ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 7, pp. 1434–1441. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © I.A. Zvereva, O.I. Silyukov, M.V. Chislov, 2011, published in Zhurnal Obshchei Khimii, 2011, Vol. 81, No. 7, pp. 1083–1091.

Ion-Exchange Reactions in the Structure of Perovskite-like Layered Oxides:
I. Protonation of $NaNdTiO_4$ Complex Oxide

I. A. Zvereva, O. I. Silyukov, and M. V. Chislov

St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia
e-mail: irinazvereva@yandex.ru

Received December 20, 2010

Abstract—The behavior of perovskite-like $NaNdTiO_4$ complex oxide in acid aqueous solutions was studied. By the X-ray and thermogravimetry analyses the instability of $NaNdTiO_4$ in aqueous solutions was found, which is determined by the sodium cation exchange for protons and by water molecules intercalation into the interlayer space of the crystal structure. The proton-containing layered oxides $HNdTiO_4$ and $H_xNa_{1-x}NdTiO_4 \cdot yH_2O$ were obtained ($1 < x < 0.64$, $0 < y < 0.47$). The structure of the $H_{0.73}Na_{0.27}NdTiO_4 \cdot 0.3H_2O$ compound was refined.

DOI: 10.1134/S1070363211070061

From the moment of discovery up to now layered perovskite-like oxides have been the subject of rapt attention of researchers. The obtained compounds have such properties as catalytic activity, ionic conductivity, high-temperature superconductivity, and colossal magnetoresistance [1–5]. Materials based on layered oxides found commercial application in the chemical and electronic industries, and also in power engineering.

By now the procedures are developed for obtaining layered perovskite-like oxides with various composition and structure. The main method of preparation of these compounds is the high-temperature solid-phase synthesis. However the possibilities of this method are limited by thermodynamic stability of the compounds at high temperatures. A number of methods of so-called “mild chemistry” appears to be more adaptable and universal. These methods include a series of low-temperature chemical reactions: ion exchange in the crystal structure of perovskite-like layered oxides [6–8], topochemical condensation [8–11], intercalation [12–15], and splitting [16–18]. In the course of these processes the required compound can be obtained via a sequence of chemical transformations from precursors synthesized, as a rule, by a high-temperature procedure.

The main method of low-temperature solid-phase synthesis of layered perovskite-like oxides is ion-exchange reactions. The first ion exchange reactions were carried out with the compounds falling in the class of Dion–Jakobson phases [19]. In these compounds large cations Cs^+, Rb^+, and K^+ occupying sites in the layers located between blocks with perovskite structure were replaced by smaller cations Na^+, Li^+, NH_4^+, and Tl^+. Such reactions were carried out in nitrate melts [20–23], and with their help it was possible to obtain compounds instable under conditions of high-temperature synthesis. Aside from single-charged cation substitution, an exchange for a double-charged cation is possible [24, 25], and also substitution for protons in solutions of acids [14, 15, 20].

Ruddlesden-Popper phases [26] also can take part in ion-exchange reactions. In these phases, as in the case of Dion–Jakobson phases, interlayer cations of alkali metals (K^+ and Rb^+) can be replaced by smaller cations (Na^+, Li^+, NH_4^+, and Ag^+) in the salt melts [25, 27–30] and in acid solutions by protons [20, 32–34]. The ion exchange of an alkali cation for a double-charged cation of an alkaline-earth element in Ruddlesden Popper phases occurs essentially easier than in Dion–Jakobson phases [31]. There is also a possibility of other, more complex structural units, such as $Bi_2O_2^{2+}$ and $PbBiO_2^{2+}$ [35], VO^{2+} [36], CuX^+ and FeX^+ (X is a halogen) [37] substitution for interlayer cations of Ruddlesden-Popper and Dion–Jakobson phases.

In the case of Aurivillius phases the ion exchange reactions with the retention of the structural type are not known. The ion exchange in Aurivillius phases resembles reactions of acid decomposition. For example, Sugimoto et al. [7, 38] transformed an Aurivillius phase into a protonated form of Ruddlesden-Popper phases by dissolving interlayer bismuth oxide in an acid without touching the layers with perovskite structure.

The interlayer space of some layered oxides can include molecules of organic and inorganic substances, which results in a possibility of intercalation. The most typical are the reactions of penetration of organic amines [14, 18] and water molecules [35, 39] into the interlayer space. Whereas alkali and especially protonated forms of the majority of Dion–Jakobson phases are easily intercalated with organic bases and water molecules, the compounds with the structure of Ruddlesden–Popper phases often do not show such properties [14].

The substitution of proton for metal cations in the interlayer space is of special interest, and protonated forms of layered perovskite-like oxides attract attention of the researchers for a long time. This is associated with a number of unique physical and chemical properties shown by hydrogen-substituted analogs of layered oxides. For example, aside from participating in ion exchange [12, 40] and intercalation reactions [12, 41], they show proton-conducting properties [42], photocatalytic activity [43], and can be split to give perovskite monolayers [18] and undergo topochemical dehydration [10, 11]. However, such solid acids are primarily used as precursors for low-temperature ion-exchange reactions. For example, Schaak et al. [44] report on the transformation of hydrogen-substituted forms of Ruddlesden-Popper phases $HLnTiO_4$ (Ln = La, Nd, Sm, Eu, Gd, Dy) into alkali forms $ALnTiO_4$ (A = K, Li). Similar transformations can be carried out with other protonated forms of layered oxides [41, 45]. The cases of obtaining both completely and partially substituted compounds depending on the starting compound chosen and pH of the medium have been described in the literature [13].

This paper opens a series of works on the study of ion-exchange reactions occurring in the crystal structure of solid samples of layered oxides belonging to various classes of perovskite-like layered phases. In this work we give the results of studying the processes occurring in water and in acid aqueous solutions with the simplest (from the point of view of structural type) layered $NaNdTiO_4$ oxide. The urgency of this study is due, first, to the prospects of using layered oxides as catalysts of chemical processes in aqueous medium, since the stability of a catalyst is an important characteristic defining the possibility of its application to a particular catalytic system, and second, with the possibility of using $NaNdTiO_4$ as a precursor for obtaining new compounds by the low-temperature solid-phase synthesis.

In the structure of the $NaNdTiO_4$ oxide which belongs to Ruddlesden-Popper phases, there is a complete ordering of Na^+ and Nd^{+3} cations owing to essential differences in sizes and charges (Fig. 1a). It is the complete ordering of cations of alkali and rare earth elements with different charges which distinguishes $ALnTiO_4$ compounds from alkaline earth compounds, in which only a local ordering of cations takes place, as for example, in the $CaLnAlO_4$ and $SrLnAlO_4$ aluminates [46, 47], or a partial positional ordering of Sr^{+2} and Ln^{+3} atoms in the $SrLn_2Al_2O_7$ structure [48–50]. The Na^+ cations in the structure of $NaNdTiO_4$ are bound to the perovskite layers weaker and have a substantial mobility, which defines high ionic conductivity and ion exchange activity of $NaNdTiO_4$ [51–53].

In this work we studied the ion-exchange reactions occurring in the crystal structure of the complex oxide $NaNdTiO_4$ submerged into aqueous solution. We used the methods of X-ray, thermogravimetric analysis, and ionometry. The $NaNdTiO_4$ oxide was obtained by high-temperature solid-phase synthesis under conditions found earlier when studying the mechanism of its formation and its thermal stability [54, 55]. We studied possible changes in the morphology of complex-oxide particles resulting from ion-exchange processes with the help of scanning electron microscopy.

The ion exchange in the crystal structure of $NaNdTiO_4$ occurred in a suspension in distilled water (1 mmol of $NaNdTiO_4$ in 100 ml of water), and also on adding hydrochloric acid (1 mmol of $NaNdTiO_4$ in 100 ml of a solution containing 0.2–1 mmol of HCl). The suspension of $NaNdTiO_4$ in water was found to have an alkaline reaction. The pH of the solution attains 11.5 within several seconds and 11.7 in 5 min, which corresponds to almost 50% substitution of H^+ for Na^+ ions. The substitution of protons for sodium ions is also confirmed by pNa of 2.26 for the obtained

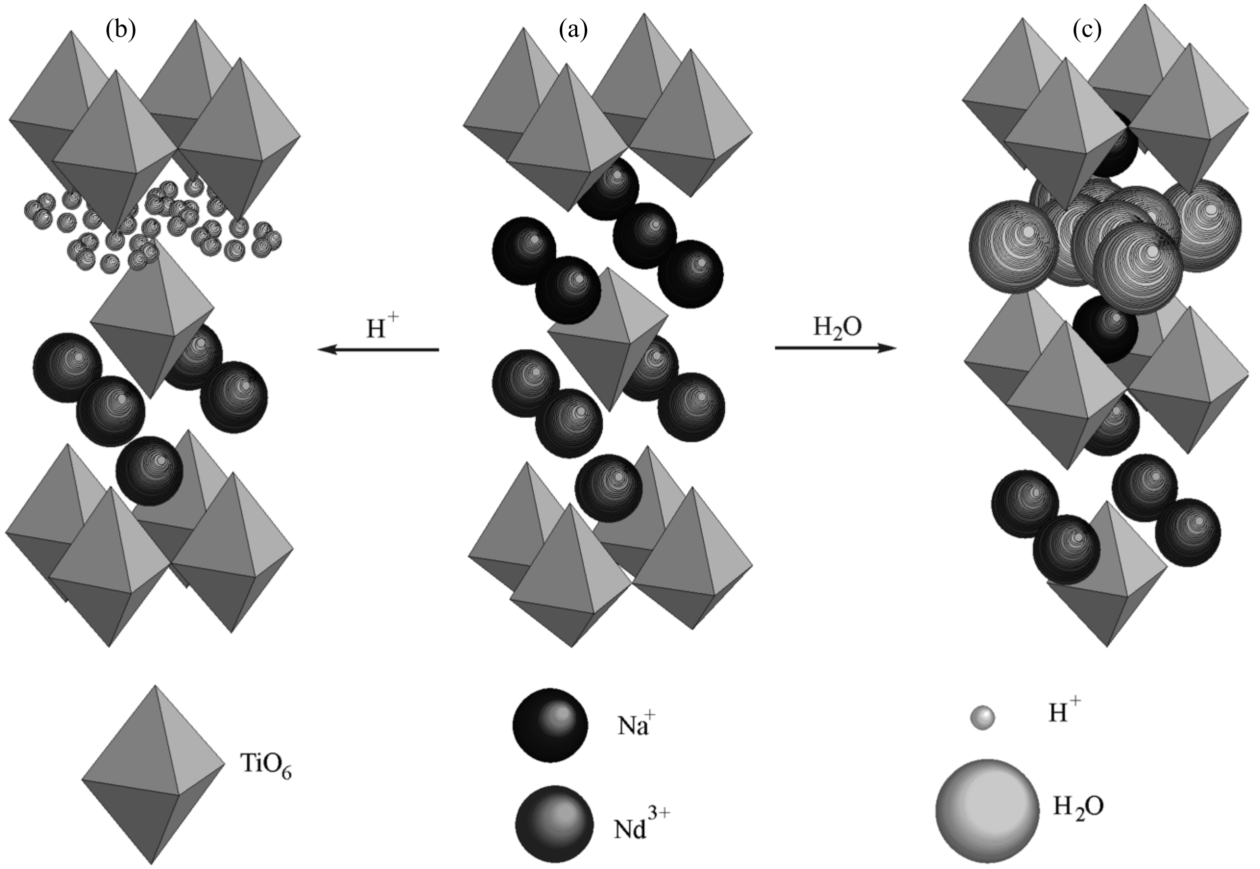

Fig. 1. Fragments of (a) $NaNdTiO_4$, (b) $HNdTiO_4$, and (c) $H_{0.73}Na_{0.27}NdTiO_4·0.3H_2O$ structures. (Location of protons in $HNdTiO_4$ is taken from [56]).

suspension. The pH 11.78 of the filtrate obtained after a week exposure of $NaNdTiO_4$ in water corresponded to the substitution degree of 60%.

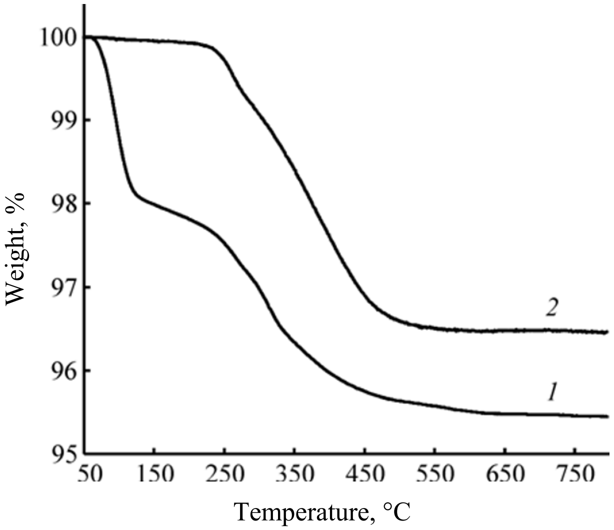

Fig. 2. Curves of thermogravimetric analysis of $NaNdTiO_4$ maintained in water [(*1*) $H_{0.73}Na_{0.27}NdTiO_4·0.3H_2O$) compared to (*2*) $NaNdTiO_4$].

The results of thermogravimetric analysis allowed us to determine the degree of proton substitution for sodium cations with a higher accuracy. The weight-loss curves are given in Fig. 2 for the sample stored in water for 7 day (curve *1*). As follows from the thermogram of this sample, the weight loss occurs in the temperature ranges of 70–130°C and 230–500°C. The weight loss in the 230–500°C range is assignable to the decomposition of the substituted compound, as this temperature range coincides with the decomposition temperature of the completely protonated $HNdTiO_4$ oxide (curve *2*). Accordingly, we assigned the weight loss in the 70–130°C range to the release of water sorbed in the interlayer space of the $NaNdTiO_4$ oxide crystal structure. These conclusions are confirmed by the data of the X-ray and differential thermal analyses.

The decomposition of $Na_{1–x}H_xNdTiO_4·yH_2O$ can be represented conventionally by scheme (1):

$$Na_{1-x}H_xNdTiO_4·yH_2O \rightarrow Na_{1-x}H_xNdTiO_{4-0.5x} + (x/2)\,H_2O\uparrow + yH_2O\uparrow. \quad (1)$$

Table 1. Degree of substitution (x), amount of intercalated water (y), and unit cell parameters (a, c, Å) of $Na_{1-x}H_xNdTiO_4\cdot yH_2O$ of samples obtained from $NaNdNiO_4$ under various conditions (in water or in acid solutions) compared to the parameters of the $NaNdNiO_4$ and $HNdNiO_4$ compounds

Sample	Solution volume, ml	Amount of HCl, mmol	pH of the filtrate	Space group	*a*	*c*
$NaNdTiO_4$	–	–	–	*P*4/*nmm*	3.7895	13.014
$H_{0.73}Na_{0.27}NdTiO_4\cdot 0.3H_2O$	100	0	11.8	*I*4/*mmm*	3.7359	27.684
$H_{0.73}Na_{0.27}NdTiO_4$[a]	–	–	–	*P*4/*nmm*	3.7084	12.601
$H_{0.64}Na_{0.36}NdTiO_4\cdot 0.43H_2O$	100	0.2	11.5	*I*4/*mmm*	3.7381	27.810
$H_{0.7}Na_{0.3}NdTiO_4\cdot 0.47H_2O$	100	0.4	11.2	*I*4/*mmm*	3.7385	27.811
$H_{0.66}Na_{0.34}NdTiO_4\cdot 0.43H_2O$	100	0.6	9.7	*I*4/*mmm*	3.7384	27.811
$H_{0.85}Na_{0.15}NdTiO_4\cdot 0.21H_2O$	100	0.8	6.47	*P*4/*nmm*	3.7223	12.957
$H_{0.99}Na_{0.01}NdTiO_4\cdot 0.06H_2O$	100	1	5.67	*P*4/*nmm*	3.7124	12.530
$HNdTiO_4$	–	–	–	*P*4/*nmm*	3.7088	12.262

[a] Product of dehydration of the $H_{0.73}Na_{0.27}NdTiO_4\cdot 0.3H_2O$ compound.

The decrease (2) in the weight of the sample under study occurs at the expense of the release of intercalated water and the removal of water resulting from the decomposition of the proton-containing compound.

$$m[Na_{1-x}NdTiO_{4-0.5x}]/m[(x/2)H_2O] = F$$

$$= \frac{A(\mathrm{Nd}) + A(\mathrm{Ti}) + A(\mathrm{Na})\cdot(1-x) + A(\mathrm{O})\cdot(4-0.5x)}{(x/2)M(\mathrm{H_2O})}. \quad (2)$$

The content of sodium ions in the substance remaining after complete water release depends on the degree of substitution in the sample under study. The dependence between the degree of substitution, x, and the weight loss in the second section of the curve can be expressed by expression (3).

$$x = \frac{2A(\mathrm{Nd}) + 2A(\mathrm{Ti}) + 8A(\mathrm{O}) + 2A(\mathrm{Na})}{F\cdot M(\mathrm{H_2O}) + 2A(\mathrm{Na}) + A(\mathrm{O})}. \quad (3)$$

Here m is the weight of the substance, M and A are molecular and atomic weights, respectively, the F parameter is the ratio of the weight of the substance remaining after the complete water release to the water weight released during the decomposition of the substituted compound.

From expression (2) the degree of substitution, x, and the amount of intercalated water can be calculated by formulas (3) and (4).

$$y = x\cdot m[y\,\mathrm{H_2O}]/2m[(x/2)\,\mathrm{H_2O}]. \quad (4)$$

The values of the degree of substitution for sodium ions, x, and the amount of intercalated water, y, calculated from the results of thermogravimetric analysis for all $NaNdTiO_4$ samples stored in water or acid solutions are given in Table 1. For example, the degree of substitution for sodium ions in the sample obtained after storing $NaNdO_4$ in water calculated from the thermogravimetric analysis was 73%, the amount of intercalated water, 0.3 mol per 1 mol of Ti^{+4} ions. Then a rational formula of the compound resulted from ion exchange may be presented as $H_{0.73}Na_{0.27}NdTiO_4\cdot 0.3H_2O$.

The X-ray patterns of the hydrated $H_{0.73}Na_{0.27}NdTiO_4\cdot 0.3H_2O$ and unhydrated $H_{0.73}Na_{0.27}NdTiO_4$ compounds, and also of the $NaNdTiO_4$ and $HNdTiO_4$ oxides are given in Fig. 3. The reflexes of the unhydrated partially substituted $H_{0.73}Na_{0.27}NdTiO_4$ oxide are described in the *P*4/*nmm* space group with the unit cell parameters: $a = b = 3.7084$ and c 12.601 Å, whereas the hydrated $H_{0.73}Na_{0.27}NdTiO_4\cdot 0.3H_2O$ compound crystallizes in the *I*4/*mmm* space group with the parameters: $a = b = 3.7359$ and c 27.684 Å (Fig. 1c). This points to the fact that after removing water from interlayer space perovskite layers (octahedral network) are displaced by 1/2 a,b and the width of interlayer space decreases.

Calculated unit cell parameters of the compounds under study are given in Table 1. The increase in the

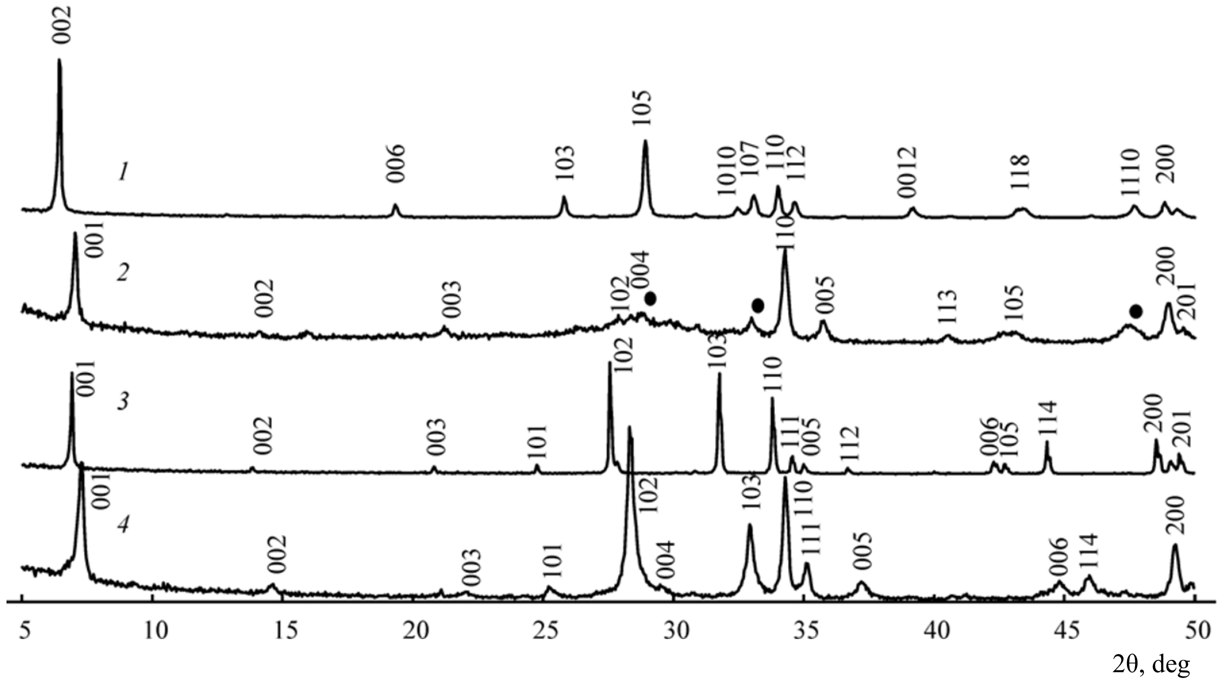

Fig. 3. X-ray patterns of (*1*) $H_{0.73}Na_{0.27}NdTiO_4 \cdot 0.3H_2O$, (*2*) $H_{0.73}Na_{0.27}NdTiO_4$, (*3*) $NaNdTiO_4$, and (*4*) $HNdTiO_4$.

c parameter of the lattice in the obtained compound compared to starting $NaNdTiO_4$ points to a widening of interlayer space resulting from intercalation of water molecules. This assumption was checked by sintering an $H_{0.73}Na_{0.27}NdTiO_4 \cdot 0.3H_2O$ sample at 150°C for 1.5 h. In this process as the result of releasing intercalated interlayer water on heating a partially substituted $H_{0.73}Na_{0.27}NdTiO_4$ compound was obtained without water molecules in the interlayer space.

For the $H_{0.73}Na_{0.27}NdTiO_4 \cdot 0.3H_2O$ compound we have fulfilled the full-profile X-ray structural analysis and refined the coordinates of cations and oxygen anions including oxygen in the water molecule. However, it appears impossible to determine sites of protons from the data of powder X-ray diffraction. A more detailed study of the structure of protonated compounds is scheduled to carry out within the context of a neutron diffraction study. The results of structural calculations are given in Table 2. A widened unit cell of the $H_{0.73}Na_{0.27}NdTiO_4 \cdot 0.3H_2O$ compound is given in Fig. 1c. It can be seen that the intercalation of water is accompanied by a rearrangement of the structure with the shift of perovskite layers relative to each other.

The study of particle morphology of hydrated $H_{0.73}Na_{0.27}NdTiO_4 \cdot 0.3H_2O$ sample and $NaNdTiO_4$ and $HNdTiO_4$ oxides showed that the ion exchange and intercalation do not result in the macrostructure destruction. Particles of synthesized $NaNdTiO_4$ consist of crystals in the form of plates 100–300 nm thick and from 500 nm to 1.5 μm in width. For $H_{0.73}Na_{0.27}NdTiO_4 \cdot 0.3H_2O$ and $HNdTiO_4$ a similar anisotropic shape of crystals is preserved, which is typical for layered oxides as a whole (Fig. 4).

The examination of the degree of substitution and of the amount of intercalated water in compounds resulting from the $NaNdTIO_4$ reaction with water in an acid medium (Table 1) indicates that on adding no more than 0.6 mmol of HCl to a $NaNdTiO_4$ suspension (1 mmol per 100 ml) the amount of intercalated water in $H_xNa_{1-x}NdTiO_4 \cdot yH_2O$ compounds is almost the same, and the degrees of substitution of protons for sodium cations also coincide. In more acidic solutions a decrease in the amount of intercalated water is observed along with an increase in the substitution degree.

The data of powder X-ray diffraction showed the identity of the X-ray patterns of samples obtained on adding no more than 0.6 mmol of HCl to the $NaNdTiO_4$ suspension and of samples of $H_{0.73}Na_{0.27}NdTiO_4 \cdot 0.3H_2O$ obtained in the reaction of $NaNdTiO_4$ with water. For the samples obtained in more acidic solutions the unit cell *c* parameter decreases, which indicates a compression of interlayer space as the degree of H^+ substitution for Na^+ increases. The X-ray pattern of the sample in the most

Table 2. Population of structural sites (g), coordinates of atoms (*x, y, z*), thermal parameters *U* (Å^2) for layered $H_{0.73}Na_{0.27}NdTiO_4\cdot 0.3H_2O$ oxide (*I*4/*mmm*, *a* 3.7359(5) Å, *c* 27.684(4) Å, *R* 0.08, R_w 0.11)

Atom	Site	*g*	*x*	*y*	*z*	*U*
Na	4*e*	0.27(1)	0	0	0.423(3)	0.12(2)
Nd	4*e*	1	0	0	0.3001(1)	0.035(6)
Ti	4*e*	1	0	0	0.1249(2)	0.031(1)
O_1	4*e*	1	0	0	0.0551(7)	0.102(7)
O_2	8*g*	1	0	0.5	0.1392(3)	0.038(3)
O_3	4*e*	1	0	0	0.2048(9)	0.101(7)
O(water)	8*j*	0.31(1)	0.39(2)	0.5	0	0.51(2)

acidic of the solutions under study (equivalent amounts of acid and oxide) almost completely coincides with the X-ray pattern of completely substituted anhydrous $HNdTiO_4$.

Therefore, the reaction of $NaNdTiO_4$ with water gives the following results depending on the acid content. In the acid medium with excess HCl a completely substituted $HNdTiO_4$ compound free from intercalated water is formed, which is proved by the fact that no weight loss occurs during the thermogravimetric analysis up to 250°C. This is in agreement with the published data for $HLnTiO_4$ compounds (Ln = La, Nd, Sm, Gd) obtained in a 0.1 N HNO_3 solution and sintered at 120°C [32]. The data of neutron diffraction of powders showed that $DLnTiO_4$ oxides containing La and Nd are crystallized in the *p*4/*nmm* group, and protons in the structure of these compounds statistically occupy sites in the interlayer space near axial oxygen atoms of the octahedral surrounding of titanium atoms [56], as shown in Fig. 1b.

In the neutral and weakly acid medium $NaNdTiO_4$ transforms into partially protonated $H_xNa_{1-x}NdTiO_4\cdot yH_2O$ compounds, in which along with the exchange of sodium ions for protons (the degree of substitution for sodium ions is more than 60%), intercalation of water into the interlayer space is also observed. Intercalated water in accordance with its amount occupies sites in the space between two layers containing Na^+ (Fig. 1c). Intercalated water is released from the samples on heating to 100–130°C, which results in a new phase of anhydrous partially substituted $H_xNa_{1-x}NdTiO_4\cdot yH_2O$ compound.

These results are close to the available published data for the La-containing $NaLaTiO_4$ compound [13], which was found to undergo the substitution of protons for sodium at pH < 2 (to give $HLaTiO_4$ at pH 1 and $H_{0.83}Na_{0.17}LaTiO_4$ at pH 2) and the substitution-intercalation at pH > 3 resulting in the $H_{0.34}Na_{0.66}LaTiO_4\cdot 0.59\,H_2O$ compound. However, in our opinion, the data of [13] on the weight loss in the of thermogravimetric plots given in the paper for $H_{0.34}Na_{0.66}LaTiO_4\cdot 0.59H_2O$ do not agree with the suggested formula, and, according to our calculations, the obtained compound has the formula close to $H_{0.7}Na_{0.3}LaTiO_4\cdot 0.5H_2O$, which is in better agreement with the data for the neodymium-containing $H_{0.7}Na_{0.3}NdTiO_4\cdot 0.47H_2O$ compound.

Therefore, in this study the ion-exchange properties of $NaNdTiO_4$ in aqueous solutions were studied using the methods of X-ray phase analysis and thermogravimetric analysis. Instability of the layered $NaNdTiO_4$ oxide in aqueous solutions was found. By ion exchange of sodium ions for hydrogen atoms in the $NaNdTiO_4$ matrix layered proton containing perovskite-like $HNdTiO_4$ and $H_{0.73}Na_{0.27}NdTiO_4\cdot 0.3H_2O$ oxides and also a series of $H_xNa_{1-x}NdTiO_4\cdot$

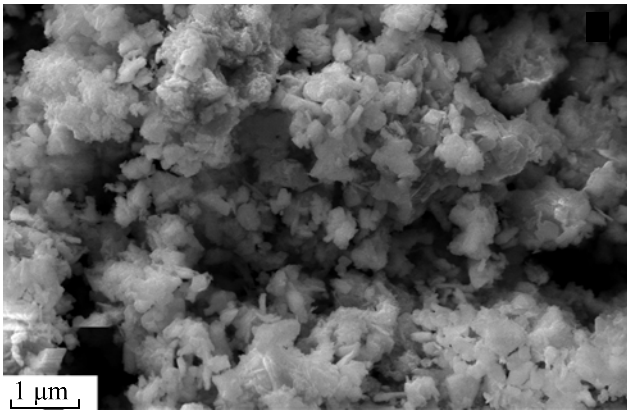

Fig. 4. Electron microphotograph of $NaNdTiO_4$ particles.

yH$_2$O compounds with the parameters: $1 < x < 0.64$, $0 < y < 0.47$ were obtained.

The study showed that more detailed information is required on the ion exchange for a wide series of layered compounds depending on their cation composition and the type of layered structure. The lack of such information will be compensated in the following studies.

EXPERIMENTAL

We synthesized the NaNdTiO$_4$ oxide by ceramic technique in air at atmospheric pressure. As the starting substances we used neodymium oxide Nd$_2$O$_3$ (containing 99.95% of the main component, previously sintered at 750°C for 3 h), finely dispersed TiO$_2$ (99.9%) in the anatase modification, and sodium carbonate Na$_2$CO$_3$, (99.5%). We carried out the synthesis from a stoichiometric mixture of the starting reagents.

$$Na_2CO_3 + 2TiO_2 + Nd_2O_3 \rightarrow 2NaNdTiO_4 + CO_2.$$

We thoroughly ground the reagents in an agate mortar, pressed the mixture into pellets of 0.5 g in weight and 0.7 cm in diameter. The mixture was sintered in a Silit furnace in corundum crucibles for 3 h at 780°C. The temperature regime was controlled by a platinum-rhodium thermocouple. The isothermal regime of the heat treatment was ensured accurate to ±1°C with the help of a TP 403 programmed heat controller.

We obtained the HNdTiO$_4$ compound by substituting H$^+$ for Na$^+$ in NaNdTiO$_4$ according to the reaction: NaNdTiO$_4$ + HCl → HNdTiO$_4$ + NaCl. With this aim we thoroughly ground NaNdTiO$_4$ in an agate mortar, put the obtained powder into a flask, and poured over a five-old excess of a 0.1 N solution of hydrochloric acid. We stirred the thus obtained suspension at room temperature for 24 h. Then we filtered off the substance and dried at room temperature in a desiccator above CaCl$_2$ for 24 h.

We studied the action of water on NaNdTiO$_4$ in a suspension with distilled water and also by adding various amounts of hydrochloric acid.

a. 0.279 g (1 mmol) of the substance was suspended in 100 ml of water. The obtained suspension was stirred at room temperature for a week.

b. 1 mmol of the substance was suspended in 100 ml of a solution containing 0.2, 0.4, 0.6, 0.8, or 1 mmol of HCl. Then we stirred the suspension at room temperature for 24 h. Changes in the cation composition of aqueous solutions were determined by an IPL-103 ionometer using H$^+$ and Na$^+$ selective ESL-43-07 and ESL-51-07 electrodes, respectively. The obtained samples were filtered off using cellulose-acetate filters and dried for 24 h in a desiccator above CaCl$_2$.

The control over the results of the synthesis and the study of the ion-exchange reactions in the solid samples were carried out by the methods of X-ray and thermogravimetric analyses. The X-ray study was carried out on an ARL XTRA powder diffractometer (CuK_α emission), the quantitative analysis of water sorption and of Na$^+$ substitution, on a Netzsch TG 209 F 1 Iris theromomicrobalance with the accuracy of 10^{-7} g.

We carried out the structural calculations (unit cell parameters, atom coordinates, occupation of structural sites) by the total profile of X-ray patterns with the refinement by Rietveld method using the GSAS program package [57]. The microphotographs of the samples were obtained on a Carl Zeiss EVO 40EP electron scanning microscope.

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for fundamental researche (grant no. 09-03-00853) and Federal target program “Scientific and scientific-pedagogical staff for innovation Russia” for 2009-2013 (contract no. P58).

REFERENCES

1. Rao, C.N.R. and Raveau, B., *Transition Metal Oxides: Structure, Properties, and Synthesis of Ceramic Oxides*, New York: Villey-VCH, 1998.
2. MacChesney, J.B., Potter, J.F. and Sherwood, R.C., *J. Appl. Phys*., 1969, vol. 40, p. 1243.
3. Moritomo, Y., Asamitsu, A., Kuwahara H., and Tokura, Y., *Nature,* 1996, vol. 380, p. 141.
4. Battle, P.D. and Rosseinsky, M.J., *Current Opinion in Solid State and Materials Science*, 1999, vol. 4, p. 163.
5. Battle, P.D., Green, M.A., Laskey, N.S., Millburn, J.E., Murphy, L., Rosseinsky, M.J., Sullivan, S.P., and Vente, J.F., *Chem. Mater*., 1997, vol. 9, p. 552.
6. Gopalakrishnan, J. and Bhatt, V., *Inorg. Chem*., 1987, vol. 26, p. 4299.
7. Sugimoto, W., Shirata, M., Sugahara, Y., and Kuroda, K., *J. Am. Chem. Soc*., 1999, vol. 121, p. 11601.
8. Ollivier, P.J. and Mallouk, T.E., *Chem. Mater*., 1998, vol. 10, p. 2585.
9. Schaak, R.E. and Mallouk, T.E., *J. Solid State Chem*., 2000, vol. 155, p. 46.

10. Thangadurai, V., Subbanna, G.N., and Gopalakrishnan, J., *J. Chem. Commun*., 1998, vol. 29, p. 1299.
11. Sivakumar, T., Lofland, S.E., Ramanujachary, K.V., Ramesha, K., Subbanna, G.N., and Gopalakrishnan, J.T., *J. Solid State Chem*., 2004, vol. 177, p. 2635.
12. Jacobson, A.J., Johnson, J.W., and Lewandowski, J.T., *Inorg. Chem*., 1985, vol. 24, p. 3727.
13. Nishimoto, S., Matsuda, M., and Miyake, M., *J. Solid State Chem*., 2005, vol. 178, p. 811.
14. Jacobson, A.J., Johnson, J.W., and Lewandowski, J.T., *Inorg. Chem*., 1985, vol. 24, p. 3727.
15. Uma, S. and Gopalakrishnan, J., *Chem. Mater*., 1994, vol. 6, p. 907.
16. Schaak, R.E. and Mallouk, T.E., *Chem. Mater*., 2000, vol. 2, p. 2513.
17. Chen, Y., Zhao, X., Mac, H., Maa, S., Huang, G., Makita, Y., Bai, X., and Yang, X., *J. Solid State Chem*., 2008, vol. 181, p. 1684.
18. Treacy, M.M.J., Rice, S.B., Jacobson, A.J., and Lewandouski, J.T., *Chem. Mater*., 1990, vol. 2, p. 279.
19. Dion, M., Ganne, M., and Tournoux, M., *Mater. Res. Bull*., 1981, vol. 16, p. 1429.
20. Richard, M., Brohan, L., and Tournoux, M., Abstract of Papers, *Soft Chemistry International Symposium*, 1994, vols. 152–153, p. 245.
21. Rouxel, J., Sato, M., Abo, J., and Jin, T., *Solid State Ionics*, 1992, vol. 57, p. 285.
22. Toda, K. and Sato, M., *Mater. Chem*., 1996, vol. 6, p. 1067.
23. Gopalakrishnan, J., Uma, S., and Bhat, V., *Chem. Mater*., 1993, vol. 5, p. 132.
24. Mahler, C.H., Cushing, B.L., Lalena, J.N., and Wiley, J.B., *Mater. Res. Bull*., 1998, vol. 33, p. 1581.
25. Cushing, B.L. and Wiley, J.B., *Mater. Res. Bull*., 1999, vol. 34, p. 271.
26. Ruddlesden, S.N. and Popper, P., *Acta Crystallogr*., 1957, vol. 10, p. 538.
27. Toda, K., Watanabe, J., and Sato, M., *Solid State Ionics*, 1996, vol. 90, p. 15.
28. Toda, K., Watanabe, J.,and Sato, M., *Mater. Res. Bull*., 1996, vol. 31, p. 1427.
29. Schaak, R.E., Afzal, D., and Mallouk, T.E., *Chem. Mater*., 2002, vol. 14, p. 442.
30. Schaak, R.E. and Mallouk, T.E., *J. Am. Chem. Soc*., 2000, vol. 122, p. 2798.
31. Hyeon, K. and Byeon, S., *Chem. Mater*., 1999, vol. 11, p. 352.
32. Byeon, S.-H., Park, K., and Itoh, M.J., *J. Solid State Chem*., 1996, vol. 121, p. 430.
33. Richard, M., Brohan, L., and Tournoux, M., *J. Solid State Chem*., 1994, vol. 112, p. 345.
34. Bhuvanesh, N.S.P. and Gopalakrishnan, J., *Inorg. Chem*., 1995, vol. 34, p. 3760.
35. Schleich, D.M., *Solid State Ionics*, 1994, vol. 70, p. 407.
36. Gopalakrishnan, J., Sivakumar, T., Ramesha, K., Thangadurai, V., and Subbanna, G.N., *J. Am. Chem. Soc*., 2000, vol. 122, p. 6237.
37. Kodenkandath, T.A., Lalena, J.N., Zhou, W.L., Carpenter, E.E., Sangregorio, C., Falster, A.U., Simons, W.B., O'Connor C.J., and Wiley, J.B., *J. Am. Chem. Soc*., 1999, vol. 121, p. 10743.
38. Tsunoda, Y., Shirata, M., Sugimoto, W., Liu, Z., Terasaki, O., Kuroda, K., and Sugahara, Y., *Inorg. Chem*., 2001, vol. 40, p. 5768.
39. Kinomura, N., Kumada, N.I., *Solid State Ionics*, 1992, vol. 51, p. 1.
40. Gopalakrishnan, J. and Bhat, V., *Mater. Res. Bull*., 1987, vol. 22, p. 769.
41. Nunes, L.M., de Cardoso, V.A., and Airoldi, C., *Mater. Res. Bull*., 2006, vol. 41, p. 1089.
42. Mangamma, G., Bhat, V., Gopalakrishnan, J., and Bhat, S.V., *Solid State Ionics*, 1992, vol. 58, p. 303.
43. Kim, Y.I., Salim, S., Huq, M.J., and Mallouk, T.E., *J. Am. Chem. Soc*., 1999, vol. 1113, p. 9561.
44. Schaak, R.E., and Mallouk, T.E., *J. Solid State Chem*., 2001, vol. 161, p. 225.
45. Schaak, R.E. and Mollouk, T.E., *Chem. Mater*., 2002, vol. 14, p. 1455.
46. Zvereva, I., Smirnov, Yr., and Choisnet, J., *Mater. Chem*. Phys., 1999, vol. 2466, no. 1, p. 63.
47. Smirnov, Yu.E. and Zvereva, I.A., *Zh. Obshch. Khim*., 2001, vol. 71, no. 6, p. 901.
48. Zvereva, I.A., Smirnov, Yu.E., Vagapov, D.A., and Choisnet, J., *Zh. Obshch. Khim*., 2000, vol. 70, no. 12, p. 1957.
49. Zvereva, I., Smirnov, Yu., Gusarov, V., Popova, V., and Choisnet, J., *Solid State Sciences*, 2003, vol. 5, no. 2, p. 343.
50. Zvereva, I., Smirnov, Yr., and Choisnet, J., *Int. J. Inorg. Mater*., 2001, vol. 3, no. 3, p. 95.
51. Byeon, S.-H., Yoon, J.-J., and Lee, S.-O., *J. Solid State Chem*., 1996, vol. 127, p. 119.
52. Toda, K., Kurita, S., and Sato, M.J., *Ceram. Soc. Japan*., 1996, vol. 104, p. 140.
53. Byeon, S.-H., Park, K., and Itoh, M.J., *J. Solid State Chem*., 1996, vol. 121, p. 430.
54. Zvereva, I.A., Silyukov, O.I., Markelov, A.V., Missyul', A.B., Chislov, M.V., Rodionov, I.A., and Liu, D.-Sh., *Phizika i Khimiya Stekla*, 2008, vol. 34, no. 6, p. 984.
55. Zvereva, I.A., Sankovich, A.M., and Missyul', A.B., *Zh. Obshch. Khim*., 2010, vol. 80, no. 7, p. 1076.
56. Nishimoto, S., Matsuda, M., Harjo, S., Hoshikawa, A., Kamiyama, T., Ishigaki, T., and Miyake, M., *J. Solid State Chem*., 2006, vol. 179, p. 1892.
57. Larson, A.C. and Von Dreele, R.B., *General Structure Analysis System (GSAS),* Los Alamos National Laboratory Report LAUR, 2000, p. 86.