INTRODUCTION

The continuing demand in technology for new effective nonlinear-optical and lasing materials is stimulating the further synthesis of noncentrosymmetric crystals in complex borate systems with rare earth elements and the study of their structures and properties. Some promising dehydrated rare earth borates have already been discovered in these systems [1, 2]. At present, only three aqueous borates are known—mineral braitshite (complicated calcium- and borate) with unknown structure [3], synthetic LiNd [B$_6$O$_9$(OH)$_3$] crystals [4], and recently synthesized and studied Ln[B$_4$O$_6$(OH)$_3$]Cl (Ln = Pr, Nd) borates [5] showing high optical nonlinearity. Below, we describe the study of the structure and dielectric and nonlinear optical properties of Ho and Gd borates (denoted as I and II, respectively).

SYNTHESIS OF CRYSTALS AND THEIR PROPERTIES

Single crystals of new Ln borates were obtained during the study of phase formation in Ln$_2$O$_3$−B$_2$O$_3$−H$_2$O systems (Ln = Sm, Eu, Gd, Ho, Tm, Yb, and Lu). The experiments were performed in standard 5–6-cm$^3$-large Teflon-futerated autoclaves. The synthesis parameters were $t = 270–280^\circ$C, $P = 70$ atm; the lowest temperature was limited by the kinetics of the hydrothermal reaction, and the highest temperature, by the apparatus used. The experiment duration (18–20 days) was selected to ensure the reaction completion. The filling coefficient of the autoclave was selected in such a way as to maintain a constant pressure during the whole experiment. The weight ratio of the oxides was Ln$_2$O$_3$ : B$_2$O$_3$ = 1 : 1. The mineralizers were Cl$^-$ and CO$_3^{2-}$ ions. The highest transparency was recorded for 4-mm-long pale yellow or colorless Ho- and Gd-containing crystals with a cubic habit.

The diffraction patterns of all the phases with the Ln elements indicated above were identical and had no analogues in the PDF database, which allowed us to consider these crystals as new crystals. To determine the composition of crystals I, qualitative X-ray spectral analysis of the crystals was performed on a CAMSCAN 4DV scanning electron microscope with an attachment for energy-dispersive analysis (LINK Co.) at the Department of Petrography of the Geology Faculty of Moscow State University. The presence of Ho atoms in crystals I indicated the formation of a new borate, whereas the phases isostructural to this borate were borates containing the elements from the middle and end parts of the Ln series.

The powder samples were tested for noncentrosymmetry by the method of second harmonic generation. The measurements on I and II crystals performed with the use of the pulsed Nd-activated YAG laser (backscattering scheme) [6] showed that, depending on the powder dispersion, the second-harmonic yield ranged within one to three and five to ten units of the quartz standard for crystals I and II, respectively. This uniquely indicated the absence of center of inversion in the structure. A more pronounced signal from crystals II in comparison with that from crystals I correlates with a higher transparency of crystals II in the green range of the spectrum at the wavelength of the second...
harmonic, $\lambda_{2\omega} = 0.532 \mu m$. The comparable intensities of the second-harmonic generation obtained on very fine powders of compounds I and II and on a quartz powder with the same dispersion (3–5 $\mu m$) allows us to state that the effective optical nonlinearity of newly synthesized borates is close to the value of nonlinear state that the effective optical nonlinearity of newly activated Y AG laser radiation.

With an increase in temperature up to 300°C, the nonlinear optical activity of crystals I and II decreases, then attains a constant value, and, finally, at temperatures exceeding the critical temperature, $T_c$ (~610°C for I and 630°C for II), it irreversibly disappears (Fig. 1). Heating to the temperatures higher than $T_c$ results in crystal turbidity and cracking, i.e., in effects usually accompanying the decomposition of hydrated compounds.

The electrical conductivity was measured on a polycrystalline sample of compound II having the form of a dense intergrowth of randomly oriented small single crystals. The intergrowth was used to prepare a 2.1 $\times$ 2.4 $\times$ 0.8-mm-plate with large surfaces metallized at room temperature by the application of Degussa silver-containing paste. The electrical measurements were made in the temperature range 20–400°C using an E7–12 a.c. bridge at a frequency of 1 MHz. Grown crystals I showed an elevated conductivity of the order of $10^{-6}$ S/cm characteristic of numerous ionic and, in particular, protonic conductors. An important fact is that crystals I showed elevated conductivity in the above temperature range only after the first cycle of heating (Fig. 2). The following heating–cooling cycles did not result in such a high conductivity in the low-temperature range, but the conductivity was preserved above 300°C. The temperature dependence of conductivity was similar to the temperature dependence characteristic of ionic conductors with low activation energies (~0.2 eV).

STRUCTURAL STUDY

The parameters of as-grown I and II crystals were determined and refined on a Syntex P-1 diffractometer ($\lambda$MoK$_\alpha$, graphite monochromator). Of all the possible vectors, we chose three mutually perpendicular vectors with the length ~11.9 Å corresponding to a possible cubic unit cell. The refinement of angles showed that the differences between the $a$, $b$, and $c$ values exceed the standard deviations and that the angles between the vectors considerably differ from 90° (in tenths of a degree), which indicates the pseudocubicity of the crystals and that the true symmetry of the crystals is lower than cubic (hexagonal, orthorhombic, or, probably, monoclinic). In experiments with an Sm-containing crystal, its habit corresponded to a half-cube with a fused base and the body diagonal being parallel to the threefold axis. This brought us to the assumption that the lattice has a trigonal distortion. Single crystal I selected for the diffraction experiment also corresponded to a half-cube with the edge ~0.125 mm. A single crystal of compound II was selected for the diffraction experiment under a polarization microscope, where most of the crystals examined showed a twin boundary along the diagonal of the cube face. The dimensions of the selected crystal having the appropriate quality and the shape of a flattened cube were ~0.175 $\times$ 0.175 $\times$ 0.1 mm. In the pseudocubic $F$ lattice of crystals I and II, some vectors corresponded to the