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The Effect of Melting and Crystallization of Indium within Pores on Properties of Photonic Crystals at Different Pore Fillings

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Abstract—Acoustic properties of synthetic opal filled with indium at different factors of pore filling is investigated using the pulse-interference technique in the frequency range from 4 to 8 MHz and in the temperature range of 300–480 K. A shift to lower temperatures and widening of the indium melting region in nanopores depending on the factor of pore filling is observed. It is shown that melting and crystallization of indium in pores during heating and cooling are accompanied with variations in velocity and absorption of longitudinal ultrasonic waves, respectively, under conditions that the filling factor exceeds the threshold value.

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1. INTRODUCTION

Interest in nanostructured composite materials has intensified lately, which is attributed, first of all, to wide prospects of their practical application. One type of nanocomposites includes porous materials filled with different substances (liquid crystals, polymers, ferrielectrics, semiconductors, etc.). At that, special attention is paid to the problems of sensitivity of the techniques to changes in the substance properties under conditions of confined geometry, in particular, to phase transformations in these substances.

Acoustic methods were used to study nanocomposites based on porous matrices filled with organic liquids, liquid nitrogen, water, ferroelectric sodium nitrite, as well as with metals, namely mercury and gallium (see [1–4] and references herein). The data on the parameters of nanocomposites and the substances filling the pores were obtained by measuring velocities and attenuation of shear and longitudinal acoustic waves. Studies of the melting-freezing phase transitions in substances within pores revealed a high informative value of acoustic methods characterized by such advantages as simplicity of experimental equipment, fast obtaining of a result, and a possibility to vary such experimental conditions as temperature changes within a wide range.

The present paper presents the results of acoustic investigations of melting and crystallization of metallic indium introduced into the pores of an opal photonic crystal. Melting and crystallization of indium in the pores of synthetic opals has not been studied before. Lowering of melting and crystallization temperatures (as compared to the melting point of bulk

indium $T_b = 429.6$ K [5]), smearing of these processes over temperature and changes in the melting and crystallization regions depending on the factor of pore filling with indium was revealed. In addition, the threshold value of the pore's filling factor for sensitivity of the used acoustic methods to indium phase transformations was found.

2. EXPERIMENT

A matrix of an opal photonic crystal is a dense packing of silicate balls 210 nm in diameter. (A description of the structure of synthetic opals can be found, e.g., in [6]). An ideal packing of balls of such sizes is to have octahedral and tetrahedral pores whose diameters are determined by relationships $d_1 = 0.414D$ and $d_2 = 0.224D$, where D is the diameter of contacting balls. Mercury porosimetry revealed for the photonic crystal under study a pore size distribution from 38 up to 70 nm with distinct maxima near 40 and 60 nm. The opal matrix's porosity (the ratio of the total pore's volume to the sample volume) was $31 \pm 2\%$. This value is slightly greater than the porosity of the ideal dense packing of identical balls (~26%), which points to irregularity of the sample structure.

Metallic indium was introduced into the pores in a melted state under high pressure. The pore's filling factor Z (the ratio of the volume of filled pores to the total pore's volume) was determined by comparing the weights of an empty sample and that filled with indium. The degree of pore filling was adjusted by prolonged keeping of the sample at temperatures, which were higher than the melting temperature of bulk indium, with some amount of indium flowing out of
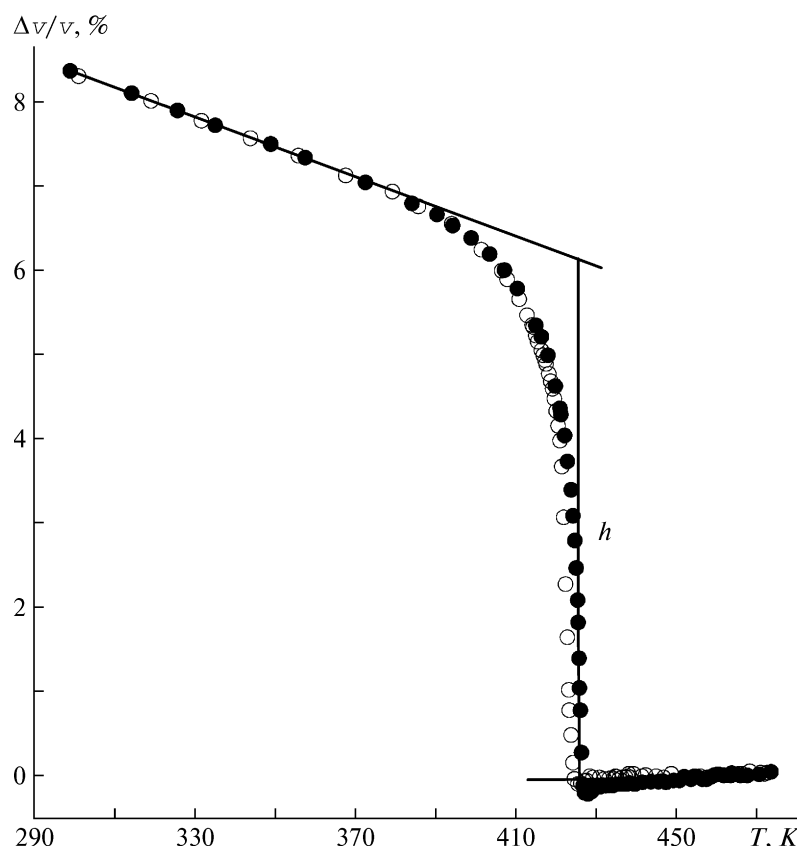
Fig. 1. Temperature dependence of relative velocity of longitudinal ultrasonic waves in the sample with the filling factor $Z = 79\%$ during heating (filled symbols) and cooling (empty symbols). Straight lines explain how the parameter h was introduced.

the pores. The values of Z, at which acoustic experiments were performed, were 93 ± 6, 79 ± 5, 51 ± 3, 35 ± 2, and 0%.

The investigations were carried out using a pulse-interference acoustic technique in the frequency range of 4–8 MHz and the temperature range of 295–480 K. Due to strong sound attenuation in the sample a variety of the technique with a single-pulse version of an acoustic path proposed in [7] was utilized. Temperature dependences of the relative variations of velocity $\Delta v/v \equiv [v(T) - v(T_0)]/v(T_0)$ of longitudinal ultrasonic waves where $v(T)$ and $v(T_0)$ are the velocities at the current temperature T and the fixed temperature T_0, respectively, were measured. The temperature T_0 was chosen to be 430 K for convenient comparison of experimental results at different factors of pore filling with indium, and the velocity variations were calculated with respect to $v(T_0)$ obtained during cooling. The accuracy of measuring the relative variations of velocity was $10^{-2}\%$. The error of temperature determination and the temperature gradient in the sample did not exceed 0.2 K and 0.08 K/cm, respectively. The measurements were performed in a quasi-stationary mode of slow heating and cooling whose rate did not

exceed 0.5 K/min and decreased in the region of phase transitions up to 0.2 K/min.

3. RESULTS

The relative velocity for an unfilled opal matrix linearly decreased with a temperature increase with the regression coefficient 5.3×10^{-4} K^{-1} within the entire analyzed temperature range. The velocity's temperature dependences for indium-containing opals significantly varied within the range below the melting point of bulk indium, and then again, the linear dependence of temperature was recovered. Figure 1 exemplifies the temperature dependence of ultrasound velocity in an opal sample with indium for the pore's filling factor $Z = 79\%$. In accordance with the earlier-performed acoustic studies of melting and crystallization of the substances introduced into nanoporous matrices [1–4] the observed nonlinear behavior should be attributed to variations in elastic properties of a composite material due to phase transitions in indium. At that, the difference in the curves of the velocity's temperature dependences directly in the region of phase transitions during heating and cooling is attributed to hysteresis between the processes of melting and crystallization of indium in confined geometry. The lower and
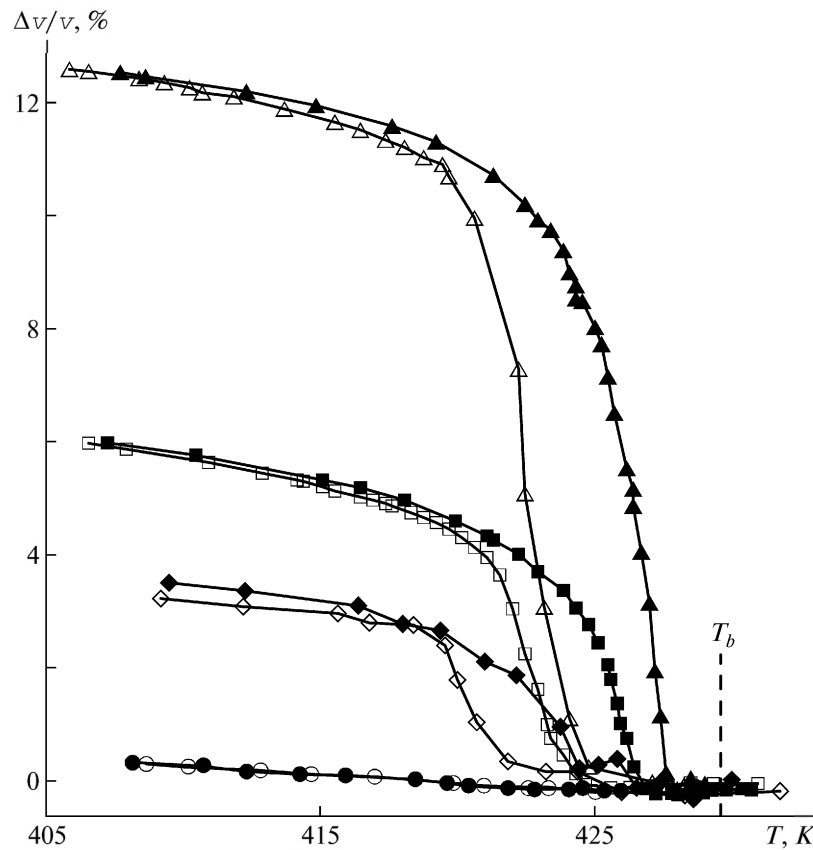
Fig. 2. Temperature dependences of relative velocity of longitudinal ultrasonic waves during heating (filled symbols) and cooling (empty symbols). Triangles, squares, diamonds and circles correspond to filling factors $Z = 93, 79, 51$ and 35%. Solid lines connect experimental points.

the upper temperature, at which velocity curves obtained during heating and cooling merge, are the temperatures of crystallization and melting completion, respectively. Note a significant widening of melting and crystallization of indium within pores which

Fig. 3. Dependence of effective melting temperature in the sample on pore filling factor.

shows up as smearing of the velocity step during phase transitions.

As apparent from Fig. 2, velocity anomalies which appeared in the region of indium melting and crystallization depended on the filling factor. With a decrease of Z the velocity's step value decreased and the loop of the velocity's temperature hysteresis observed during heating and cooling narrowed and shifted towards lower temperatures.

As the process of indium melting in pores is diffused, the temperature at which the derivative $d(\Delta v/v)/dT$ reaches its maximum, is recognized as the effective temperature of indium melting T_m. Figure 3 shows the dependence of T_m on the pore's filling factor.

To quantitatively characterize the value of the velocity step during phase transformations of indium we introduced the magnitude h determined as a difference of the values of $\Delta v/v$ lying on linear extrapolation of the velocity's temperature dependences far off indium melting and crystallization at the temperature T_m as shown in Fig. 1. The values of h are shown in Fig. 4 as functions of the filling factor of pores with indium.
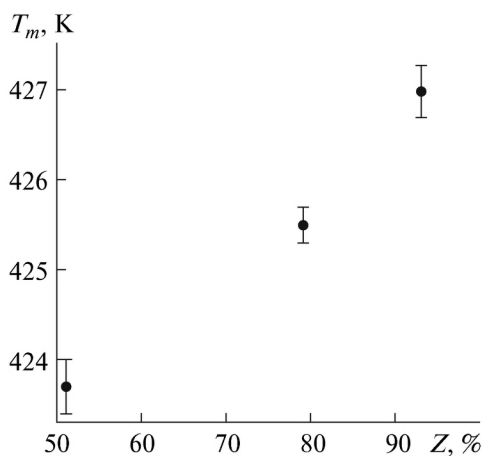
4. DISCUSSION

Lowering of melting temperatures of indium particles introduced into the pores of synthetic opals as compared to the melting point of bulk indium is explained by the size effects whose analysis is given, e.g., in [8–10]. All dimensional effect models for melting of small spherical particles proposed by now yield either an inversely proportional dependence of the melting temperature's shift $\Delta T_m = T_b - T_m$ on the particle diameter D ($\Delta T_m \propto 1/D$) or a close monotonous dependence within the framework of the model which assumes formation of a liquid layer on the surface of a melting particle. Diffusion of the melting region in this case is attributed to spread of small particle sizes.

Earlier, researchers studied the melting of thin indium films on germanium substrates [11], discontinuous indium films on amorphous silicon nitrite substrates [12], indium threads and nanoparticles, indium in an aluminum matrix (see references in [13, 14]), indium nanoparticles in porous glass [15], and indium nanoparticles on the surface of quartz glass [14] on the surface of graphite [16] and on the surface of WSe_2 [17]. For zero-, one-, and two-dimensional nanostructures of indium with a free surface a decrease in the melting temperature was revealed. For the particles with nonfree surfaces an increase in the melting temperature was observed, which was attributed to the effect of the interaction of an indium particle with a matrix. Thus, based on the data found in the literature we can make a conclusion that behavior of indium particles in the pores of an opal photonic crystal observed in the present study is close to that of the particles with free surfaces.

Lowering of the effective temperature of indium melting in opal pores with a decrease in the pore's filling factor should be paid attention to. This effect has not been mentioned earlier. Dependence of the melting temperature on the filling factor can be explained by indium redistribution inside the opal pore network in the process of Z variations. A decrease in Z took place when the sample was kept at temperatures above the melting temperature of bulk indium and indium in the pores was in a melted state. Since liquid indium partially wets the walls of a silicate matrix (the wetting angle at the contact surface of liquid indium with quartz glass being $40°$), the melt tends, first of all, to fill the pores of small sizes. Thus, with a decrease in Z indium frees large pores which yield a decrease in the particle sizes within pores. As the temperature of particle melting is related to particle sizes, the process of indium redistribution in pores leads to lowering of the effective melting temperature with a decrease in Z.

It follows from the results shown in Fig. 4 that a decrease in the pore's filling factor also yields a decrease in the velocity step h observed in the process of indium melting and crystallization in opal. However, h nonlinearly depends on Z and an acoustic reac-
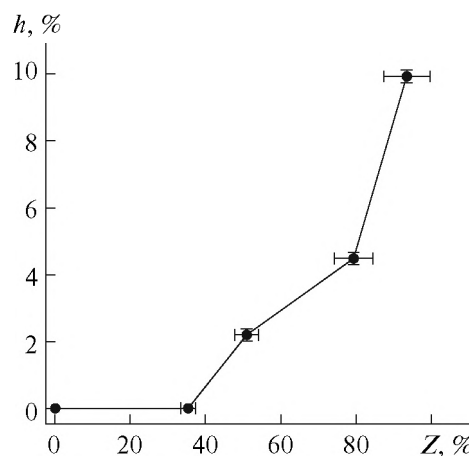
Fig. 4. Dependence of the step of ultrasonic velocity on pore filling factor. Solid line connects experimental points.

tion of the sample is not observed when the pore's filling factor is as large as 35%. The existence of the threshold value of the filling factor Z shows that the velocity step of ultrasound is not a simple consequence of variations of indium's elasticity moduli during melting and crystallization in pores as was assumed earlier in [2]. Probably connection of indium in the pore network, which is broken at small Z, is especially important for sensitivity of sample acoustic properties to phase transitions in indium.

Thus, acoustic studies of indium melting and crystallization in opal photonic crystals revealed variations in the velocities of the acoustic wave through phase transitions depending on the factor of pore filling with indium. Lowering of the temperature of melting completion with a decrease in the filling factor is explained by indium redistribution into the pores with smaller sizes and consequent decrease in indium's particle sizes in pores. The threshold value of the pore's filling factor for sensitivity of the acoustic wave's velocity to melting and crystallization of indium in pores was revealed.

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