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«HIGH REFRACTIVE INDEX GLASSES WITH A HIGH CONTENT OF LANTHANUM OXIDE»

Abstract

The relevance of the work. In the period of rapid development of optical and information technologies, in particular optoelectronic and photonic devices, the demand for optical components and materials is increasing. Optical glasses, as an integral part of most optical systems, need to be continuously improving both in terms of key parameters and in terms of material quality. A key factor in the development of modern optical systems is the use of glasses with various combinations of optical and physical-chemical characteristics. For example, glasses with high refractive indices n_d (> 1.7) or dispersion ν_d (> 60); high n_d and ν_d simultaneously or with high n_d and low ν_d; with a special course of partial dispersion; with reduced density ρ; transparency in the UV region; low T_g value, etc.

Today the development of high refractive index glasses is one of the most demanded tasks in the entire sector of optical instrumentation. The high refractive power of glass can be used not only to minimize spherical and chromatic aberration, but also to reduce the size of lens systems and the number of used components.

Lanthanum oxide containing glasses are widely used in optical materials science, since high values of the refractive index and dispersion are well combined with their manufacturability, with the possibility of obtaining optically homogeneous blanks. However, their potential is far from being exhausted, since La_2O_3 can enter in large amounts (>25 mol.%) into the composition of many glasses of silicate, aluminosilicate, borate, aluminoborate, phosphate, and germanate systems. But systematic studies of glass formation have been carried out only for a very narrow range of compositions.

The purpose of the research work is to identify the structural features and related possibilities for the synthesis of glasses with a high content of lanthanum oxide, to establish concentration limits that allow to obtain glasses of optical quality, and to expand the range of technological optical glasses with a high refractive index $n_d \approx 1.75–1.95$; dispersion coefficient $\nu_d \geq 30$ in combination with a density of less than 5 g/cm^3, and to confirm their applicability as materials for optical instrumentation.

Achievement of this purpose is ensured by the following key **tasks**:

1. Determination of the regions of stable glass formation in the systems La_2O_3–Al_2O_3–B_2O_3–SiO_2 (LABS) and La_2O_3–Nb_2O_5–B_2O_3 (LNB) with a high content of lanthanum oxide;
2. Study of the near atomic environment in LNB glasses near La and Nb atoms by XANES and EXAFS X-ray absorption spectroscopy;
3. Search for promising matrix compositions for the introduction of modifying additives Nb_2O_5, BaO, Ga_2O_3, TiO_2, ZrO_2, Ta_2O_5, CaO, ZnO in amounts at which it is possible to obtain optically homogeneous glasses with a high refractive index ($n_d \geq 1.95$);
4. Study of the influence of the nature and content of modifying additives on the structure and basic physical and chemical properties of the studied glasses;
5. Development of a laboratory technology for melting, manufacturing and annealing multicomponent high refractive index LABS glasses, which makes it possible to obtain glasses of optical quality;
6. Determination of the optimal parameters of laser modification for the formation of stable waveguide structures in the volume of multicomponent high refractive index glass.

Scientific novelty. The regions of glass formation in the 4-component LABS system with a high content of lanthanum oxide (27 mol.%) and the ternary LNB system were determined. The composition areas were determined as promising for subsequent modification in order to achieve high refractive indices and optimal technological parameters of synthesis.

The XANES and EXAFS methods were used to determine the bond lengths and coordination numbers (CNs) for oxygen of the main structural units of LNB glasses. The stability of the short-range order near Nb atoms was proved based on distorted NbO_6 octahedra, predominantly connected by vertices, and an increase in the CNs of La atoms from ~7 to ~10 with an increase in the content of Nb_2O_5 in the range of 5–30 mol.%, which provides an acceptable glass-forming ability of melts with a low content of B_2O_3.

The optimal parameters of femtosecond laser radiation are determined to ensure the stable formation of structures in the volume of multicomponent high refractive index glass based on the LABS system with a local change in the refractive index $\Delta n = -5 \times 10^{-3}$. This confirms the possibility of recording optical waveguides in the volume of these glasses.

Theoretical and practical significance of the work. By modifying the original LABS and LBN matrices, multicomponent glasses with refractive indices n_d = 1.81–2.04 and a density of no more than 4.8 g/cm^3 have been developed, which can be successfully synthesized under miniaturized production conditions to obtain optical quality blanks.

An experimental laboratory technology for obtaining multicomponent high refractive index glasses of optical quality based on the LABS system has been developed and successfully tested. The technology allows to obtain glass of the 2nd category of looseness and 2nd category of blistering with a glass melting crucible volume of 300 ml at a maximum melting temperature of no more than 1450 °C.

Models of the short-range order structure for high refractive index lanthanum-containing glasses are proposed. They provide the possibility to predict glass formation processes, which can be used in the development of new optical glasses.

The main provisions for the defense.

1. Results of determination of glass formation regions in LABS and LNB systems and principles for selecting promising compositions for modification.

2. Results of modifying the composition of the initial LABS and LBN matrices and the development of multicomponent glasses based on them with refractive indices n_d = 1.81–2.04, which can be implemented under industrial conditions.

3. Analysis results of the structure of glasses in the LNB system, which made it possible to describe the short-range order around the atoms of lanthanum and niobium and, thereby, to clarify the increased glass-forming ability of the compositions in the LNB system in the case of a high content of non-glass-forming components.

4. Laboratory technology for obtaining multicomponent high refractive index glasses based on the LABS system, which makes it possible to obtain optically homogeneous glass (weighing up to 1 kg) in a glass melting crucible with a volume of 300 ml.

5. Results of femtosecond laser micromodification in the volume of multicomponent high refractive index glass of the LABS system, which ensures the formation of stable waveguide structures.

6. Models of the short-range order structure of high refractive index lanthanum-containing glasses.