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X-RAY AND OPTICAL SPECTROSCOPY STUDY OF SYNTHETIC OPALS SUFFERED THE MELTING-IN OF LITHIUM TETRABORATE

A possibility of the fabrication of new composites based on synthetic opals and lithium tetraborate $\text{Li}_2\text{B}_4\text{O}_7$ is investigated. An embedding of the nonlinear-optical material into opal matrix pores is performed by soaking initial opal into the $\text{Li}_2\text{B}_4\text{O}_7$ melt at temperature slightly higher than lithium tetraborate melting temperature ($T_m = 1190$ K) with the following cooling of sample to the room temperature. The duration of soaking is varied from 0.5 to 15 minutes. The characterization of the samples is made by using the X-ray analysis, reflection, and Raman spectroscopy methods. In Raman spectrum of opal with a shortest duration of soaking, the shift and broadening of bands compared to the $\text{Li}_2\text{B}_4\text{O}_7$ single crystal spectrum and appearance of a new band, typical for the α -quartz spectrum, are observed. No indications of any lithium borate phase in Raman spectra of opals placed into the $\text{Li}_2\text{B}_4\text{O}_7$ melt during more than two minutes are found. The structure of these samples is the α -quartz phase together with amorphous SiO_2 phase of initial opal. It is suggested that formation of crystalline phases is possible by melting of amorphous SiO_2 globules of initial opal due to the energy appeared at the reaction between lithium in $\text{Li}_2\text{B}_4\text{O}_7$ melt and oxygen in air.

Keywords: synthetic opal, α -quartz, X-ray analysis, Raman scattering.

Досліджено можливість отримання нових композитів на основі синтетичних опалів і тетраборату літію $\text{Li}_2\text{B}_4\text{O}_7$. Введення нелінійно-оптичного матеріалу до пор опалової матриці здійснювалось шляхом просочення вихідного опалу в розплав $\text{Li}_2\text{B}_4\text{O}_7$ при температурі дещо вищій за температуру плавлення тетраборату літію ($T_m = 1190$ К) з наступним охолодженням зразка до кімнатної температури. Тривалість просочення варіювалась від 0.5 до 15 хвилин. Характеризація зразків проводилась із використанням методів рентгенівського аналізу, спектроскопії відбивання та раманівського розсіяння. У раманівському спектрі опалу з найменшою тривалістю просочення спостерігалися зсув і розширення смуг порівняно зі спектром монокристала $\text{Li}_2\text{B}_4\text{O}_7$, а також поява нової смуги, характерної для спектру α -кварцу. У раманівському спектрі опалів, витриманих у розплав $\text{Li}_2\text{B}_4\text{O}_7$ більше 2 хвилини, ознаки існування будь-якої фази борату літію відсутні. Структура цих зразків являє собою фазу α -кварцу разом із аморфною фазою SiO_2 вихідного опалу. Є припущення, що формування кристалічних фаз стає можливим при розтопленні аморфних SiO_2 глобул вихідного опалу за рахунок енергії, яка виникає при реакції літію в розплав $\text{Li}_2\text{B}_4\text{O}_7$ з киснем у повітрі.

Ключові слова: синтетичний опал, α -кварц, рентгенівський аналіз, раманівське розсіяння.

Изучена возможность получения новых композитов на основе синтетических опалов и тетрабората лития $\text{Li}_2\text{B}_4\text{O}_7$. Введение нелинейно-оптического материала в поры опаловой матрицы производилось путем пропитки исходного опала в расплаве $\text{Li}_2\text{B}_4\text{O}_7$ при температуре несколько выше температуры плавления тетрабората лития ($T_m = 1190$ К) с последующим охлаждением образца до комнатной температуры. Длительность пропитки варьировалась от 0.5 до 15 минут. Характеризация образцов проводилась с использованием методов рентгеновского анализа, спектроскопии отражения и рамановского рассеяния. В спектре рамановского рассеяния опала с наименьшей длительностью пропитки наблюдались смещение и уширение полос по сравнению со спектром монокристаллов $\text{Li}_2\text{B}_4\text{O}_7$, а также появление новой полосы, характерной для спектра α -кварца. В рамановском спектре опалов, выдержанных в расплаве $\text{Li}_2\text{B}_4\text{O}_7$ более двух минут, признаки существования какой-либо фазы бората лития отсутствуют. Структура этих образцов представляет собой фазу α -кварца вместе с аморфной фазой SiO_2 исходного опала. Предполагается, что формирование кристаллических фаз возможно при плавлении аморфных SiO_2 глобул исходного опала за счет энергии, выделяемой при реакции лития в расплаве $\text{Li}_2\text{B}_4\text{O}_7$ с кислородом в воздухе.

Ключевые слова: синтетический опал, α -кварц, рентгеновский анализ, рамановское рассеяние.

1. Introduction

The search for new materials with managed optical properties is in progress now. In this sense, one of the prospective directions is a creation of photonic crystals, a new class of materials characterized by the 3D modulation of dielectric susceptibility with the period close to the visible light wavelength [1]. In case of the proper values of dielectric contrast in such structures with definite space symmetry, an energy gap in the photonic spectrum appears in all space directions, similar to the gap in the electron spectrum in semiconductor [2].

Among all possible structures considered as photonic crystals, the globular photonic crystals created on the base of synthetic opals is of a special interest [3, 4]. Regular arrangement of cavities and channels in initial opals allows getting 3D periodical structures for a wide range of organic and inorganic compounds. A typical embedding procedure is a soaking of initial opal into the compound solution at temperatures close to room temperature or into the melt of compound with the following crystallization by cooling. The latter procedure is applied to fill the opal pores with active dielectrics. An interest in such structures is due to the fact that crystallization conditions into opal pores are quite different from those as usual. It may result in forming the other crystalline phases if the embedded substance is polymorph [5 - 7]. Besides, new features of the known nonlinear optical phenomena may be expected for opals filled with nonlinear optical dielectrics because of the regular space arrangement of nano-sized objects with nonlinear susceptibility [8].

This work is devoted to the obtaining and characterization of new composite based on opal and lithium tetraborate $\text{Li}_2\text{B}_4\text{O}_7$ (LB4). A choice of lithium tetraborate among other borates (LiB_3O_5 , BaB_2O_4 , $\text{CsLiB}_6\text{O}_{10}$ etc.) is due to its wide transparency region, high laser damage power, and strongly pronounced nonlinear optical properties [9, 10].

2. Samples and methods

Bulk synthetic opals were grown by natural sedimentation of a colloidal solution of monodisperse SiO_2 globules synthesized by modified Stöber method. To extract water and organic residuals from the obtained precipitates they were dried in air and then annealed at 400 K and 1025 K for one and two hours, respectively.

The filling of opal pores was carried out by melting-in a fine dispersive polycrystalline LB4 powder. For this purpose, a thin uniform layer of the powder was placed on (or under) the surface of initial opal and the whole system on various (diffuse silica or silicon) substrates was held in the air resistance furnace at temperatures above the melting temperature ($T_m = 1190$ K) for 0.5 – 15 min. After this the samples were cooled down to the room temperature with an average cooling rate of 3 K/min.

The structure and chemical composition of initial opals and opals subjected to the procedure of LB4 melting-in were characterized by X-ray diffraction (Cu K_α radiation), optical reflection and Raman spectroscopy methods.

3. Results and discussion

The X-ray diffraction pattern and Raman spectrum of initial opal indicate its amorphous structure (Fig. 1). A broad diffusive halo in the X-ray diffraction pattern and wide bands in Raman spectrum are inherent features of disordered structures. The obtained Raman spectrum of initial opal is quite similar to the one presented in paper [11], where it coincides with the Raman spectrum of fused quartz. The size of coherently diffracting domains estimated from the X-ray data is 3 nm. This value is well correspondent to the diameter of SiO_2 nuclei which appear at the first stage of globule

growth as a result of the polymerization of silicon acid monomers. After aggregation, these nuclei form the opal structural unit, the SiO_2 globule with a mean diameter D of about 300 nm [12].

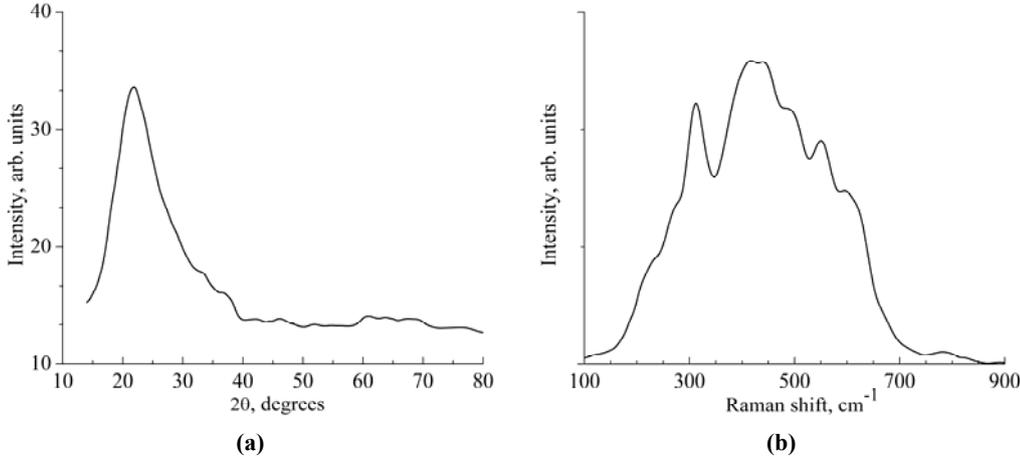


Fig. 1. Cu K α X-ray diffraction pattern (a) and Raman spectrum (b) of initial synthetic opal.

As known from earlier investigations [13], SiO_2 globules are placed in hexagonal close-packed layers which are perpendicular to the sedimentation direction. These layers form a face-centered cubic lattice structure with a preferred [111] direction. The fact, that period of these structures is close to the visible light wavelength, allow us to use optical diffraction technique in determining the diameter D and distance Λ between planes formed by globules. The value of Λ is estimated from the Bragg diffraction spectra by defining a spectral position λ_m of the reflection peak (Fig. 2, a). In our case the connection between these parameters is as follows

$$\lambda_m(\theta) = 2\Lambda\sqrt{\varepsilon_{eff} - \sin^2\alpha} \quad (1)$$

where α is an incident angle of light beam on system of the {111} planes, $D = \Lambda\sqrt{3/2}$, ε_{eff} is an effective dielectric constant. The latter is determined by the dielectric constants ε_i of substances forming composite and the volume part of substance f_i as follows

$$\varepsilon_{eff} = 0.74 \cdot \varepsilon_{\text{SiO}_2} + \sum_i f_i \cdot \varepsilon_i, \quad \sum_i f_i = 0.26. \quad (2)$$

For opals in study the values of D and Λ are within the range of 250 – 270 nm and 204 – 220 nm, respectively. An average linear size of pores is about of 70 nm.

As refraction index of LB4 crystal ($n \approx 1.58$) is higher than that of SiO_2 globules ($n_{\text{SiO}_2} = 1.47$) the filling of opal pores with LB4 should result in shifting the reflection peak towards the longer wavelengths, in accordance with expression (2). At higher concentration of embedded substance f_i the shift may be even to the infrared region [6]. This is why the reflection spectrum of opal suffered the melting-in was measured at two different incident angles ($\alpha = 15^\circ, 55^\circ$). However, there are not any Bragg reflection peaks in both cases (Fig. 2, b). It means that optical contrast in the composite is vanished, and the possible reason for it is the changes in structure of composite compounds.

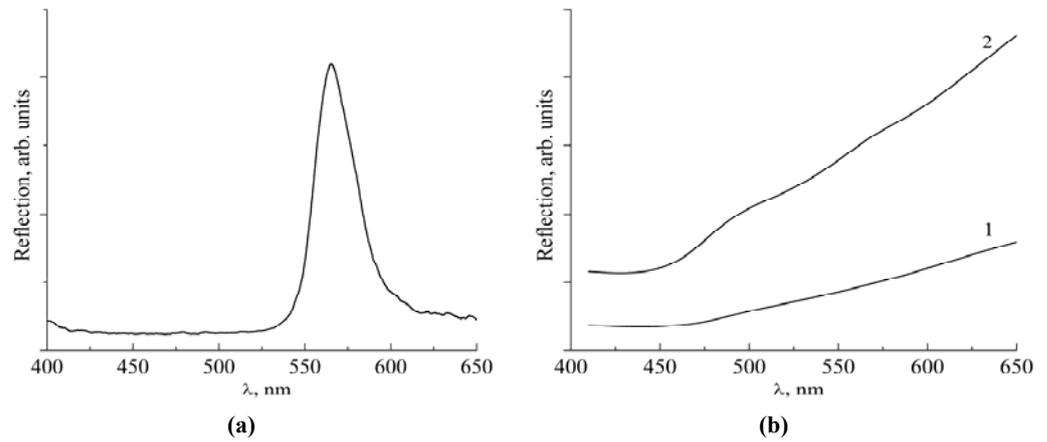


Fig. 2. Reflection spectra of initial opal at $\alpha = 15^\circ$ (a) and of the same opal after the LB4 melting-in procedure (b) at $\alpha = 15^\circ$ (1) and 55° (2).

The Raman spectrum of opal soaked into the melt for a shortest time (0.5 min) contains bands which are broadened (up to 20 cm^{-1}) and shifted to the low-frequency region (up to 70 cm^{-1} , depending on the spectral region) compared with those in Raman spectrum of LB4 single crystal (curves 1, 2 in Fig. 3). The smallest broadening (less than 5 cm^{-1}) is observed for the 469 cm^{-1} band in the opal-LB4 spectrum. Its spectral position is well correlated with a position of very intensive band of the α -quartz at 464 cm^{-1} [14].

In Raman spectra of opals with a soaking duration longer than 0.5 min the bands assigned as the shifted LB4 ones, except for the 469 cm^{-1} band, disappear. The spectrum becomes absolutely identical to the α -quartz Raman spectrum with a weak background formed by the spectrum of amorphous phase of initial opal (curves 3, 4 in Fig. 3).

The X-ray diffraction pattern proves the formation of some crystalline phase together with residual of amorphous state of initial opal (Fig. 4). The values of interplanar distances d_{exp} , calculated from angular positions 2θ of the X-ray diffraction peaks by using the Bragg

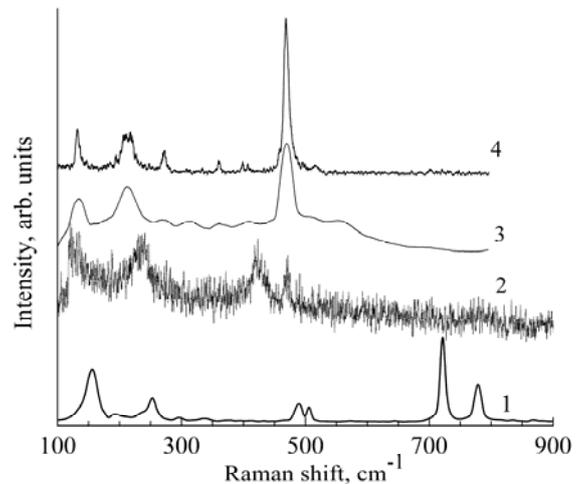


Fig. 3. Raman spectra of LB4 single crystal (1), opals with the soaking duration for 0.5 min (2) and for 3 min (3), and α - quartz (4).

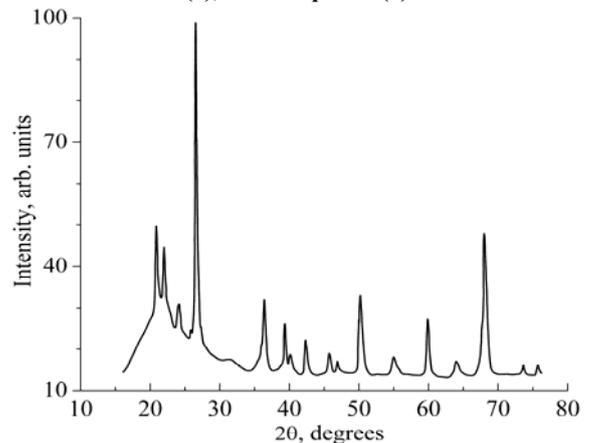


Fig. 4. $\text{Cu } K_\alpha$ X-ray diffraction pattern of opal with the 3 min soaking duration.

law ($d\sin\theta = k\lambda$, λ is the X-ray radiation wavelength, k is the diffraction order, $k = 1$), together with distances d_{tabl} for different phases of SiO_2 and lithium borates in ASTM PDF2 and in [15] are shown in the Table 1.

Table 1

Identification of the X-ray diffraction pattern of opal with the 3 min soaking duration

No.	2 θ , degrees	d_{exp} , Å	d_{tabl} , Å	Phase	No.	2 θ , degrees	d_{exp} , Å	d_{tabl} , Å	Phase
1	20.8	4.27	4.26	α -quartz	9	45.9	1.979	1.980	α -quartz
2	22.0	4.05	4.04	α -cristobalite	10	50.2	1.817	1.817	α -quartz
3	24.1	3.70	3.68	β -LiBO ₂	11	55.0	1.670	1.672	α -quartz
4	26.7	3.345	3.343	α -quartz	12	60.0	1.542	1.541	α -quartz
5	36.6	2.458	2.458	α -quartz	13	64.1	1.453	1.453	α -quartz
6	39.6	2.282	2.282	α -quartz	14	68.3	1.374	1.375	α -quartz
7	40.3	2.242	2.237	α -quartz	15	73.6	1.287	1.288	α -quartz
8	42.5	2.130	2.128	α -quartz	16	75.7	1.256	1.256	α -quartz

As can be seen from the Table 1, there is a well coincidence between d_{exp} and d_{tabl} for the α -quartz phase within the accuracy of data. Two peaks may be assigned to α -cristobalite and β -LiBO₂ phases. However, the appearance of the only peak, typical for some phase, is not enough to prove the presence of this phase. It may indicate the residuals of the phase, but it may be caused by the impurity presence, too. Thus, the α -quartz phase formation in the studied samples is no doubt only.

The following model for explanation of the obtained results may be proposed. When lithium tetraborate is melted, some part of lithium may contact with oxygen in air. It results in the known exothermic reaction between lithium and oxygen ($4\text{Li} + 2\text{O}_2 = \text{Li}_2\text{O}$) with the heat reaction effect $\Delta H = -1198$ kJ. Due to the low thermal conductivity of synthetic opals [5] this heat is accumulated into a small volume near by (or inside) opal, and cause its local heating up to temperatures at which the melting of amorphous silica dioxide is possible with the further transition to the α -quartz phase under cooling. (Our previous estimations of the local temperature of globules in the vicinity of exothermic reaction source give the value up to several thousands of K.)

On the basis of obtained data one can suggest that the main factor in such mechanism is the value of temperature at which exothermic reaction starts. Similar procedure of embedding LiKB₄O₇ into opal matrix in such a way did not result in the α -quartz phase formation, as the Raman spectrum of obtained sample evidenced. The probable reason for it is the lower temperature of LiKB₄O₇ melting (953 K). The dominant role of lithium in the proposed mechanism is proved by the absence of similar transformations by embedding non-lithium borate BaB₂O₄ into opal in such a way at temperatures higher than the LB4 melting temperature.

4. Conclusions

Characterization of opals contacted with the LB4 melt was made by X-ray and optical spectroscopy methods. The obtained results indicate the decomposition of lithium borate during the procedure and the α -quartz phase formation. For time of soaking opals into the LB4 melt shorter than 0.5 min the existence of the LB4 phase in opal matrix is proved by Raman spectrum. The structure of opals subjected to the procedure of LB4 melting-in for a longer time is the mixture of α -quartz with amorphous SiO_2 phase of initial opal. The existence of α -cristobalite and β -LiBO₂ phases in a very small quantity is not excluded. The mechanism of the α -quartz phase formation due to the local heating of opal matrix which is caused by exothermic lithium-oxygen reaction is proposed.

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