INTRODUCTION

In our previous study [1], we considered possible mechanisms of structural transitions in undoped lanthanum manganite. The emphasis was on the transitions from the rhombohedral modification to the orthorhombic phases \( \text{Pnma}^I \) and \( \text{Pnma}^II \) with a change in the oxygen concentration. A two-step scheme of the noted diffusionless transitions through a virtual cubic configuration (\( \text{mmm} \)) was discussed. In addition, it was noted that the experimental investigation of the structural processes occurring with a decrease in temperature had begun.

The subject of this study is the evolution of the basic rhombohedral structure of the \( \text{LaMnO}_3 + \delta \) compound having a specified constant oxygen concentration with a decrease in temperature.

EXPERIMENTAL

The technique of preparation of powder samples of oxides of specified composition was described in [2]. The excess of oxygen \( \delta \) (or the ratio of \( \text{Mn}^{4+} \) and \( \text{Mn}^{3+} \) ions) was determined by either direct weighting or titration with potassium iodide. It was found that the value of \( \delta \) depends not only on the synthesis temperature and the type of gas atmosphere but also on the rate of sample cooling. The rhombohedral phase (sp. gr. \( R\bar{3}c \)) was obtained by cooling a sample from 1100°C at a rate of 10 K/h. The composition of the sample grown under these conditions was \( \text{LaMnO}_{3.13} \) (29.5 and 70.5% of \( \text{Mn}^{4+} \) and \( \text{Mn}^{3+} \) ions, respectively).

The X-ray diffraction analysis was performed on a SIEMENS D500 diffractometer (\( \text{CuK}_{\alpha} \) radiation); a continuous-flow liquid-helium cryostat, designed and fabricated at the Institute of Solid-State Physics of the Russian Academy of Sciences, served as a low-temperature attachment. The cryostat design ensures precise measurements of diffraction patterns in a wide angular range. The accessible temperature range is 4.2–300 K, the rate of sample cooling can be varied in a specified range, and a specified temperature is stabilized accurate to 0.1 K [3, 4]. The cryostat was installed on the goniometer of the X-ray diffractometer. The sample holder was mounted on a rod, which was installed in the cryostat well. In the working cell, powder samples were tightened up by a thin polyethylene film to retain a planar surface. (This amorphous film gave rise to a halo reflection at \( \sim 25^\circ \) in the diffraction patterns in Fig. 1.) Varying temperature step by step, we reached a specified temperature, after which a diffraction pattern was measured with thermal stabilization of the sample during the measurement.

The X-ray diffraction experiments were carried out in the temperature range 93.4–300 K in the cooling mode; the design of the measuring system also made it possible to use, when necessary, heating and thermal-cycling modes.

RESULTS AND DISCUSSION

The X-ray diffraction pattern of a powder sample of \( \text{LaMnO}_3 + \delta \) measured at room temperature is shown in Fig. 1a. Analysis shows that the diffraction lines at room temperature correspond to the rhombohedral phase with the lattice parameters \( a_{\text{rhom}} = 5.455 \) Å and \( \alpha = 60.74^\circ \). The diffraction pattern at 93.4 K is shown in Fig. 1b. The additional splitting of some lines (beginning with 200 K) is indicative of a decrease in the sym-
The most characteristic changes in the diffraction pattern were observed in the angle ranges near $2\theta = 32.5^\circ$ and $2\theta = 68^\circ$–$69^\circ$. Figure 2 shows as an example an additional reflection arising between the $(220)$ and $(422)$ peaks. The intensity of this reflection increases with a decrease in temperature. Heating a sample led, accordingly, to the disappearance of this line and the recovery of the initial pattern. This fact indicates that a reversible low-temperature phase transition occurs in lanthanum manganite crystals.

Table 1 contains the experimental and calculated data on the characteristic groups of lines in the X-ray diffraction patterns recorded at two temperatures according to Figs. 1a and 1b. To understand the genesis of crystalline modifications, we found it useful to add to Table 1 the calculated values of the positions of the lines corresponding to a “virtual” cubic phase ($Pm\bar{3}m$). The lattice constants of this perovskite configuration were calculated from the experimental data on the structures of other modifications. The relationship