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M. P. Dergachov\*, V. N. Moiseyenko, O. O. Spichak, N. A. Kutseva

*Oles Honchar Dnipropetrovsk National University, Dnipropetrovsk, Ukraine*

*\*e-mail: dergachov-mp@dsu.dp.ua*

## THE PECULIARITIES OF THE LITHIUM BORATES STRUCTURE FORMATION INTO SYNTHETIC OPAL PORES

A possibility of the embedding of nonlinear optical materials from lithium borates group ( $\text{Li}_2\text{B}_4\text{O}_7$ ,  $\text{LiKB}_4\text{O}_7$ , and  $\text{LiB}_3\text{O}_5$ ) in pores of synthetic opals from the melt is investigated. The solid state formation in opal pores is made by slow cooling the opal – dielectric sample. The phase composition identification of lithium borates in opal pores is performed by the powder X-ray diffraction and Raman scattering methods. The filling grade of embedded substance is determined by measuring Bragg reflection spectra. An existence of  $\text{Li}_2\text{B}_4\text{O}_7$  and  $\alpha\text{-SiO}_2$  crystalline phases in opal pores is found. A mechanism of the  $\alpha$ -quartz phase formation as a consequence of the opal globule surface melting, caused by the local discharge of additional heat due to lithium – oxygen exothermic reaction, with the following crystallization of the melt. Temperature of the warming-up of opal globule surface is estimated. Crystalline phase in the pores of opals soaked with  $\text{LiKB}_4\text{O}_7$  or  $\text{LiB}_3\text{O}_5$  melts is not detected in the corresponding Raman scattering spectra. Difficulties in obtaining of “opal -  $\text{LiKB}_4\text{O}_7$ ,  $\text{LiB}_3\text{O}_5$ ” composites are discussed with taking into account the values of melting temperature of the embedded substances and viscosity of their melts.

**Keywords:** synthetic opal, lithium borates,  $\alpha$ -quartz, powder X-ray diffraction, Raman scattering.

Досліджується можливість введення нелінійно-оптичних матеріалів групи боратів літію ( $\text{Li}_2\text{B}_4\text{O}_7$ ,  $\text{LiKB}_4\text{O}_7$  і  $\text{LiB}_3\text{O}_5$ ) у пори синтетичних опалів з розплаву. Утворення твердої фази у порах опала здійснювалось у процесі повільного охолодження зразків опал-діелектрик. Ідентифікація фазового складу боратів літію у порах опалової матриці проводилась методами рентгенофазового аналізу та спектроскопії комбінаційного розсіювання світла. Ступінь заповнення пор речовиною, що вводиться, визначалась шляхом вимірювання спектрів брегівського відбивання. Встановлено наявність у порах опала кристалічної фази  $\text{Li}_2\text{B}_4\text{O}_7$  та  $\alpha\text{-SiO}_2$ . Запропонований механізм утворення кристалічної фази  $\alpha$ -кварцу, який ґрунтується на плавленні поверхні глобул опала внаслідок локального виділення додаткової теплової енергії за рахунок протікання екзотермічної літій – кисневої реакції, та наступної кристалізації розплаву. Наведена оцінка температури розігріву поверхні глобул опала. За результатами вимірювань спектрів комбінаційного розсіювання світла зразків, просочених у розплавах  $\text{LiKB}_4\text{O}_7$  або  $\text{LiB}_3\text{O}_5$ , кристалічна фаза у порах опала не виявлена. Труднощі в отриманні композитів “опал -  $\text{LiKB}_4\text{O}_7$ ,  $\text{LiB}_3\text{O}_5$ ” обговорюються з врахуванням значень температури плавлення речовин, що вводиться, та в'язкості їх розплавів.

**Ключові слова:** синтетичний опал, борати літію,  $\alpha$ -кварц, рентгенофазовий аналіз, комбінаційне розсіювання світла.

Изучена возможность введения нелинейно-оптических материалов группы боратов лития ( $\text{Li}_2\text{B}_4\text{O}_7$ ,  $\text{LiKB}_4\text{O}_7$  и  $\text{LiB}_3\text{O}_5$ ) в поры синтетических опалов из расплава. Формирование твердой фазы в порах опала осуществлялось в процессе медленного охлаждения образцов опал-диэлектрик. Идентификация фазового состава боратов лития в порах опаловой матрицы проводилась методами рентгенофазового анализа и спектроскопии комбинационного рассеяния света. Степень заполнения пор вводимым веществом определялась путем измерения спектров брегговского отражения. Установлено наличие в порах опала кристаллической фазы  $\text{Li}_2\text{B}_4\text{O}_7$  и  $\alpha\text{-SiO}_2$ . Предложен механизм образования кристаллической фазы  $\alpha$ -кварца, основанный на плавлении поверхности глобул опала вследствие локального выделения дополнительной тепловой энергии за счет протекания экзотермической литий – кислородной реакции, и последующей кристаллизации расплава. Приведена оценка температуры разогрева поверхности глобул опала. По результатам измерений спектров комбинационного рассеяния света образцов, промоченных в расплавах  $\text{LiKB}_4\text{O}_7$  или  $\text{LiB}_3\text{O}_5$ , кристаллическая фаза в порах опала не выявлена. Трудности в получении композитов “опал -  $\text{LiKB}_4\text{O}_7$ ,  $\text{LiB}_3\text{O}_5$ ” обговариваются с учетом значений температуры плавления вводимых веществ и вязкости их расплавов.

**Ключевые слова:** синтетический опал, бораты лития,  $\alpha$ -кварц, рентгенофазовый анализ, комбинационное рассеяние света.

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## 1. Introduction

One of the promising trends in photonics and nonlinear optics is a creation of photonic crystals (PCs) - nanostructures which are characterized by 2D or 3D modulation of refractive index with a period, comparable to the light wavelength. The dispersion law of photons in such medium is radically different from that in ordinary crystals. The main feature is an existence of energy gap in photon spectrum due to a multiple interference of electromagnetic waves [1].

One of the representatives of PCs may be globular synthetic opals (SO's) composed of amorphous  $\text{SiO}_2$  globules with a diameter about 200-250 nm. The globules form a face-centered lattice with a period  $\sim 165$ -205 nm. Octahedral and tetrahedral pores between the globules are connected with each other through channels. An average size of the pores is varied from 50 nm to 200 nm [2, 3]. Such porous structure can be filled with different compounds whose properties may be controlled by varying the globule diameter and, respectively, the pore linear size. Moreover, nanostructures obtained in such a way may exhibit unique properties which are not inherent to composing materials.

The embedding of materials with a high nonlinear optical susceptibility  $\chi^{(2)}$  and  $\chi^{(3)}$  into opal pores is of a particular interest. The second optical harmonic generation in SO's filled with  $\text{BaTiO}_3$  or  $\text{NaNO}_2$  has been observed in [4], and a possibility of parametric down - conversion in SO's with  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{LiIO}_3$  or  $\text{KH}_2\text{PO}_4$  have been discussed in [5]. So, the searching for other nonlinear optical materials which can fill the opal pores and the working out of methods of their embedding are topical. Some substances from lithium borates family such as  $\text{Li}_2\text{B}_4\text{O}_7$  (LB4),  $\text{LiKB}_4\text{O}_7$  (LKTb), and  $\text{LiB}_3\text{O}_5$  (LBO) were chosen for solving these purposes in the work. These compounds are very wide transparent (from vacuum ultraviolet to near-infrared spectral region); they have sufficient nonlinear optical susceptibility together with a good radiation resistance and high damage threshold [6]. LBO and LB4 single crystals are prospective for generation of the higher order optical harmonics [7]. LKTb is a new piezoelectric material with nonlinear optical properties no worse than other lithium borates [8, 9].

## 2. Samples and characterization technique

Initial bulk SO's were grown by sedimentation of  $\text{SiO}_2$  globules in accordance with the Stöber method [10]. After solvent evaporating, the samples were dried in air and then annealed at 400 K and 1025 K for one and two hours, respectively, in order to extract water and organic residuals. The samples were in the form of plates with mean dimensions about  $1.0 \times 1.0 \times 0.1 \text{ cm}^3$ .

The globule diameter  $D$  and the distance  $\Lambda$  between the (111) growth planes formed by the globule layers were determined from the spectral position  $\lambda_m$  of the reflection peak as follows  $\lambda_m(\theta) = 2\Lambda\sqrt{\varepsilon_{eff} - \sin^2\alpha}$  where  $\alpha$  is an angle of the incidence light beam,  $\varepsilon_{eff}$  is an effective dielectric constant, and  $D = \Lambda\sqrt{3/2}$ .

Raman spectra of the initial and infiltrated opals were excited by a 532 nm DPSS laser radiation with an average power of 100 mW. The spectra were measured in the backward scattering geometry. The scattered radiation was collected in the [111] direction of opal by using lens with an aperture no more than  $0.17\pi$  sr. Analysis of scattered radiation was performed with the use of modernized spectrometer DFS-12. Registration of a useful signal was carried out in a regime of photon counting with accumulation. X-ray diffraction patterns of the samples were obtained with using the diffractometer DRON-2 (Cu  $K_\alpha$  radiation).

### 3. Pore filling procedure

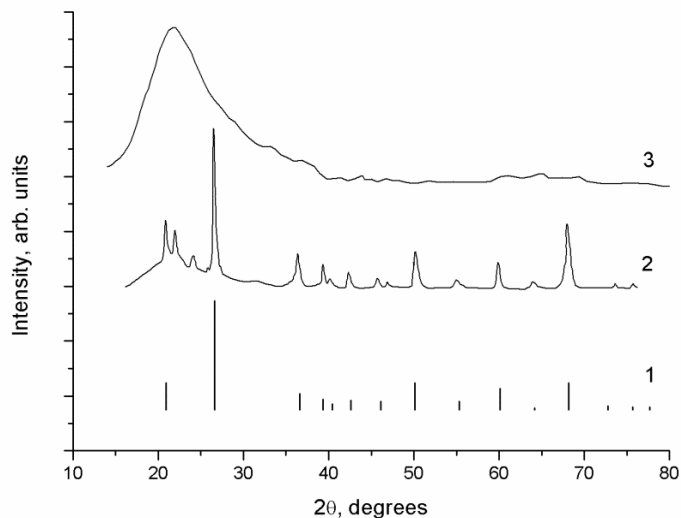
The pore filling is usually carried out either by soaking opal with a melt (or a solution) of the desired compound [11] or by the melt synthesis method, when the desired compound is synthesized in opal pores through chemical reaction [12]. The first way was chosen in our case.

At first, LB4 or LKTB polycrystalline powder with a thickness up to 0.25 mm was placed on or under opal surface, and then the whole system was placed on various substrates such as fused quartz or silicon. As it was difficult to make LBO polycrystalline powder due to its great hardness, the small rocks of LBO single crystals were used. At the second stage, each system was slowly heated in a resistance furnace up to the melting temperature of the filler ( $T_m = 1190$  K for LB4,  $T_m = 913$  K for LKTB, and  $T_d = 1108$  K for LBO, the last value is a decomposition temperature), and then was maintained at temperatures higher than the melting one by 5-10 K for an interval from 0.5 minutes to 15 minutes. Thereafter, the samples were cooled down to room temperature at an average cooling rate of 3 K/min.

### 4. Results and discussion

The reflection spectra of the obtained samples may serve as a criterion of the filling grade of embedded substance. One weak broad band with maximum at 630 nm is observed in the spectra. An independence of its spectral position on light incident angle may testify that it is originated rather from Rayleigh multiple scattering than Bragg diffraction.

The evolution of Raman spectrum of opal soaked with the LB4 melt via the time soaking was previously discussed in [13]. For the shortest soaking time (0.5 min) it contains broadened bands which are shifted to the low-frequency region compared with those in Raman spectrum of LB4 single crystal. For a soaking duration longer than 0.5 min the bands assigned as the shifted LB4 ones disappear and the spectrum becomes absolutely identical to the  $\alpha$ -quartz Raman spectrum. The X-ray diffraction pattern demonstrates the formation of a crystalline phase with the remains of amorphous phase of initial opal (Fig. 1).

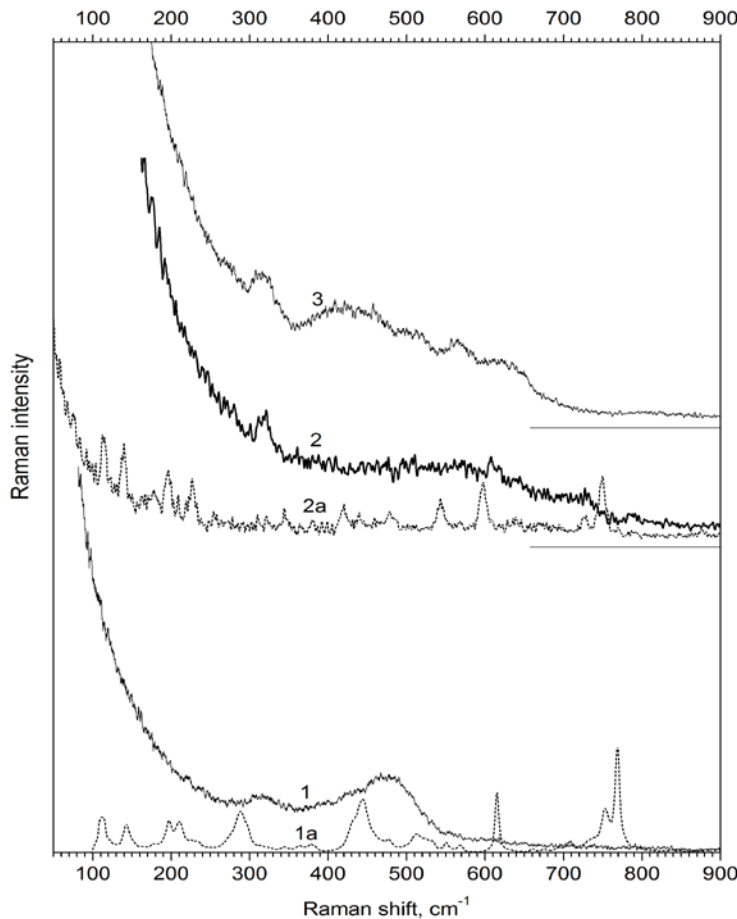


**Fig. 1.** X-ray diffraction spectrum of the crystalline  $\alpha$ -quartz (1) [14], the opal-LB4 composite with a duration of the soaking for 3 minutes (2), and the initial opal (3).

To explain the results let us consider phenomena in contact zone of the LB4 melt with opal globules. While maintaining temperature slightly above the LB4 melting one, lithium ions start reacting with oxygen in the air. It is an exothermic reaction with heat

releasing of  $\Delta H = -1198 \text{ kJ}$  for 4 moles of Li. Due to its low thermal conductivity, the nearest opal surrounding is locally heated up to the melting temperature of fused silica with the following crystallization in  $\alpha$ -quartz phase under cooling. The value of local heating temperature can be estimated by the expression  $T = T_m + \beta \cdot \Delta H / (4 c_\mu)$  where  $\beta$  is the Li number in chemical formula, and  $c_\mu$  is a molar heat conductivity. The latter may be calculated by the expression  $c_\mu = a + bT + cT^{-2}$  where  $a$ ,  $b$ , and  $c$  are constants taken from [15]. The value of  $\beta \cdot \Delta H / (4 c_\mu)$  is estimated for LB4 as no more than 1120 K. It is quite enough to exceed the melting temperature of fused quartz (assigned as 2000 K). This explanation may be examined for opals filled with other lithium-containing substance. No structural transformations were observed in opals which were filled with  $\text{LiIO}_3$  by using similar melted technique [16]. The possible heating should not result in melting the surface of globules because of the lower values of  $\text{LiIO}_3$  melting temperature ( $T_m = 693 \text{ K}$ ) and  $\beta \Delta H / (4 c_\mu)$  (evaluated as 1033 K).

The Raman spectra of opals soaked with the LKTB and LBO melt are quite different from the spectra of corresponding crystalline powders, and have several wide overlapped bands (Fig. 2).



**Fig. 1. Raman spectra of opals soaked with LKTB (1) and LBO (2) melts, polycrystalline powders of LKTB (1a) and LBO (2a), and initial opal (3).**

These spectra are similar to the initial opal spectrum, but not absolutely identical. This fact allows proposing the embedding of LKTb and LBO into opal matrix and the existence of these substances in amorphous state. Besides, the high viscosity of the selected compounds [17] should prevent their deep penetration into pores of synthetic opal. A crystalline  $\alpha$ -quartz phase is not formed in both cases. For LKTb, the estimated values of the melting temperature and  $\beta\Delta H / (4c_{\mu})$  are not enough in order to start melting the globule surface. In case of LBO, the decomposition at 1108 K may result in forming the new compounds and the mechanism discussed above may not be effectively realized.

## 5. Conclusions

The mechanism of the  $\alpha$ -quartz phase formation in opals soaked with the LB4 melt is most probably due to the local melting of opal globules due to lithium-oxygen exothermic reaction with the following crystallization. The possible reasons for an absence of any crystalline phase in opals filled with other lithium borates are the lower melting temperature (in case of LKTb) and possible chemical decomposition of LBO. The obtaining of perfect “opal – lithium borates” composites is also complicated by the high viscosity of the melts of mentioned compounds.

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