INTRODUCTION

Investigations of mixed alkali phosphates are associated with the solution of the fundamental problem of modern materials science, i.e., the design of new vitreous and glass-ceramic materials with a wide range of controlled properties. For example, new composite materials with high elastic moduli, increased strength, low volume thermal expansion coefficients, low thermal conductivity, and good heat stability and moisture resistance have been developed using alkali zinc phosphates [1]. Alkali zinc diphosphate glasses have an especially high chemical durability and low glass transition temperatures ($T_g$).

In order to elucidate the factors responsible for these valuable characteristics of the above materials, it is expedient to investigate the crystal structures of compounds formed in the Me$_2$O–ZnO–P$_2$O$_5$ system and to establish their interrelations with the corresponding vitreous diphosphates.

The crystal structures of some alkali zinc diphosphates are described in [2–9]. They can be assigned to compounds with heterovalent cations condensed in the form of layers or three-dimensional frameworks. In this case, the [PO$_4$]$^{3-}$ and [ZnO$_4$]$^{6-}$ tetrahedra serve as the main building blocks. A nonuniform charge distribution in the structure and the presence of channels and holes in the anion make these compounds promising in the search for new solid materials for nonlinear optics and electrical engineering. High-temperature X-ray diffraction studies have revealed that the majority of the compounds under investigation are characterized by a strong anisotropy of thermal expansion [10].

This paper reports on the results of the determination of the crystal structure of the Li$_{12}$Zn$_4$(P$_2$O$_7$)$_5$ compound. This compound was synthesized for the first time when studying the phase relationships in the Zn$_2$P$_2$O$_7$–Li$_4$P$_2$O$_7$ system [11]. According to the phase diagram of the above system, the Li$_{12}$Zn$_4$(P$_2$O$_7$)$_5$ compound exists in two polymorphic modifications with a reversible-transition temperature of 640°C and an incongruent-melting temperature of 720°C [11, 12]. The refractive indices of the low-temperature ($\alpha$) modification are as follows: $n_g = 1.560$ and $n_p = 1.548$ (the birefringence is equal to 0.012). According to the preliminary data [10], the Li$_{12}$Zn$_4$(P$_2$O$_7$)$_5$ compound up to a temperature of 600°C is indexed in the orthorhombic crystal system. However, it has been revealed that the heating of a sample above 300°C leads to a change in the intensities of lines in diffraction patterns and an abrupt change in the thermal expansion coefficient, which indicates that the ion conductivity can appear in this compound.

SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Synthesis

The Li$_{12}$Zn$_4$(P$_2$O$_7$)$_5$ compound was synthesized from the following reactants: NH$_4$(H$_2$PO$_4$) (special-purity grade), Li$_2$CO$_3$ (reagent grade), and ZnO (reagent grade). In order to prevent the formation of impurity phases, the synthesis was performed in several stages. Initially, the Zn$_2$P$_2$O$_7$ compound was synthesized by the solid-phase reaction between ZnO and NH$_4$(H$_2$PO$_4$) and the Li$_4$P$_2$O$_7$ compound was prepared from Li$_2$CO$_3$ and NH$_4$(H$_2$PO$_4$). The reactants in the form of powders were mixed in a stoichiometric ratio in alcohol, dried, and pelletized. Annealing of the prepared samples was repeatedly performed in sev-
eral stages in the temperature range from 400 to 800°C with intermediate grinding of the cakes between annealings to their complete homogenization. The synthesized samples were identified using X-ray powder diffraction analysis by comparing their interplanar distances with those listed in the ICDD database for Zn$_2$P$_2$O$_7$ and Li$_4$P$_2$O$_7$.

Then, the mixture of Zn$_2$P$_2$O$_7$ and Li$_4$P$_2$O$_7$ prepared by the above procedure was annealed at a temperature of 600°C for 20 h. The X-ray diffraction and crystal optical data for the prepared sample corresponded to the low-temperature modification of the Li$_{12}$Zn$_4$(P$_2$O$_7$)$_5$ compound [11, 12].

**X-Ray Diffraction Analysis**

The structure of the α-Li$_{12}$Zn$_4$(P$_2$O$_7$)$_5$ modification was determined using a polycrystalline sample. The X-ray diffraction pattern of the compound under investigation was recorded on a Siemens D-500 X-ray powder diffractometer (CuK$_α$ radiation; X-ray tube; operating voltage, 40 kV; operating current, 30 mA; 2θ$_{\text{min}}$, 10°; 2θ$_{\text{max}}$, 80°; scan step 2θ, 0.02°; exposure time per point, 40 s; scintillation counter). The highest intensity of the peak in the X-ray diffraction pattern amounted to ~155000 counts.

The X-ray diffraction pattern was indexed with the Bail program [13]. The best indexing results were obtained for the orthorhombic crystal system and the unit cell parameters $a = 5.145(1)$ Å, $b = 13.454(2)$ Å, and $c = 8.186(1)$ Å, which are close to the unit cell parameters of the monoclinic phase of lithium diphosphate Li$_4$P$_2$O$_7$ (ICSD no. 39814, space group $P2_1/n$, $Z = 4$, $a = 5.190(2)$ Å, $b = 13.902(3)$ Å, $c = 7.901(3)$ Å, $β = 89.97(3)^\circ$ [14]). This circumstance indicated that these compounds can be structurally similar to each other. Moreover, the analysis of the phase diagram of the Zn$_2$P$_2$O$_7$–Li$_4$P$_2$O$_7$ system [11] demonstrated that the prepared compound lies in the concentration region that is close to the region of Li$_{4(1-x)}$Zn$_{2x}$P$_2$O$_7$ solid solutions ($0 \leq x \leq 0.35$) based on Li$_4$P$_2$O$_7$, even though there is a miscibility gap between them. In accordance with the aforesaid, the lithium diphosphate structure was taken as the initial model for the refinement of the structure under investigation by the Rietveld method (with the SIMREF 2.5 program [15]). After the refinement of the structure, we obtained the following unit cell parameters: $a = 5.130(1)$ Å, $b = 13.454(1)$ Å, $c = 8.205(1)$ Å, $β = 90.36(1)^\circ$, space group $P2_1/n$, and $Z = 4$.

Figure 1 shows the experimental, calculated (after the structure refinement), and difference X-ray powder diffraction patterns. Figure 2 presents the projection of the structure of the α-Li$_{12}$Zn$_4$(P$_2$O$_7$)$_5$ compound along the $a$ axis. The results of the refinement are given in Table 1. The atomic positions are presented in Table 2. The selected bond lengths and bond angles are listed in Table 3.

**DISCUSSION OF THE RESULTS**

It can be seen from Fig. 2 that, in the structure of the α-Li$_{12}$Zn$_4$(P$_2$O$_7$)$_5$ compound, there are layers that are formed by diphosphate groups, separated by the distance 1/2 $c$ from one another, and perpendicular to the $c$ axis. The neighboring layers are related by the