Manifestation of metastable γ-TeO_2 phase in the Raman spectrum of crystals grown in synthetic opal pores

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Abstract. 'Opal–tellurium dioxide' nanocomposite has been obtained by filling opal pores with a melt of fine dispersive polycrystalline α-TeO_2 powder. The Raman spectrum of the composite has been measured in the region of 50–1100 cm^{-1} and compared with the spectra peculiar for polycrystalline α-TeO_2 powder and the corresponding single crystals. Besides of the Raman bands corresponding to α-TeO_2 lattice vibrations, other bands have been detected in the spectrum of the composite. Their spectral positions coincide fairly well with those available in the spectrum of γ-TeO_2.

Keywords: synthetic opal photonic crystals, Raman scattering, polymorphs of tellurium dioxide

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1. Introduction

Creation and investigation of active nanosized dielectric crystals attracts great attention in the physics of low-dimensional systems. Physical properties of such nanocrystals should be essentially different from those typical for the bulk crystals because of quantum-size effects in both electronic and vibrational spectra [1]. On the other hand, in case of some periodical arrangement of nanocrystals, the effects attributed to photonic crystals should also be expected. Therefore such structures can expand our possibilities for controlling light [2].

As a basic matrix for obtaining these structures, synthetic opals have been widely used. Regular arrangement of cavities and channels in the initial synthetic opals allows for getting 3D periodic structures for a wide range of organic and inorganic compounds. A typical embedding procedure is soaking of the initial opal into a compound solution at temperatures close to the room one or into a melt of the compound, with following crystallisation by cooling [3, 4]. By embedding active dielectrics from a melt, higher degrees of filling can be achieved (up to 60% of the pores volume), and both a surface and interior pores are filled with almost equal quantities of a compound [3]. Besides, a solid phase of the embedded compound is formed in this case. The special conditions involve high temperatures, a limited volume of pores, and a lack of atmosphere in the interior pores. Taking these factors into account, one should not exclude a possibility for forming metastable polymorphs of dielectrics in the pores due to interaction between a melt and a globule surface of SiO_2.

The present work is devoted to a growth of tellurium dioxide in the pores of synthetic opals and to studies of Raman spectrum of the composite obtained this way. This is aimed at revealing possible structural changes and the size effects occurring in the vibrational spectrum. A choice of the tellurium dioxide is caused by its strongly pronounced piezoelectric, acousto-optic and nonlinear optical properties [5, 6]. This stipulates its wide applications as a material for optical fibres and nonlinear optical elements [7]. Besides, three crystalline polymorphs of the tellurium dioxide have been obtained up to date (see [8–11]). One of them, γ-TeO_2, has been synthesised from TeO_2-rich glasses with different initiating oxides (WO_3, Nb_2O_5, PbO, etc.) and is known to be metastable (see [11]).

2. Samples and experimental setup

Bulk opals were grown by slow crystallisation of a colloidal solution of monodisperse SiO_2 globules synthesised using a modified Stöber's method [12]. After drying in the air, the precipitate obtained was annealed at 125°C for 1 h and then at 750°C for 2 h. The opal structure was characterised with a face-centred cubic lattice formed by hexagonal closely packed layers of monodisperse globules. In order to determine the structural parameters of the opal matrix (the diameter of the globules D and the interplanar distance d) and, consequently, to estimate the geometrical sizes of those pores, the Bragg diffraction spectra in the reflected beams were measured. According to the Bragg's law, the spectral position λ_m of the reflection peak is associated with the interplanar distance d by the relationship $\lambda_m(\theta) = 2d\sqrt{\varepsilon_{eff} - \sin^2\theta}$, where θ is the angle of incidence of the light beam upon the system of $\{111\}$ planes and ε_{eff} is the effective dielectric constant. The latter is determined by the dielectric constants ε_i of substances which form the composite and the volume part of a substance f_i as follows: $\varepsilon_{eff} = 0.74 \times \varepsilon_{SiO_2} + \sum_i f_i \times \varepsilon_i$. The connection between the globule diameter D and the interplanar distance d is defined by the geometry of arrangement of the globules and is simply equal to $D = d\sqrt{3/2}$ in our case. For different opal samples under study the diameters D and the interplanar distances d were varied in the regions of 250–270 nm and 204–220 nm, respectively. The average linear size of the pores was about 70 nm.

The sample pores were filled by melting-in a fine dispersive polycrystalline α-TeO_2 powder. For this purpose, a thin uniform layer of the substance powder was placed on a surface of the synthetic opal and the whole system was held in the air-resistant furnace at the temperatures above the melting temperature of the substance (T_{melt} = 733°C) for 15–30 min. After this the samples were cooled down to the room temperature with the average cooling rate of 3°C/min. At first, we performed the procedure described above at the temperature close to the melting temperature during a shorter time period, in order to test the moistening of TeO_2 melting with the silica globules. In this case a part of the substance was rested on the opal surface, as high viscosities of the melt prevented full suction, and was crystallised in a drop. The form of the drop pointed to a good moistening of the TeO_2 melting with the silica globules. After that, the melt was completely soaked up by increasing the temperature. An additional evidence of the fact that the pores are filled was vanishing of iridescence of the opal after its illumination with the visible light. It is caused by a shift of the spectral position λ_m of the Bragg reflection peak towards longer wavelengths due to increasing ε_{eff} caused by embedded TeO_2 ($n_o = 2.2931$ and $n_e = 2.4520$ at the wavelength of $\lambda = 546.1$ nm).

The Raman spectra of the TeO_2 powder and the nanocomposites obtained by us were excited with a continuous multimode light radiation of a diode-pumped solid-state laser (the wavelength of 532 nm and the average power of 120 mW). The spectral width of the excitation line was approximately 1 nm. The measurements were performed in the back-scattering geometry. The diameter of the laser spot focused on a sample surface did not exceed 0.1 mm. The scattered radiation was collected in the direction [111] using a lens with the aperture not larger than 0.17 π sr. The Raman spectra were detected with the aid of a modified laser spectrometer based on a double monochromator DFS-12 in the photon counting mode with accumulation. The spectral slot width was 4 cm^{-1}. The Raman spectra of the powder and the nanocomposites obtained by us were non-polarised. The polarised Raman spectra of the single crystals TeO_2 were measured using a Cary 82 laser Raman spectrometer, with the Ar^+-ion laser excitation at 514.2 nm. All the spectra were measured at the room temperature.

3. Results and discussion

In order to identify the experimental spectra, we have performed a preliminary group-theoretical analysis of the vibrations peculiar for the α-TeO_2 (the point symmetry group 422). The results of our analysis are shown in Table 1, together with the corresponding selection rules. The frequencies of the bands observed in the Raman spectra of the α-TeO_2 single crystals are presented in the first columns of Table 2. The number of the bands observed in the polarised spectra is larger than that predicted by the group-theoretical analysis. This is caused by interference of the spectra of the other polarisations due to a wide collection aperture used in the laser Raman spectrometer Cary 82 in order to gather as much scattered light as possible.

Table 1. Results of group-theoretical analysis and selection rules for the point symmetry group D_4.

D_4	n	T	n_i	Infrared	Raman
A_1	4		4		$X^2 + Y^2 + Z^2$
A_2	5	1	4	T_Z	
B_1	5		5		$X^2 - Y^2$
B_2	4		4		XY
E	9	1	8	T_X, T_Y	XZ, YZ

Table 2. Frequencies of the bands observed in the Raman spectra for different phases of tellurium dioxide (in cm^{-1}).

α-TeO_2 single crystals			α-TeO_2 poly-crystalline powder	TeO_2 nanocrystals in the opal pores	γ-TeO_2 single crystals [11]
$X(ZZ)Y$	$X(YZ)Y$	$X(YX)Y$			
	56			51	
60	60	60	62	62	
					66
					116
121	121	121	123	121	
				142 (shoulder)	140
	151	150	150	150	
	170	176	175	176	174
190	194		196		
		204			
	229	230	231	227	226

α-TeO_2 single crystals			α-TeO_2 poly-crystalline powder	TeO_2 nanocrystals in the opal pores	γ-TeO_2 single crystals [11]
X(ZZ)Y	X(YZ)Y	X(YX)Y			
				290	291
				311	307
	333	334	341	336	
392	388	390	396	398	
				426	426
	586	590	593	588	
				609	611
652	645	648	647	647	645
				682	683
	714		718	718	
					752
	761		763	760	
	781	779	785	785	
	807		806		
				816	812

The Raman spectra of the polycrystalline α-TeO_2 powder and the tellurium dioxide embedded in the pores of synthetic opal are shown in Fig. 1. The frequencies of the bands observed in these spectra are also presented in Table 2. As seen from Fig. 1, the Raman spectrum of the nanocomposite obtained by us consists of the bands corresponding to the crystalline state. The spectrum is quite different from that measured for the α-TeO_2 powder. When compared to the spectrum of the latter powder, one can see new bands in the nanocomposite spectrum appearing at 51, 290, 311, 426, 609, 682 and 816 cm^{-1}. Besides, some spectral redistribution inside the region of 100–180 cm^{-1} and a total enhancement of the Raman spectrum are observed for the case of the nanocomposite.

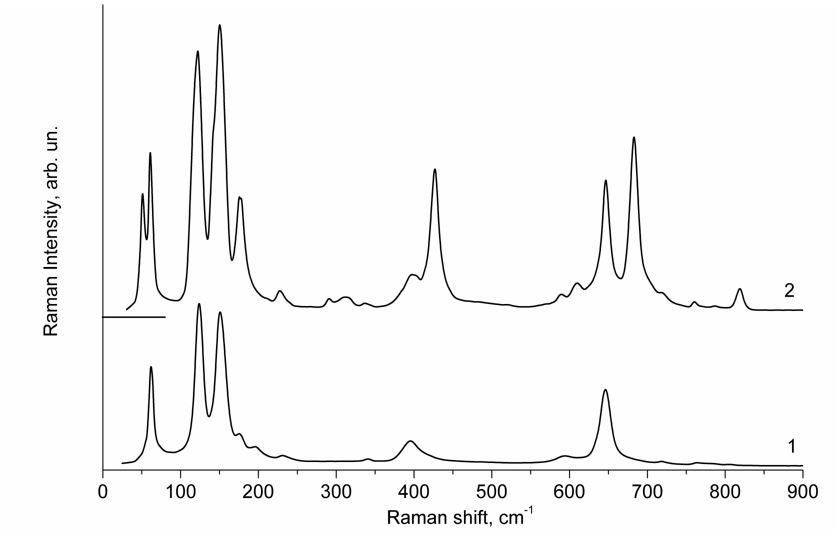

Fig. 1. Raman spectra of (1) polycrystalline powder of α-TeO_2 and (2) TeO_2 crystals embedded in the pores of synthetic opal. All the spectra correspond to the same quantity of tellurium dioxide in the excitation volume.

According to the results of our previous studies, one can exclude any ‘mixing’ of the Raman spectrum of the initial opal from further consideration. The reason for this is that the intensities of wide diffuse bands observed in its Raman spectrum are very small when compared with those typical for the spectra of the powder and the nanocomposite. We can also neglect the influence of the photonic stop-band since it is located far from the spectral region under study.

Thus, the changes observed in the Raman spectrum of the 'opal–tellurium dioxide' system may be caused by the quantum-size effect and/or by changes in the crystalline structure of TeO_2. In the first case, one should expect a broadening (or an asymmetry) and shifts of the Raman bands, and an appearance of new bands corresponding to the phonons from the other points of the Brillouin zone. According to the confinement criterion suggested in the study [13], the quantum-size effect occurs in the nanocrystals with their linear sizes not larger than the length of twelve unit cells along a given direction. For the tellurium dioxide this condition is realised for the nanocrystals with the sizes not exceeding 11 nm. For the synthetic opals under study, this requires that at least seven nanocrystals were formed in each pore in the case of full filling. As seen from Fig. 1 and Table 2, the bands in the both spectra do not undergo any noticeable broadening or shifting, whose values are larger than the experimental accuracy. This can be explained while suggesting that larger nanocrystals are formed in the opal pores.

Then the appearance of the new bands should testify some changes occurring in the crystalline structure. It is quite possible that the frequencies of the new bands appearing in the Raman spectrum of the 'opal–tellurium dioxide' system (except for the band located at 51 cm^{-1}) coincide with the majority of the frequencies of the bands observed in the spectrum of γ-TeO_2 (see the two last columns in Table 2). Hence, one can conclude that both the α- and γ-phases are formed in the tellurium dioxide crystals grown in the pores of the synthetic opal. Basing on comparison of the spectral intensities of the bands observed at 647 and 682 cm^{-1} (assigned to the vibrations of the α- and γ-TeO_2 lattices, respectively), which are measured from different volumes of the samples, the irregular distribution of these phases over the sample volume is found. As for the band located at 51 cm^{-1}, which is absent in the spectra of the both crystalline phases, its appearance may be associated with folding up of acoustic phonon branch owing to decreasing Brillouin zone for the TeO_2 nanocrystals embedded in the opal pores. The spectral redistribution inside the region of 100–180 cm^{-1} is probably due to appearance of a new band at 142 cm^{-1} typical for γ-TeO_2, which enlarges the total intensity observed in the region of 140–180 cm^{-1}. The total 'enhancement' of the Raman spectrum seen for the nanocomposite can be explained by multiple reflections of the exciting photons from disordered elements present in the synthetic opal structure, which result in increasing temporal intervals of radiation-substance interactions [4].

4. Conclusion

In the present work we have worked out a method for embedding tellurium dioxide from the melt into the pores of synthetic opal. Basing on the studies of the Raman spectra for the samples thus obtained, we have found that the substance available in the opal pores is of a crystalline form. When compared with the Raman spectra typical for the polycrystalline powder and the corresponding single crystals, the changes seen in the spectra of the 'opal–tellurium dioxide' nanocomposites are caused by crystallisation of a metastable phase of γ-TeO_2 in the pores of opal matrix.

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Анотація. *Нанокомпозит “диоксид телуру–опал” одержано заповненням пор опалу розплавом тонкодисперсного полікристалічного порошку* α*-*TeO_2*. Спектри комбінаційного розсіяння композиту досліджено в області 50–1100 см*$^{-1}$ *і порівняно зі спектрами полікристалічного порошку та монокристалів* α*-*TeO_2*. Окрім раманівських смуг, що відповідають ґратковим коливанням* α*-*TeO_2*, виявлено нові смуги в спектрі композиту. Спектральне положення цих смуг збігається зі смугами для* γ*-*TeO_2*.*