OPTICAL PROPERTIES AND STRUCTURE OF ULTRADISPERSED PARTICLES OF CuInSe$_2$Te$_2$(1−x) IN A SILICATE GLASS MATRIX

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We investigate silicate glasses that contain nanodimensional particles of the ternary semiconductor compounds CuInSe$_2$ and CuInTe$_2$ and the solid solution CuInSeTe. Based on the data of x-ray examination, it is assumed that the particles of the indicated compounds have a cubic lattice rather than the tetragonal one typical of these compounds in a macroscopic state. In the spectra of optical absorption of the glasses (irrespective of the dimensions of the particles) there is a band at $\lambda_{\text{max}} \approx 550$ nm which can be associated with partial oxidation of copper on the surface of the glasses.

Keywords: absorption spectrum, x-ray analysis, nanodimensional particle, silicate glass, solid solution.

Introduction. Optical materials synthesized on the basis of amorphous dielectric matrices and containing particles of semiconductor compounds are of considerable interest from the point of view of both investigation of the dimensional effects of semiconductors manifested in their optical properties and production of materials with new properties which can be regulated within rather wide limits [1-5] due to a change in the chemical nature of the semiconductor, the concentration of particles, their dimension, the composition of matrices, specific features of the localization of particles in a matrix, etc. This kind of material is developed on the basis of different dielectric matrices (polymeric films, inorganic glasses, composite systems with organic substances, zeolites, opals). The glasses based on inorganic oxides (first of all, silicon) produced by means of the generally accepted technology of melting [6-10] and by the sol-gel method [11-15] are a rather convenient matrix in view of their high transparency within the 0.3-2.0-$\mu$m wavelength region and their stability, chemical inertness, and simple technology of production.

In a number of works [16-20], the possibility of synthesizing glass-like matrices (GM) doped with nanocrystals (NC) of ternary semiconductor compounds CuInS$_2$ and CuInSe$_2$ and with CuInS$_2$Se$_{2(1-x)}$ solid solutions (0 $\leq$ x $\leq$ 1) based on them is shown. The conditions for the production of matrices and the influence of the chemical composition of the glass and of semiconductor particles on the linear and nonlinear optical properties of synthesized materials were investigated. The results of investigation of the structure of the particles formed at different concentrations of a semiconductor in a glass made it possible to suggest that a crystal lattice with cubic symmetry can be realized in CuInS$_2$ particles, although in a conventional state a lattice of chalcopyrite with tetragonal symmetry is typical of this class of compounds. The change in the crystal lattice was observed for binary semiconductors [21-23]. This change can be associated with the excess surface energy.

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of particles, the mechanical or thermal stresses inside of the glass-like matrix [24], and also with the formation of a shell of new composition chemically bonded with the surface of the particles [25].

In our work, we present the results of investigation of glass-like media doped with CulnSe₂ and CulnTe₂ nanocrystals and with a solid solution of CulnSeTe. Previously, this class of tellurium-containing semiconductors as activators of silicate glasses had not been studied. These semiconductors are of interest in view of the possibilities of an additional change in the optical absorption edge due to the decrease in the forbidden-band width in the series CulnS₂–CulnSe₂–CulnTe₂ and the possibility of creating new optical materials [26].

**Experimental.** As glass-like matrices, we used two compositions (in what follows they will be denoted by GM1 and GM2), based on the SiO₂–CaO–M₂O (M = Li, Na, K) system, that differ only by the oxides of alkali metals at a constant total content of M₂O equal to 15 mole%. In GM1, 15 mole% Na₂O is present; in GM2, a partial equimolar replacement of Na₂O by K₂O + Li₂O in a 1:1:1 ratio is performed. As shown in [16, 17], the character of light absorption (in the region of the matrix transparency) for the glasses doped with semiconductors depends not only on the chemical nature of the activator but also on the nature of the cations that enter into the composition of the glass-like matrix due to their polarizing action on the semiconductor particles and on the specific features of the formation of the glass/semiconductor interface. In the matrix with three alkaline components, more favorable conditions can be created for retaining the chemical individual property of the semiconductor-activator particles [27].

The crystalline compounds CulnSe₂, CulnTe₂, and CulnSeTe used as activators were synthesized from elementary components [28] and identified radiographically. The content of CulnSe₂ and CulnTe₂ in the glass-like matrix was 0.75 wt.%, while the content of CulnSeTe varied from 0.1 to 1.0 wt.%. The glass-like matrices doped with semiconductors were synthesized at 1620 ± 20 K by a procedure described in [16-18]. The glasses were colored directly in melting and cooling of melts. The coloration intensity was regularly enhanced with increase in the content of the semiconductor that at concentrations of up to 1 wt.% was completely dissolved in the glass-like matrix.

In order to determine the phase composition of the particles in the glasses, the glass-like matrix was attacked by a hydrofluoric acid with subsequent washing out of the fluorides (except for CaF₂) formed, since x-ray examination of the glasses without their destruction did not allow one to reveal the presence of any