Research Article

Low-Temperature Transformations of Protonic Forms of Layered Complex Oxides HLnTiO_4 and $\text{H}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$ ($\text{Ln} = \text{La}, \text{Nd}$)

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In the present work protonic forms of layered $n = 1, 3$ Ruddlesden-Popper oxides HLnTiO_4 and $\text{H}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$ ($\text{Ln} = \text{La}, \text{Nd}$) were used as the starting point for soft chemistry synthesis of two series of perovskite-like compounds by acid leaching and exfoliation, promoted by vanadyl sulfate. The last route leads to the nanostructured VO^{2+} containing samples. Characterization by SEM, powder XRD, and TGA has been performed for the determination of the structure and composition of synthesized oxides.

1. Introduction

Layered perovskite-like oxides are compounds which consist of intergrowths of perovskite and other structures, and they are formed by two-dimensional nanosized perovskite slabs interleaved with cations or cationic structural units. Perovskite-like compounds can exhibit a wide range of important physical and chemical properties, such as superconductivity [1, 2], colossal magnetoresistance [3], ferroelectricity [4, 5], and catalytic and photocatalytic activity [6, 7].

In recent years, there has been a growing interest in using the soft chemistry methods for development of new layered perovskite-like compounds with specified physicochemical properties, as well as design of these materials based on the perovskite structure [8]. This is mostly due to the ability to preserve most of the structural and physical features of the initial substance in the course of these transformations.

Layered compounds HLnTiO_4 and $\text{H}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$ ($\text{Ln} = \text{La}, \text{Nd}$) are representatives of the Ruddlesden-Popper layered perovskite-type phases. They are formed by polyanion sheets of transition metal oxides (in case of HLnTiO_4 polyanion sheets consist of a single layer of oxygen octahedral [9] and, in case of $\text{H}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$, three layers of oxygen octahedral [10]) and protons in the interlayer space.

Protonic forms of transition metal-layered perovskite-like oxides attract great attention due to their interesting and variable properties, in particular the proton conductivity [11, 12]. Such protonated compounds are interesting in terms of their application as precursors for low-temperature reactions and as starting compounds for building nanostructured materials. Ion-exchange reactions of interlayer protons, acid leaching, and topochemical dehydration are the most important soft chemistry routes.

2. Experimental

2.1. Precursor Synthesis. Alkaline forms NaLnTiO_4 and $\text{K}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$ ($\text{Ln} = \text{La}, \text{Nd}$) of a powder were produced by ceramic technique as precursors for further synthesis of protonic forms. Stoichiometric mixtures of Ln_2O_3 ($\text{Ln} = \text{La}, \text{Nd}$), TiO_2 , and sodium or potassium carbonate (40% excess, since it is volatilized at high-temperature synthesis) were taken as initial compounds; all substances were calcined to remove traces of moisture.

In case of NaLnTiO_4 , following temperature mode has been used: fast heating to 780°C , calcinating at 780°C for 2 hours, fast heating to 900°C , and calcinating at 900°C for 3 hours [13]. This temperature mode was selected regarding the

FIGURE 1: X-ray powder patterns: (a) precursor NaLaTiO₄; (b) HLaTiO₄; (c) precursor NaNdTiO₄; (d) HNdTiO₄.

formation beginning of NaLnTiO₄ at 780°C, while Na₂CO₃ does not yet melt at this temperature. After NaLnTiO₄ formation, the temperature is increased to 900°C to obtain pure phase. For K₂Ln₂Ti₃O₁₀ fast heating to 1100°C was used, with calcinations for 6 hours. Syntheses took place according to the following reactions:

Protonic forms HLnTiO₄ (Ln = La, Nd) were obtained by substitution of Na⁺ ions in NaLnTiO₄ (Ln = La, Nd) to H⁺, according to the following reaction:

Initial alkali metal-containing layered compounds were treated in 0.1 H HCl acid medium, as described in [14].

XRD analysis (powder X-ray diffraction, CuKα radiation) was carried out to control the reaction and to determine structural parameters of substances (Figure 1).

Calculated unit cell parameters of obtained samples (a) NaLaTiO₄, tetragonal, P4/nmm: $a, b = 3,775 \text{ Å}$; $c = 13,018 \text{ Å}$; (b) NaN₂TiO₄, tetragonal, P4/nmm: $a, b = 3,771 \text{ Å}$; $c = 12,832 \text{ Å}$; (c) HLaTiO₄, tetragonal, P4/nmm: $a, b = 3,753 \text{ Å}$; $c = 12,417 \text{ Å}$; (d) HNdTiO₄, tetragonal, P4/nmm: $a, b = 3,708 \text{ Å}$; $c = 12,261 \text{ Å}$ are in agreement with the literature data [9].

The degree of substitution of Na⁺ by H⁺ is estimated by means of TGA analysis using TG 209 F3 Iris, Netzsch [14, 15]. For example, the decomposition process of Na_(1-x)H_xNdTiO₄·yH₂O can be represented by the following reaction:

The weight loss of the sample results from the sorbed water release (intercalated/adsorbed) and from water formed by decomposition of protonic form HNdTiO₄. The content of sodium ions remaining after release of all water substance depends on the degree of substitution of the sample. Dependence between the degree of substitution of x and mass loss in mass loss curve can be expressed by the following relationship:

$$\begin{aligned} \frac{m[\text{Na}_{1-x}\text{NdTiO}_{4-0.5x}]}{m[(x/2)\text{H}_2\text{O}]} \\ = F = \frac{A(\text{Nd}) + A(\text{Ti}) + A(\text{Na}) \cdot (1-x) + A(\text{O}) \cdot (4-0.5x)}{(x/2)M(\text{H}_2\text{O})}, \end{aligned} \quad (5)$$

where m is the mass of sample and M and A the molecular and atomic mass, respectively. F parameter is the ratio of the mass remaining after the release of all water substances to the mass of water released during the decomposition of substituted compounds.

From (5), the degree of substitution x and quantity of sorbed water y can be calculated using the following formulas:

$$\begin{aligned} x = \frac{2 * A(\text{Nd}) + 2 * A(\text{Ti}) + 8 * A(\text{O}) + 2 * A(\text{Na})}{F * M(\text{H}_2\text{O}) + 2 * A(\text{Na}) + A(\text{O})}, \\ y = \frac{x * m[y\text{H}_2\text{O}]}{2 * m[(x/2)\text{H}_2\text{O}]}. \end{aligned} \quad (6)$$

Calculated degrees of substitutes were found to be nearly 100% (±2%) for both HLaTiO₄ and HNdTiO₄.

SEM images (Zeiss Supra 40VP) show that the protonated samples keep the morphology of their layered Na precursors, where the particles are composed of layered plates that are typical for all layer compounds. The average thickness of the particles is about 300 nm. According to the X-ray microanalysis data, Na reflexes were not observed for all protonated substances.

FIGURE 2: X-ray powder patterns: (a) HNdTI₄; (b) HNdTI₄ (4 days, excess of 0.1 H HCl); (c) Nd_{2/3}TiO₃ (7 days, excess of 0.1 H HCl); (d) HLaTiO₄; (e) HLaTiO₄ * nH₂O (star) + La_{2/3}TiO₃ (triangle) (7 days, excess of 0.1 H HCl).

2.2. Acid Leaching Processes. Cation-deficient perovskites Ln_{2/3}TiO₃ (Ln = La, Nd) were obtained for the first time by leaching of Ln³⁺ ions from HLnTiO₄ in acid solution (10x excess of HCl solution (0.1 H) for 7 days):

During the leaching in HCl solution of varying concentrations, it was found that the right product can be obtained only under conditions. Ln_{2/3}TiO₃ dissolved at higher concentration and reaction does not have time to pass through at lower concentration. In case of Nd_{2/3}TiO₃ pure phase of the product was obtained, while for La_{2/3}TiO₃ the impurity of stable HLnTiO₄ * nH₂O phase was observed [16] (Figure 2).

The SEM shows that the initial morphology is not preserved for defect perovskites Ln_{2/3}TiO₃ obtained by acid leaching. The resulting phase is characterized by irregularly shaped particles with dimensions less than 100 nm (Figure 3(c)).

The process of acid leaching of Ln³⁺ cations was also observed in reaction of a perovskite-oxide K₂Ln₂Ti₃O₁₀ (Ln = La, Nd) with a solution of hydrochloric acid of different concentrations. Initial compound K₂Ln₂Ti₃O₁₀ was treated by 5.5x excess of 2 M hydrochloric acid for 5 days. In the process, K⁺ ions are replaced by H⁺, according to the following reaction:

XRD analysis data showed that in case of the initial K₂La₂Ti₃O₁₀ the resulting compound contains a large number of impurity cation-deficient perovskite La_{2/3}TiO₃ (Figure 4, b). In case of the initial K₂Nd₂Ti₃O₁₀, an amount of the Nd_{2/3}TiO₃ is noticeably smaller (Figure 4, f). The main phase in both cases is partially hydrated compound H₂Ln₂Ti₃O₁₀ * γH₂O.

Further, it was proposed to reduce the concentration to 0.1 M solution of 10x excess HCl. This concentration was

chosen by analogy with the reaction of a single-layer perovskite NaLnTiO₄ with hydrochloric acid solution, where the result is a pure phase HLnTiO₄. But in the case of three-layer perovskite oxides the desired product was also obtained with impurities of Ln_{2/3}TiO₃ (Figure 4, c). Only short time treatment (24 hours, 0.1 M solution of 10x excess HCl) leads to the product with satisfactory amount of impurity (Figure 4, a and d).

The SEM images of samples show that the leaching results in the formation of square holes on the surface of the particles; the initial morphology of the layered oxide particles is preserved.

2.3. HLnTiO₄ (Ln = La, Nd) Exfoliation Promoted by VOSO₄. Treatment of NaLnTiO₄ (Ln = La, Nd) by aqueous solution of VOSO₄ leads to partial substitution of Na⁺ by (VO)²⁺ as described in [17] with preservation of layered structure and only partial exfoliation (Figure 5(a)). A similar reaction is known for the K₂La₂Ti₃O₁₀, as described in [18]. In case of protonic compound, the reaction goes another way; VOSO₄ causes exfoliation and reassembling of HLnTiO₄ particles.

Exfoliated HLnTiO₄ (Ln = La, Nd) were prepared by treatment of initial HLnTiO₄ in a double excess of VOSO₄ aqueous solution at 80°C for 3 days. As a result a dark green powder was obtained. The particles of the obtained samples consist of a number of interconnected flat crystallites less than 10 nm width (Figure 5(b)).

The X-ray powder patterns (b) of obtained substances are close to the initial HLnTiO₄ (Figure 6). Exfoliated compounds contain significant amounts of adsorbed VO²⁺ cations (more than 15% mass) according to the X-ray microanalysis.

TGA shows that samples lose water during heating from 30 to 700°C, and in both La and Nd cases the mass loss is nearly the same, 12-13% of the total mass of the substance. The porous nature of the particles explains the continuous nature of mass loss on the TGA curves. This is in contrast with HNdTI₄ and HLaTiO₄ dehydration from 250°C and 350°C, respectively (Figure 7).

FIGURE 3: SEM images: (a) NaNdTiO₄; (b) HNdTiO₄; (c) Nd_{2/3}TiO₃.

FIGURE 4: X-ray powder patterns: (a) K₂La₂Ti₃O₁₀ + 10x excess of HCl (0.1 M), 24 h; (b) K₂La₂Ti₃O₁₀ + 5.5x excess of HCl (2 M), 5 d (H₂La₂Ti₃O₁₀ (rhombus), La_{2/3}TiO₃ (star)); (c) K₂La₂Ti₃O₁₀ + 10x excess of HCl (0.1 M), 5 d; (d) K₂Nd₂Ti₃O₁₀ + 10x excess of HCl (0.1 M), 24 h; (i) K₂Nd₂Ti₃O₁₀ + 5.5x excess of HCl (2 M), 5 d (H₂Nd₂Ti₃O₁₀ (rhombus), Nd_{2/3}TiO₃ (star)); (f) K₂Nd₂Ti₃O₁₀ + 10x excess of HCl (0.1 M), 5 d.

XRD patterns of dehydrated (VO)_xH_{1-2x}LnTiO₄ * γH₂O compounds are nearly the same for 150°C, 300°C, and 600°C temperatures. Total reduction of peaks intensity and 001 reflex displacement in small angle region to large angles (c) is natural because a new phase is formed, identified as

Ln₂□Ti₂O₇. It has cell parameters close to the obtained by pyrolysis of the HLnTiO₄ substance, but less peak broadening on the XRD pattern. The SEM images of dehydrated phases are close to the images of corresponding hydrated (VO)_xH_{1-2x}LnTiO₄ * γH₂O samples.

FIGURE 5: SEM images: (a) $\text{NaNdTiO}_4 + \text{VOSO}_4$; (b) $(\text{VO})_x\text{H}_{1-2x}\text{NdTiO}_4 \cdot y\text{H}_2\text{O}$; (c) $(\text{VO})_x\text{H}_{1-2x}\text{NdTiO}_4 \cdot y\text{H}_2\text{O}$, calcination 300°C , 30 min.

FIGURE 6: X-ray diffraction patterns: (a) HNdTiO_4 ; (b) HNdTiO_4 exfoliated; (c) HNdTiO_4 exfoliated, calcinations at 300°C , 30 min; (d) $\text{Nd}_2\text{Ti}_2\text{O}_7$ by pyrolysis at 680°C .

2.4. $\text{H}_2\text{Nd}_2\text{Ti}_3\text{O}_{10} \cdot y\text{H}_2\text{O}$ Exfoliation Promoted by VOSO_4 .
In case of protonic form of three-layer perovskite-like oxide $\text{H}_2\text{Nd}_2\text{Ti}_3\text{O}_{10} \cdot y\text{H}_2\text{O}$, we carried out the treatment in a double excess of VOSO_4 aqueous solution at 80°C for 3 days. The resulting dark green powder was washed with distilled water and dried under CaCl_2 .

FIGURE 7: TGA analysis: (a) HNdTiO_4 ; (b) HLaTiO_4 ; (c) $(\text{VO})_x\text{H}_{1-2x}\text{NdTiO}_4 \cdot y\text{H}_2\text{O}$; (d) $(\text{VO})_x\text{H}_{1-2x}\text{LaTiO}_4 \cdot y\text{H}_2\text{O}$.

XRD analysis showed that formation of new phases was not observed during the exfoliation synthesis; diffraction patterns of the initial hydrated and protonated $\text{H}_2\text{Nd}_2\text{Ti}_3\text{O}_{10} \cdot y\text{H}_2\text{O}$ and the sample treated by VOSO_4 are almost identical,

TGA curve of $\text{H}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$ exfoliated by VOSO_4 ($(\text{VO})\text{H}_{2-2x}\text{Nd}_2\text{Ti}_3\text{O}_{10} \cdot x\text{H}_2\text{O}$) has mass area during the heating from 30 to 100°C corresponding to the surface water, which is not observed in the case of initial protonated phase (Figure 9). In other $(\text{VO})_x\text{H}_{2-2x}\text{Nd}_2\text{Ti}_3\text{O}_{10} \cdot x\text{H}_2\text{O}$

Surface analysis by SEM demonstrated that the compound in general keeps the particle size of the layered precursor, but there are significant amounts of particles with exfoliated surface layers (Figure 10) similarly as in the case of single-layer perovskite-like oxides HLnTiO_4 ($\text{Ln} = \text{La}, \text{Nd}$). And in contrast with single-layered phases, the amount of adsorbed VO^{2+} cations is less than 5% mass according to the

FIGURE 10: SEM images: (a) $\text{H}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$; (b) $(\text{VO})_x\text{H}_{2-2x}\text{Nd}_2\text{Ti}_3\text{O}_{10}$.

X-ray microanalysis. The mass ratio of Ti and Nd was not changed in contrast with initial protonated compound.

3. Conclusions

Cation-deficient perovskites $\text{Ln}_{2/3}\text{TiO}_3$ ($\text{Ln} = \text{La}, \text{Nd}$) were obtained for the first time by leaching of Ln^{3+} ions from HLnTiO_4 in acid solution (10x excess of HCl solution (0.1 H) for 7 days) (Scheme 1). In case of $\text{Nd}_{2/3}\text{TiO}_3$ pure phase of the product was obtained, while for $\text{La}_{2/3}\text{TiO}_3$ the impurity of stable $\text{HLnTiO}_4 \cdot n\text{H}_2\text{O}$ phase was observed.

Exfoliated $(\text{VO})_x\text{H}_{1-2x}\text{LnTiO}_4 \cdot y\text{H}_2\text{O}$ ($\text{Ln} = \text{La}, \text{Nd}$) have been prepared for the first time by the ion-exchange reaction of HLnTiO_4 in aqueous VOSO_4 . They consist of a large number of interconnected flat crystallites less than 10 nm in size with large amount of surface adsorbed VO^{2+} and water molecules (Scheme 1).

The process of acid leaching of Ln^{3+} cations was also observed in reaction of a perovskite-type layered oxide $\text{K}_2\text{Ln}_2\text{Ti}_3\text{O}_{10}$ ($\text{Ln} = \text{La}, \text{Nd}$) with a solution of hydrochloric acid of different concentrations. Resulting compounds contain a large number of impurity cation-deficient perovskites $\text{Ln}_{2/3}\text{TiO}_3$.

In case of three-layer perovskite-like oxide $\text{H}_2\text{Nd}_2\text{Ti}_3\text{O}_{10}$, the treatment with VOSO_4 aqueous solution at 80°C for 3 days leads to the compound with significant amount of exfoliated surface layers. But in general, it keeps the particle morphology of the precursor.

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