Synthesis of a New Layered Rb$_2$Nd$_2$Ti$_3$O$_{10}$ Oxide, Its Hydration and Protonation

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Abstract—A new perovskite-like oxide (Rb$_2$Nd$_2$Ti$_3$O$_{10}$) is synthesized by the ceramic method. Its stability in a humid atmosphere and aqueous solutions of different acidities is investigated. Under these conditions, the formation of hydrated and protonated compounds is revealed. The parameters of the unit cell of the Rb$_2$Nd$_2$Ti$_3$O$_{10}$ oxide and its derivatives and the degree of rubidium substitution by protons for the obtained protonated phases are determined.

Keywords: layered oxide, titanate, hydration, protonation
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INTRODUCTION

Layered perovskite-like titanates A$_2$Ln$_2$Ti$_3$O$_{10}$ (A is an alkali metal and Ln is a lanthanide) attributed to the Ruddlesden–Popper phases are promising photocatalysts [1]. Their high level of photocatalytic activity in the reaction of water decomposition is often explained by the possibility of intercalating water molecules into the interlayer space, which is considered, along with the crystal surface, as the reaction zone [2, 3]. Along with the increase of the radius of the alkali cation A present in A$_2$Ln$_2$Ti$_3$O$_{10}$ titanates, their capacity for water intercalation and, simultaneously, photocatalytic activity increase [4]. Thus, there is special interest in studies of Rb-containing oxides. However, they have been studied insufficiently and only the Rb$_2$La$_2$Ti$_3$O$_{10}$ compound has been obtained and characterized [2, 5].

The objective of the present work is to synthesize a new layered oxide and to describe the processes occurring at its contact with a humid atmosphere and aqueous solutions of different acidities.

EXPERIMENTAL

The layered perovskite-like Rb$_2$Nd$_2$Ti$_3$O$_{10}$ oxide (RNTO) was synthesized in accordance with the ceramic technique under atmospheric pressure in air. The general reaction equation can be written in the form

$$\text{Rb}_2\text{CO}_3 + \text{Nd}_2\text{O}_3 + 3\text{TiO}_2 \rightarrow \text{Rb}_2\text{Nd}_2\text{Ti}_3\text{O}_{10} + \text{CO}_2 \uparrow .$$

(1)

The initial reagents (Rb$_2$CO$_3$ of a chemically pure grade, Nd$_2$O$_3$ of a chemically pure grade, and TiO$_2$ of a special purity grade) were preliminarily annealed to remove humidity traces (Rb$_2$CO$_3$ and TiO$_2$ at 500°C, and Nd$_2$O$_3$ at 900°C). The oxides were used in accordance with the stoichiometric reaction (1) and rubidium carbonate with a 40% excess to compensate its losses during annealing. The reagent mixture was ground in an agate mortar under a heptane layer. The produced charge was additionally dried for 1 h at 300°C and, thereafter, compacted under a pressure of 50 atm into pellets of a mass of 1.0 to 1.5 g and a diameter of 1.5 cm, which were then placed into a corundum crucible and annealed in a silicate furnace. Thermal treatment was performed in two stages with intermediate grounding and compacting. The first stage of synthesis was carried out at 650°C for 6 h; and the second one, at 1000°C for 10 h.

The X-ray diffraction of the synthesized compounds was analyzed using a Rigaku Miniflex II device (CuK$_\alpha$-radiation, angle range 2$\theta$ = 3°–60°, scanning rate 10$^\circ$/min, increment 0.02$^\circ$); the structural parameters were determined using a Topas software package.

RNTO protonation was studied through a preparation of 0.3 g of the initial oxide in 50 mL of distilled water and subsequent pH adjustment to the preset value (in the range from 2 to 10) by the dropwise addition of hydrochloric acid. Thereafter, the suspension was stirred for 2 h to establish the ion-exchange equilibrium and centrifuged, and then the precipitate was separated and dried for 48 h over CaO for further study.

The morphology of the samples studied was investigated by the method of scanning electron micros-
copy using a Zeiss Merlin microscope with a field emission cathode, GEMINI-II column electronic optics, and oil-free vacuum system. The element analysis was performed using an Oxford Instruments INCAx-act system of energy-dispersive X-ray microanalysis (EXM).

The degree of substitution and the quantity of intercalated water were calculated based on the data of thermogravimetry analysis (TGA) using a Netzsch TG 209 F1 Libra device (heating rate 10 K/min, temperature range 30–800°C, argon atmosphere). The calculation method of the degree of protonation \(x/2\) from the TGA data was described in detail in [8] and was successfully used in studies of layered compounds [9, 10]. According to this technique, the mass decrease in the heating process is caused, first, by the reaction of dehydration (2) and, then, that of the decomposition of the protonated compound (3):

\[
\begin{align*}
H_xRb_{2-x}Nd_2Ti_3O_{10} \cdot yH_2O &= H_xRb_{2-x}Nd_2Ti_3O_{10} + yH_2O \uparrow \quad (60–200°C),
\end{align*}
\]

\[
\begin{align*}
H_xRb_{2-x}Nd_2Ti_3O_{10} &= Rb_{2-x}Nd_2Ti_3O_{10} - x/2
\end{align*}
\]

\[
\begin{align*}
+ x/2H_2O \uparrow \quad (300–500°C).
\end{align*}
\]

**RESULTS AND DISCUSSION**

The X-ray diffraction data showed that the obtained sample was single-phased and contained a perovskite-like oxide (Fig. 1). The diffractogram of the obtained oxide RNTO is most adequately indexed in the space group \(I4/mmm\), which corroborates its isostructurality to similar \(A_2Ln_2Ti_3O_{10}\) oxides and assignment to the Ruddlesden–Popper phases. The calculated unit cell parameters \(a = b = 3.891\) Å and \(c = 30.34\) Å are somewhat smaller than those of the known \(Rb_2La_2Ti_3O_{10}\) compound \((a = b = 3.90\) Å, \(c = 30.47\) Å) [5] and larger than those of \(K_2Nd_2Ti_3O_{10}\) \((a = b = 3.86\) Å, \(c = 29.66\) Å) [6].

In air, the product is hydrated because of the atmospheric humidity with the formation of the intercalate \(Rb_2Nd_2Ti_3O_{10} \cdot H_2O (RNTO \cdot H_2O)\), which is distinguishable on the diffractogram from the emergence of reflections symmetrically shifted to the small-angle range (00l). The intercalation of water molecules into the RNTO interlayer space results in the interlayer distance \(d\) increasing by 3.46 Å and the space group changing to \(P4/mmm\) because of the diagonal shift of the adjacent perovskite-like layers similarly to the case of \(K_2La_2Ti_3O_{10}\) [7]. It became possible to obtain the hydrated phase in its pure form by holding the RNTO oxide at a relative humidity of 75% for one hour at \(25°C\) (Fig. 1). More prolonged exposure did not result in any noticeable changes in the cell parameters. It was convenient to control the RNTO purity by detecting this completely hydrated phase due to its stability in air.

The preparation of an oxide suspension in water with the addition of certain amounts of hydrochloric acid resulted both in hydration and protonation (the substitution of rubidium ions by protons):

\[
\begin{align*}
Rb_2Nd_2Ti_3O_{10} + (x + y)H_2O &= H_xRb_{2-x}Nd_2Ti_3O_{10} \cdot yH_2O + xRbOH.
\end{align*}
\]

As established in complex studies by the methods of X-ray diffraction and TGA, the RNTO interaction

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**Fig. 1.** Diffractograms of \(Rb_2Nd_2Ti_3O_{10}\) samples after synthesis (RNTO), after hydration in air (RNTO \(\cdot H_2O\)), after treatment with water (\(\alpha\)-RNTO), equimolar quantity of HCl (\(\beta\)-RNTO), and excess of HCl (\(\gamma\)-RNTO).

* Hydrated phase RNTO \(\cdot H_2O\).

**Fig. 2.** Thermogravimetry curves of \(Rb_2Nd_2Ti_3O_{10}\) samples after hydration in air (RNTO \(\cdot H_2O\)), after treatment with water (\(\alpha\)-RNTO), equimolar quantity of HCl (\(\beta\)-RNTO), and excess of HCl (\(\gamma\)-RNTO).