably influence the shape and intensity of RS spectra for studied materials. New bands in the low-frequency part of the spectrum are conditioned by the nanoparticles' normal vibrations.

Key words: Raman scattering, tin dioxide, nanoscale effect.

PACS: 78.30.-j; 78.67.-n

В. С. Грінeвич, Л. М. Філевська

КОМБІНАЦІЙНЕ РОЗСІЮВАННЯ В НАНОРОЗМІРНОМУ ДІОКСИДІ ОЛОВА

Резюме

На основі власних досліджень авторів і аналізу наявної літератури в роботі розглянуті особливості спектрів комбінаційного розсіювання в нанорозмірних зразках двоокису олова. Показаний ряд відмінностей спектрів КР нанооб'єктів від таких для об'ємних матеріалів. Принципові особливості включають розширення піків, зміщення їх від основних положень, розмиття спектрів (присутність помітної дисперсії), появу нових смуг, які нехарактерні для об'ємного SnO_2. Основна причина відхилень - квантово- розмірний ефект просторового обмеження фононів. Суттєвим є вплив вакансій кисню на форму та інтенсивність спектрів комбінаційного розсіяння в досліджуваних матеріалах. Нові смуги в низькочастотній частині спектру обумовлені власними коливаннями наночастинок.

Ключові слова: комбінаційне розсіювання, діоксид олова, нанорозмірний ефект.

PACS: 78.30.-j; 78.67.-n

В. С. Гриневич, Л. Н. Филевская

КОМБИНАЦИОННОЕ РАССЕЯНИЕ В НАНОРАЗМЕРНОМ ДИОКСИДЕ ОЛОВА

Резюме

На основании собственных исследований авторов и анализа имеющейся литературы в работе рассмотрены особенности спектров комбинационного рассеяния в наноразмерных образцах двуокиси олова. Показан ряд отличий спектров КР в нанообъектах от таковых в объемных материалах. Принципиальные особенности включают в себя уширение пиков, смещение их от основных положений, размытие спектров (присутствие заметной дисперсии), появление новых полос, которые нехарактерны для объемного SnO_2. Основная причина отклонений - квантово-размерный эффект пространственного ограничения фононов. Существенно влияние вакансий кислорода на форму и интенсивность спектров КР в изучаемых материалах. Новые полосы в низкочастотной части спектра обусловлены собственными колебаниями наночастиц.

Ключевые слова: комбинационное рассеяние, диоксид олова, наноразмерный эффект.