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TRANSPARENT LITHIUM-ALUMINUM-SILICATE GLASS-CERAMICS (OVERVIEW)

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Methods of laser micro- and nano-modification of the structure of transparent dielectrics offer much for the creation of a new type of glass-crystalline materials and new applications. In the present work, after a brief excursion into the history of glass-ceramics, transparent aluminosilicate sitalls [glass-ceramics] are discussed, mainly for the example of the Li_2O–Al_2O_3–SiO_2 system, and the areas of their new applications. The recently discovered possibilities of laser micro-modification of the structure of sitalls and the writing of elements of photonics and integrated optics in their interior volume are considered. Special attention is given to transparent glass-ceramics with thermal expansion coefficient close to zero.

Keywords: transparent sitalls [glass-ceramics], thermostable sitall, directed crystallization, laser micro-processing, direct laser amorphization.

The discovery of catalytic volumetric crystallization of glass by S. D. Stookey in the USA [1, 2] and practically simultaneously by I. I. Kitaigorodskii in the USSR [3], who was awarded the Lenin Prize in 1963 for work together with N. M. Pavlushkin on sitalls, remains to this day one of the central events in glass science, which largely determined the directions of research into glass-crystalline materials and extraordinarily expanded the limits of their applications (see, for example, [4, 5]).

After S. D. Stookey's first publications, brand names and copyright names for a new class of materials began to appear in different countries — glass-ceramics, such as 'Pyroceram' (USA), 'Vitrokeram' (England), 'Devitroceram' (Japan), and many others. In the USSR, at I. I. Kitaigorodskii, glass-ceramic materials were called 'sitalls.' At the turn of the 1960s, intensive research and hunts began for the most rational ways of obtaining them. If earlier the efforts of researchers were aimed at preventing crystallization and avoiding this undesirable and poorly controlled process in the production of glass products, now, on the contrary, efforts have largely focused on the search for conditions that afford controlled production of a fine-crystalline structure, uniformly distributed in the interior volume of the original glass [4, 6].

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The development of the technology of glass-crystalline materials in general, and transparent glass-ceramic in particular, over the course of more than 70 years, effected their large-scale implementation in the most diverse industries — from household appliances to high-precision optics, astrophysics, electronics, etc. [5, 7]. The wide range of applications of transparent glass-ceramics is a result of the fact that the greater mechanical strength, wear resistance, chemical resistance, and heat resistance than that of glass are combined with high transparency and the possibility of initiating properties characteristic of active dielectrics [8 – 12].

The physical properties of glass-ceramics depend on many parameters, primarily on the composition of the matrix glass, phase composition, size and properties of crystals, degree of crystallization, etc., and the volume fraction of the crystalline phase can vary from values close to zero (nanostructured glass) up to more than 90% [13, 14]. The targeted characteristics of glass-ceramics can be adapted to a specific application by isolating certain types of crystalline phases with the desired microstructure and morphology [6, 11]. At the same time, the current level of technology development provides the ability to accurately control the temperature–time parameters of crystallization and, accordingly, a high reproducibility of properties [15, 16]. Isolation of the nuclei of any polar or even ferroelectric phase (lithium, sodium, and

potassium niobates, stillwellite-like $LaBGeO_5$, fresnoite Ba_2TiSiO_8, β-BaB_2O_4, hilgardite-like $Pb_2[B_5O_9]Br$, etc.) and their moderate growth to sizes that guarantee the preservation of transparency, causes the appearance of quadratic optical nonlinearity, electro-optical effects, and, in the case of texture formation in a temperature gradient field, piezoelectric and pyroelectric properties in a transparent glassy matrix [17 – 21]. By using glass-ceramic matrices it becomes possible to obtain highly efficient luminescent nanocrystalline materials, including in the form of optical fibers doped with ions of rare earth elements [22 – 25].

A large number of works and monographs are devoted to the development of glass-crystalline materials, including transparent glass-ceramics [4 – 7, 11, 20, 21, 26, 27]. Another direction in the science of glass-crystalline materials has been developing intensively over the past two decades: the elaboration of methods of laser micro- and nano-modification of the surface structure [28 – 30] and volume [20, 31 – 34] of glass by means of laser radiation, making it possible to create locally, according to the developer's intention, zero-dimensional, one-dimensional (including waveguide), planar crystalline or glass-crystalline structures of complex architecture, and in particular the creation of such structures with nonlinear optical properties based on active dielectrics.

Even though there is an abundance of publications on laser modification of various glasses and crystals, only a few works are devoted to investigating the effect of femtosecond (FS) laser radiation on the structure of transparent glass-ceramics [35 – 38]. Trends in research into the interaction of laser radiation with transparent glass-crystalline matrices are associated with the development of methods for recording channel waveguides in their interior volume. Waveguide structures in the volume of glass-crystalline matrices with improved mechanical characteristics and thermal stability over a wide temperature range are of great interest for the development of components of integrated optical circuits and miniaturization of aerospace-based optoelectronic devices that experience strong mechanical loads and temperature changes [36, 39].

The present work considers in more detail transparent thermally stable glass-ceramics based on the Li_2O–Al_2O_3–SiO_2 (LAS) system, mainly with reference to the work of the last decade. LAS sitalls, in our opinion, will significantly expand the capabilities of laser writing technology for elements of integrated optics and photonics in the interior volume of transparent dielectrics. Minimizing the linear thermal expansion coefficient (LTEC) and increasing the temperature range of its stability not only near room temperatures but also at up to about 500 ºC while maintaining all other advantages of the LAS system sitalls, requires a particularly precise relationship between the final properties of transparent sitalls and the composition of the original glass, the content of crystallization nucleators, and the development of precision sitallization modes.

Among the known sitall-forming systems, the transparent sitalls based on the LAS system and those based on the MgO–Al_2O_3–SiO_2 system are commonest [4, 5, 7, 40]. They have found application as a basis for the creation of navigation devices [41 – 43], substrates for UV photolithography, and the basis of telescope mirrors [44, 45], photosensitive materials [2], IR-transparent radomes of aircraft [40, 46], cooktops, kitchenware [7], dental implants [47], bioactive materials [48, 49], hard drive substrates [50], and transparent ballistic armor materials [51], and much else.

Back in 1959, D. Stookey found that in order to obtain a fine-crystalline glass-ceramic structure and a homogeneous distribution of crystalline grains, one or more crystallization nucleators must be present in the composition of the original glass [1]. Subsequently, researchers focused on the issues of heterogeneous nucleation in glasses nucleated with titanium oxide [27, 52, 53]. Direct observation of the progress of nucleation was difficult half a century ago because of the small size of the resulting nuclei, and research on the pre-crystallization stages was based mainly on the 'development' method [54] — counting the nuclei grown as a result of additional heat treatment, visible in an optical microscope [55]. The most complete understanding of the process of nucleation of the crystalline phase became possible by using powerful methods of structural analysis — primarily small-angle thermal neutron scattering [56, 57] and transmission electron microscopy (TEM) [58, 59].

For LAS-system glasses, just as for magnesium aluminosilicate glasses, ordinarily, titanium oxide was used as a crystallization nucleator, but then a combination of oxides $TiO_2 + ZrO_2$ came increasingly into use. Direct methods of structural analysis (x-ray absorption spectroscopy (XANES) and electron microscopy with the possibility of local chemical analysis) made it possible to study in detail the mechanism of action of nucleators at the early stage of crystallization and subsequent crystal growth [60, 61]. Using the LAS system as an example, the formation of a glass-ceramic structure can be divided into three stages: 1) phase separation — one of the amorphous phases is saturated with crystallization catalysts TiO_2 and ZrO_2 [58, 60, 61]; 2) growth of spherical crystals of mixed oxide $ZrTiO_4$ up to 20 nm in size [58, 62]; 3) epitaxial growth of the main crystalline phase [63]. As a result, a complex multiphase sitall structure is formed, consisting of large (about 200 nm) aluminosilicate crystals, small (up to 20 nm) $ZrTiO_4$ crystals and a residual glass phase (Fig. 1). Similar processes were described much earlier in [52, 53, 56, 64] for the case of a single nucleator, TiO_2, into glass for the sitallization of a number of aluminosilicate glasses.

An equally important technological stage in the production of transparent glass-ceramics is the determination of optimal heat-treatment conditions for the original glass, which would assure the formation of the maximum number of nuclei and the specified phase composition as well as the required degree of crystallinity and crystal size. It is known that to obtain a fine nanocrystalline structure of transparent

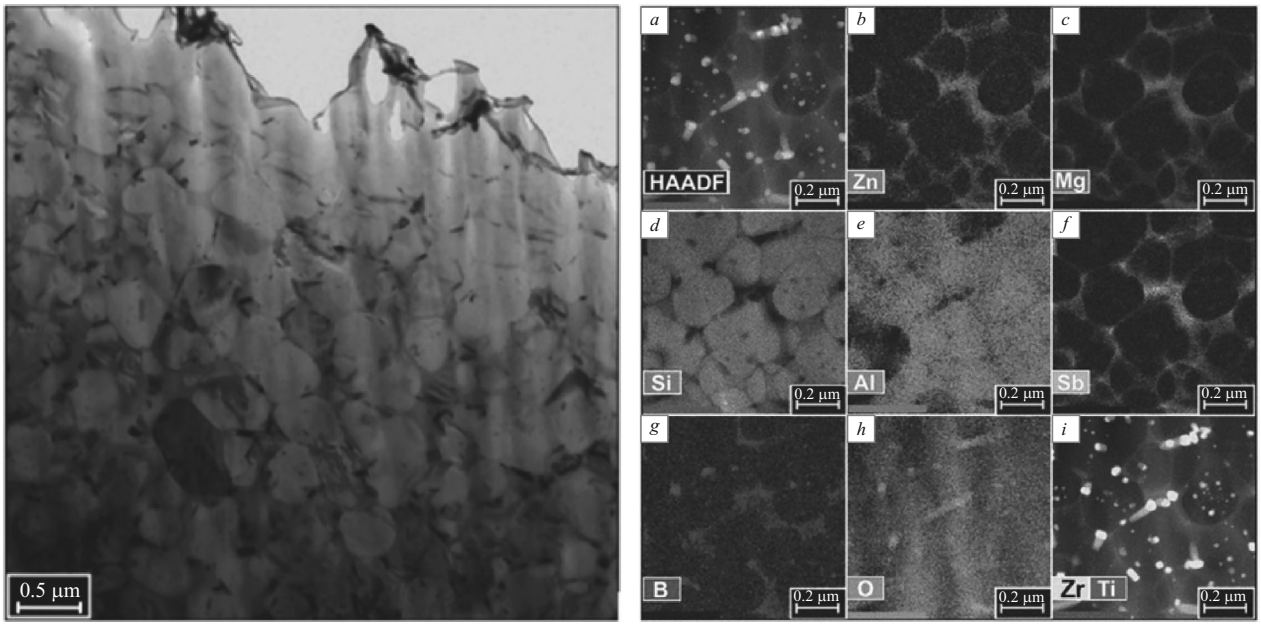

Fig. 1. Bright-field TEM image of the microstructure of sitall based on the LAS system (left); dark-field image of scanning transmission electron microscopy (STEM) with a high-angle ring detector (*a*) and elemental distribution maps (*b* – *i*) according to energy-dispersive x-ray spectroscopy data (right) [59].

glass-ceramics, as a rule, a two-stage glass crystallization regime is used, in which the release of the largest number of crystallization nuclei is assured at the first stage, and the growth of the main crystalline phase is realized at the second stage.

The nucleation stage has the greatest influence on the final structure and uniform distribution of the crystalline phase in the volume of the glass-ceramics [65], so that it is of great importance to find the nucleation heat-treatment regime for each composition of the glass subject to sitallization. In our view the simplest and most accessible method for accurately determining the nucleation temperature is the method proposed by A. Marotta, et al. [66]. It is based on a determination of the dependence of the position of the exothermic peak on differential thermal analysis (DTA) or differential scanning calorimetry (DSC) curve on the heat treatment conditions of the original glass near the glass transition temperature T_g. The application of the technique of A. Marotta and others to LAS glasses made it possible to obtain sitalls with near-zero LTEC values in a wide temperature range [67 – 69].

The leading manufacturers of optical materials (Corning Inc. (USA), SCHOTT AG (Germany), Eurocera (France), Nippon Electric Glass, OHARA (Japan), LZOS (Russia) and others) have launched serial production of a number of materials based on LAS glass-ceramics. Among the well-known brands, special mention should be made of glass-ceramics characterized by ultra-low thermal expansion: Zerodur®, Astrositall® (CO-115M), Clearceram® [70, 71]. In spite of the high degree of crystallization (about 70%), they have good transparency on account of the small size of the crystals (less than 50 nm) and the insignificant difference in refractive indices between the crystalline phase and the residual glass phase [67]. Precision control of crystallization processes greatly contributed to the production of unique materials: for example, the SCHOTT Company (Germany) introduced new grades of glass-ceramics Zerodur® Extreme with tolerances for LTEC equal to $0 \pm 0.07 \times 10^{-7}\ K^{-1}$ in a narrow temperature range from 0 to 50°C [45]. In addition, deviations of the expansion coefficient are regulated in the radial and axial directions for finished products with diameter up to 4 m.

Increasingly strict stabilization of the parameters of the optical resonator of a gyroscope under external influences also continues to be very relevant. To solve this problem it is necessary to achieve a combination of high efficiency of active stabilization with low control voltages at minimum cost, as well as the creation of housing materials with near-zero LTEC in a wide temperature range — not only including the low-temperature region from –100 to +100°C, but also the high-temperature range — up to 500°C and higher [41 – 43]. This necessitates deeper understanding of the structure of glass-crystalline materials and processes that provide ultra-stable and close to zero LTEC, requires clarification and complexity of the compositions of the original glasses and the development of precision heat treatment modes at the first and second stages of glass-ceramic formation. Accordingly, in recent years, the number of publications aimed at improving the structure and properties of optical glass-ceramics has been growing [15, 16]. As a result, in [68, 72] transparent LAS glass-ceramics were obtained with a temperature variation of the LTEC in the form of a constant

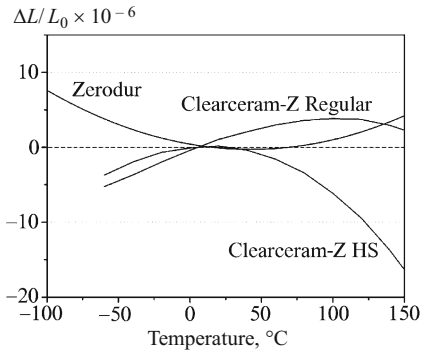

Fig. 2. Temperature dependence of elongation L/L_0 of industrial samples of optical glass-ceramics according to the data in [11] and catalogs of manufacturing companies (OHARA Inc., Japan).

near-zero up to about 500°C, while the LTEC oscillations in the temperature range from –100 to +100°C for foreign and domestic glass-ceramics Ceran, Zerodur, Clearceram, SO-115M and other brands, according to data from the catalogs of manufacturing companies, is an order of magnitude greater for relatively large-sized samples (Fig. 2)

The unique properties of LAS glass-ceramics are directly related to the possibility of isolating in their volume crystalline phases based on β-quartz, β-eucryptite ($Li_2O \cdot Al_2O_3 \cdot nSiO_2$, where $n = 2 – 10$) and β-spodumene solid solutions ($Li_2O \cdot Al_2O_3 \cdot nSiO_2$, where $n = 4 – 10$), and research into the crystallization of LAS glasses has not stopped for more than 70 years [73, 74]. The main crystalline phase that is released upon significant supercooling of the melt in a wide SiO_2 content range ($n = 2 – 8$) is a solid solution based on β-quartz [75]. The formation of solid solutions of lithium aluminosilicates is the result of the replacement of Si^{4+} atoms with Al^{3+} in [SiO_4] tetrahedra with charge compensation by Li^+, Zn^{2+}, Mg^{2+} cations. As a rule, this substitution is done by pairs (Al_2O_3, Li_2O), (Al_2O_3, MgO), or (Al_2O_3, ZnO) while maintaining the SiO_2 content in the range 50 – 80 wt.%, which ultimately shifts the stoichiometry towards solid solutions of β-eucryptite and β-spodumene [70]. This is also evidenced by the data of [59], where the microstructure of transparent LAS glass-ceramic was studied in detail using TEM and energy-dispersive x-ray microanalysis. Distortion of the crystal structure as a result of the formation of solid solutions results in the appearance of a noticeable anisotropy of thermal expansion along the *a* and *c* axes [76 – 78], which is often the source of strong deformations along the crystal interface and the appearance of microcracks in their interior volume.

The composition of the original glass directly affects the position and slope of the temperature variation of the LTEC curve. According to [79], as clockwise shift of the expansion coefficient curve is achieved by increasing the ZnO content at the expense of Li_2O; a counterclockwise shift of the LTEC curve could be due to the replacement of ZnO with MgO and an increase in the P_2O_5 content at the expense of Al_2O_3. The heat-treatment time has a direct impact on the size and amount of the released crystalline phase, which significantly changes both the thermal expansion coefficient and the thermomechanical properties of LAS sitalls. Associated with this is a large volume of recent research, including phase separation at early, nanoscale stages of crystallization [58, 60, 80], the influence of the type and number of crystallization catalysts [61, 63, 81], determination of nucleation mechanisms and crystallization kinetics [54, 59, 82 – 84], and the use of various heating methods to initiate crystal growth [85, 86].

The trend towards miniaturization of optical instruments dictates the need to create integrated micro-optical navigation systems using thermally stable optical media. Prototypes of micro-optical gyroscopes with ring resonators are successfully created using photolithography technologies and the use of polymer materials [87]. This necessitates thermal compensation and additional protection of micro-gyroscopic integrated chips. The photolithography methods used can assure stable production of only two-dimensional structures, while a promising path for the development of micro-optical gyroscopes is the implementation of the technology of multi-ring resonators located within the volume of a chip [88]. A logical step in the research and development of micro-optical gyroscopes could be the writing of waveguide structures in the interior volume of thermally stable glass-ceramic matrices using FS laser writing technology. In the future, this will provide an opportunity to create integrated optical devices and miniaturize large optical installations that are used in space astronomy and navigation, where weight and size parameters are critical factors.

Along with the problems of using thermally stable sitalls in gyroscopes, it seems relevant to create a new class of cover glasses for mobile device screens based on transparent glass-ceramics [sitalls]. Research in this area is increasingly developing [89 – 93]. Corning Inc. (USA) has developed cover glasses based on aluminosilicate glass-ceramics, produced under the brand name Ceramic Shield. The Chinese mobile device company Huawei, in collaboration with CDGM Glass (USA), has patented and announced the release of mobile devices with a new class of protection for cover glasses under the Kunlun brand, which are also based on transparent glass-ceramics [94]. There is every reason to assume that in the near future mobile devices will increasingly use sitall ceramic glass screen protectors, which will replace their glassy Gorilla® predecessors Glass (Corning Inc.) and Dragontrail® (Asahi Glass Company). Translation of the technique for writing waveguide structures in the interior volume of transparent glass-ceramics will make it possible to create photonic devices integrated directly into the screens of mobile devices [95, 96] and augmented reality displays [97].

Investigations where attempts have been made to write waveguides in LAS glass-ceramics demonstrate the fundamental possibility of implementing this idea [35 – 37]. Mo-

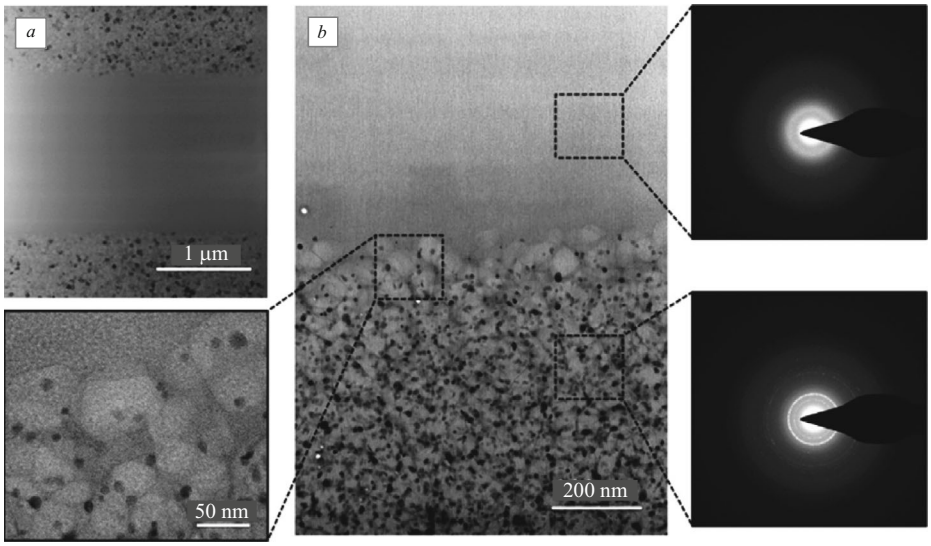

Fig. 3. Bright-field TEM images of the glass-ceramic area with a track (*a*) and the boundary of the track (*b*), recorded in LAS glass-ceramic in thermal mode by a laser beam with a pulse repetition rate 500 kHz, pulse energy 300 nJ at scanning rate 200 μm/sec, and electron diffraction pictures of selected areas [98].

dified regions in the athermal and thermal regimes of the PV recording of a transparent glass-ceramic based on a LAS system with a LTEC value close to zero were studied in detail by means of TEM [98]. The results of electron microscopy and electron diffraction demonstrate the possibility of complete amorphization of nanosized crystals of β-eucryptite-like solid solutions under the action of laser pulses (Fig. 3).

In the TEM images displayed in Fig. 3 the phase-separated structure of LAS glassware outside the laser recording region is clearly visible, including dark areas about 10 nm in size, corresponding to $ZrTiO_4$ nanocrystals, and large ones — aluminosilicate crystals, while the structure of the track turns out to be homogeneous. The directly observed disappearance of nanocrystals in the tracks correlates well with the diffraction patterns written in the area affected by the laser beam and outside this area: in regions inside the track there are no Bragg reflections, while in the diffraction pattern of the area outside the region of effect of the laser beam point reflections from individual nanocrystals are observed — they form rings, which indicates an arbitrary orientation of crystallites, and a halo around the central reflection from the amorphous matrix. The thermal effect of individual pulses is found to be sufficient to melt the nanocrystals, eliminate the multiphase structure of glass-ceramics, and restore the homogeneous structure of the glass. In this case, complete amorphization of LAS glass-ceramic results in a decrease in the refractive index in the laser processing area, which opens up the possibility of using direct laser writing of channel waveguides in a thermally stable glass-ceramic matrix.

Similar results were obtained for glass-ceramic samples based on the $ZnO–MgO–Al_2O_3–SiO_2$ system [99], for which the possibility of complete amorphization of the crystalline ganite phase in the volume of the sitall was also demonstrated. In this case, complete amorphization of the local area of glass-ceramics leads to an increase in the refractive index, thereby showing that in different glass-ceramic-forming systems very different relationships between the refractive indices of the original and modified glass-ceramic structures can be realized. Substantial differences in the results of laser micro-processing of different aluminosilicate glass-ceramics indicate that the melting of the crystalline phase under the action of FS laser pulses is not the only factor responsible for the local change in the refractive index. In developing a technology for writing wave guides sitalls of complex compositions, it is necessary to take into account the entire variety of physicochemical processes that occur under the influence of a laser beam and can compete with each other in the process of local modification of the refractive index.

Local reduction in the refractive index in the amorphized region makes it possible to record the shells of waveguide structures, in which the light-guiding role is played by the unmodified volume of thermally stable LAS sitalls [35, 39]. Changes in the focusing depth of the laser beam from pass to pass make it possible to form the core of waveguides with an almost circular cross-section centered at a depth of 150 μm below the surface of the thermostable LAS sitall sample. The shell of a waveguide channel is a set of parallel amorphized tracks written at different focusing depths (Fig. 4).

The achieved level of minimal optical losses in the formed single-mode waveguides still limits the practical significance of the method of direct laser modification of the microstructure of sitalls. It can be assumed that a reduction in optical losses will be achieved not only by optimizing the geometry of the waveguides, but also by optimizing the

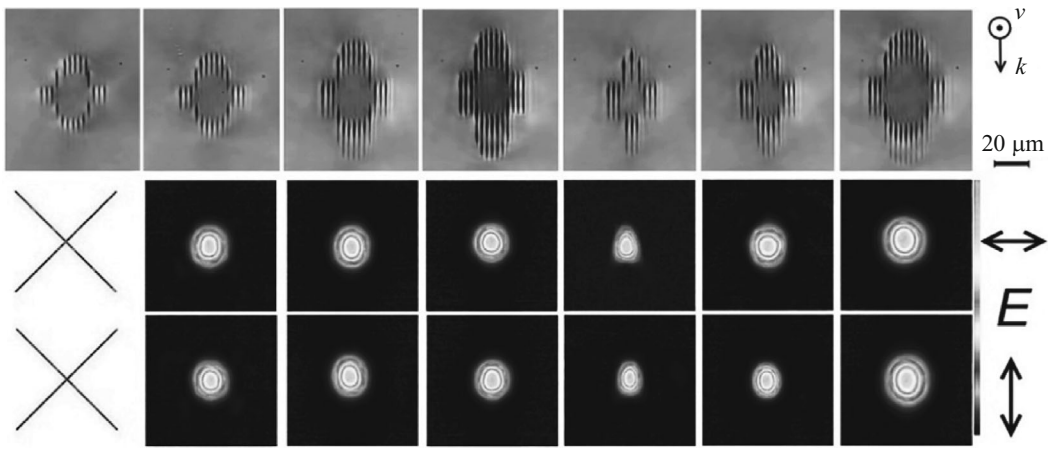

Fig. 4. Optical photomicrographs of the cross-section of waveguides with different core diameters written in LAS sitall (top), and near-field light intensity distribution profiles at the waveguide exit (bottom). The vectors *k*, *v*, and *E* show the directions of the wave vector, writing a shell, and orientation of the plane of polarization of light in the waveguide [35].

nanocrystalline structure of sitalls by adjusting the heat-treatment conditions of the original LAS glass.

In summary, transparent sitalls, and especially sitalls based on the LAS system, are successful commercial products in different fields of science and technology, and retain great potential for future applications, some of which are discussed in this work. The development of new materials with a high degree of homogeneity and the possibility of precise adjustment of the coefficient of thermal expansion, and this is exactly what optical instrument making requires, requires further research in the series "composition of the batch – conditions of melting and glass production – heat treatment with the formation of a nanocrystalline structure of a precisely specified phase composition – sitallization." A deeper understanding of the nature of the anomalous thermal expansion of both sitalls and composites, as well as quartz glass, titano-silicate binary glasses, Invar alloys, etc., together with the development of approaches to laser micromodification of their structure, will contribute to the creation of a new class of hybrid glass-crystal materials and their use in thermally stable photonic devices and integrated optics elements.

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