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Photocatalytic Properties and Hydration of Perovskite-Type Layered Titanates $A_2Ln_2Ti_3O_{10}$ (A = Li, Na, K; Ln = La, Nd)

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Abstract—Layered perovskite-type oxides $A_2Ln_2Ti_3O_{10}$ (A = Li, Na, K; Ln = La, Nd) prepared by solid-phase synthesis and their hydrated forms were characterized by the methods of TGA, XRD, and by UV-Vis spectroscopy. Photocatalytic activity of $A_2Ln_2Ti_3O_{10}$ oxides in reaction of hydrogen evolution from aqueous alcoholic suspensions irradiated by UV-light was studied. It was shown that the ability to intercalation of water into interlayer space essentially affects the rate of photoinduced hydrogen evolution and is a determining factor leading to a high photocatalytic activity.

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Photocatalysts of water decomposition into hydrogen and oxygen under the action of light draw attention of researchers from the moment of this process discovery [1] up to the present time. It is connected, first of all, with obvious practical interest to the use of sunlight energy for obtaining such ecologically pure fuel as hydrogen.

Layered perovskite-type oxides are considered as perspective photocatalysts for several reasons. Ion-exchange properties caused by high mobility of interlayer cations make it possible to vary composition of such compounds within a wide range and thus to affect their optical properties and photocatalytic activity [2, 3]. Layered oxides are nanostructured objects, and it can be expected that the recombination probability of electrons and holes induced in such semiconductor materials will be reduced. And, finally, some layered oxides are capable of reversible intercalation of water molecules into interlayer space [4–6], which results both in the increase of the specific "working" surface area of photocatalysts and in spatial separation of centers of water oxidation-reduction.

Many layered oxides, for example, like $K_4Nb_6O_{17}$ [7], $K_2La_2Ti_3O_{10}$ [8], $RbNdTa_2O_7$ [9], and $PbBi_2 \cdot Nb_2O_9$, have already proved to be effective photocatalysts for water decomposition [10]. For some of them the conditions of synthesis were optimized [11, 12] and also the influence of various ways of modification on their photocatalytic activity [13–18] was studied. However, the photocatalytic process is sensitive to a great number of experimental factors, and published data on the photocatalytic activity of isostructural layered oxides measured in identical conditions are still deficient. At the same time, such data are a key to understanding mechanisms of the influence of composition and structure of a photocatalyst on its activity. This work continues our study of photocatalytic properties of isostructural layered compounds with various cation compositions [19]. In this paper we present results of studying some perovskite-type layered titanates $A_2Ln_2Ti_3O_{10}$ (A = Li, Na, K; Ln = La, Nd): the stability of these compounds in water and in a damp atmosphere, their ability to intercalate water in interlayer space, their optical properties, and photocatalytic activity in the reaction of hydrogen evolution from aqueous suspensions with added isopropyl alcohol.

Complex oxides $A_2Ln_2Ti_3O_{10}$ belong to three-layer Ruddlesden-Popper phases and are constructed according to a block principle by joining layers with the perovskite structure and fragments of the rock-salt structure. Because of essential distinctions in sizes and charges, the cations of Ln and alkali metals with different charges are fully ordered in the structure of the oxides under consideration: Ln^{+3} ions occupy 12-coordination positions in the layers with the perovskite structure, whereas A^+ ions are located between the layers and have the coordination number nine [20].

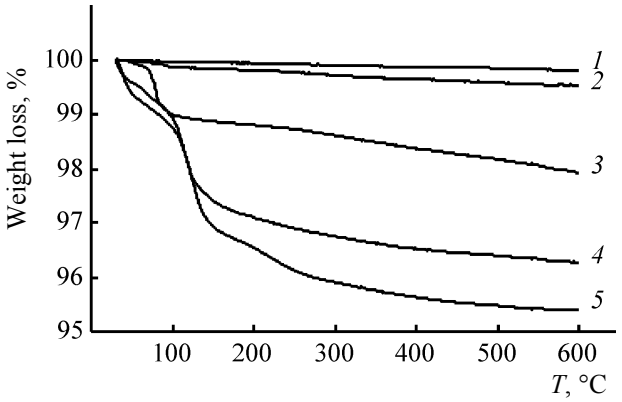

Fig. 1. Thermogravimetric curves of $A_2Ln_2Ti_3O_{10}$ samples kept in air. (*1*) $Li_2Nd_2Ti_3O_{10}$, (*2*) $Na_2La_2Ti_3O_{10}$, (*3*) $Na_2Nd_2Ti_3O_{10}$, (*4*) $K_2La_2Ti_3O_{10}$, (*5*) $K_2Nd_2Ti_3O_{10}$.

To study a possibility for sorption of water from air, we held samples in a damp atmosphere in a desiccator within a day and then subjected them to a thermogravimetric analysis (TGA). It is seen from Fig. 1 that $Li_2Ln_2Ti_3O_{10}$ samples practically do not lose weight upon heating up to 600°C and, hence, do not sorb water from air. At the same time, compounds $Na_2Ln_2Ti_3O_{10}$ and $K_2Ln_2Ti_3O_{10}$ lose weight in a wide range of temperatures. The main weight loss falls to the range 70–100°C in the case of $Na_2Ln_2Ti_3O_{10}$ and 60–170°C for $K_2Ln_2Ti_3O_{10}$. It is necessary to note that an essential distinction is observed for Na-containing samples: In the case of $Na_2La_2Ti_3O_{10}$ the weight loss is almost tenfold less than in the case of $Na_2Nd_2Ti_3O_{10}$. The difference between K-containing samples is insignificant, however here $K_2Nd_2Ti_3O_{10}$ loses more weight than the La-containing analog.

To find out, whether phenomena observed in TGA are connected with water intercalation into the interlayer space, we subjected the samples under study to the X-ray phase analysis (XRD) before and directly after heating up to 180°C. It was found that the unit cell of $K_2Ln_2Ti_3O_{10}$ after sample calcination undergoes a compression along the *c* axis, as follows from the displacement of 002 reflexes in the X-ray pattern (Fig. 2). Moreover, after a short keeping these samples in air at room temperature a gradual transition to the initial state is observed (Fig. 2a). Thus, $K_2Ln_2Ti_3O_{10}$ compounds exist in air in the form of $K_2Ln_2Ti_3O_{10}\cdot H_2O$ hydrates and contain water molecules in the interlayer space, thereby increasing parameter *c* in comparison with the dehydrated form. These data agree with the data of [20]. In the case of $Na_2Ln_2Ti_3O_{10}$ no displacement of peaks after heating was observed. For the compound $Na_2Nd_2Ti_3O_{10}$ the extraneous reflexes close in position to initial reflexes

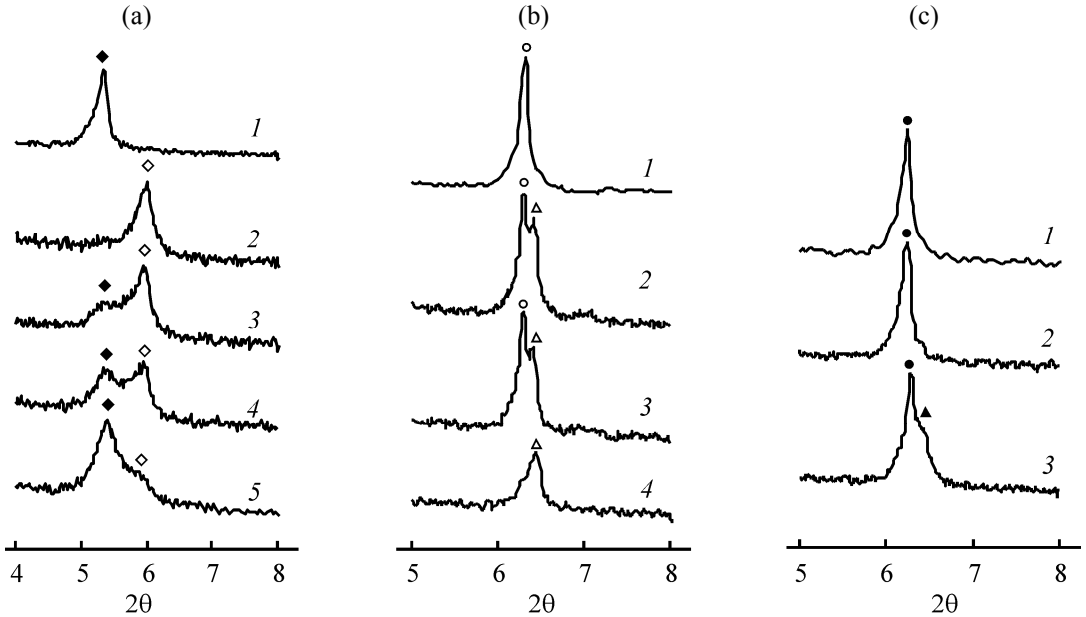

Fig. 2. Fragments of $A_2Ln_2Ti_3O_{10}$ X-ray patterns reflecting observed phase transformations. (a): (*1*) $K_2Nd_2Ti_3O_{10}$ in air; (*2*) $K_2Nd_2Ti_3O_{10}$ heated up to 280°C; (*3*) $K_2Nd_2Ti_3O_{10}$ heated up to 180°C; (*4*) $K_2Nd_2Ti_3O_{10}$ heated up to 180°C after 30 min stay in air; (*5*) $K_2Nd_2Ti_3O_{10}$ heated up to 180°C after 120 min stay in air; dark rhombs are $K_2Nd_2Ti_3O_{10}\cdot H_2O$; light rhombs are $K_2Nd_2Ti_3O_{10}$; (b): (*1*) $Na_2Nd_2Ti_3O_{10}$ after synthesis; (*2*) $Na_2Nd_2Ti_3O_{10}$ in air; (*3*) $Na_2Nd_2Ti_3O_{10}$ heated up to 180°C; (*4*) $Na_2Nd_2Ti_3O_{10}$ treated by water; light circles $Na_2Nd_2Ti_3O_{10}$; light triangles $H_xNa_{2-x}Nd_2Ti_3O_{10}$; (c): (*1*) $Na_2La_2Ti_3O_{10}$ in air; (*2*) $Na_2La_2Ti_3O_{10}$ heated up to 180°C; (*3*) $Na_2La_2Ti_3O_{10}$ treated by water; light circles $Na_2La_2Ti_3O_{10}$ treated by water; dark circles $Na_2Ln_2Ti_3O_{10}$; dark triangles $H_xNa_{2-x}La_2Ti_3O_{10}$.

appeared after keeping the sample in air. The X-ray pattern has not changed after heating the sample (Fig. 2b). It means that Na-containing phases are not exposed to intercalation of water in a damp atmosphere. The decrease in the $Na_2Nd_2Ti_3O_{10}$ weight at 70–100°C should be caused by other factors, which we discuss further.

To study stability of $A_2Ln_2Ti_3O_{10}$ compounds in water medium, we placed samples of weight 1 g in 5 ml of distilled water, kept them within a day, and washed out on a filter three times with 300 ml of water in total. After drying above alkali the samples were exposed to the X-ray phase and thermogravimetric analyses.

Samples of $Li_2Ln_2Ti_3O_{10}$ have not undergone visible changes after treatment with water, as follows from the absence of weight loss in TGA and from the identity of the X-ray patterns. At the same time, in the thermogravimetric curves corresponding to $Na_2Ln_2Ti_3O_{10}$ the weight loss at 70–100°C is not observed anymore; the formed phases lose weight at higher temperatures (Fig. 3). It points to ion-exchange processes resulting in washing away Na^+ ions from the crystal phase, which are replaced by protons from water. In this case the solution gains an alkaline reaction, which was actually observed during the experiment. This process was studied in detail in [6] by the example of layered oxide $NaNdTiO_4$. The weight loss in the temperature range 300–500°C corresponds to the decomposition of the hydrogen-substituted compounds accompanied by the condensation of the layered structure with water release. The degree of replacement of sodium ions by protons calculated from the TGA data appeared to be 40% in the case of $Na_2Nd_2Ti_3O_{10}$ and 15% in the case of $Na_2La_2Ti_3O_{10}$. Thus, ion-exchange properties of the Nd-containing phase are noticeably stronger than those of the La-containing analog. It can be explained by the fact that Nd^{3+}, possessing a smaller ionic radius than La^{3+}, gives rise to a greater distortion of titan-oxygen octahedra, which leads to a greater mobility of sodium ions in the interlayer space.

The X-ray patterns of $Na_2Ln_2Ti_3O_{10}$ samples treated by water point to the formation of new phases (Fig. 2c) with a smaller unit cell parameter *c,* which is caused by the replacement of Na^+ cations by H^+. Moreover, the reflexes corresponding to the resulting hydrogen-substituted phase were observed for the $Na_2Nd_2Ti_3O_{10}$ sample after keeping it in air (Fig. 2b). It allows us to conclude that an ionic exchange occurs upon contacting the compound $Na_2Nd_2Ti_3O_{10}$ with damp atmosphere. Sodium hydroxide formed as a result seems to be localized on the surface of the layered oxide and, due to its hygroscopicity, gives rise to the weight loss observed in the thermogravimetric curve (Fig. 1). Thus, owing to the ion-exchange process, $Na_2Ln_2Ti_3O_{10}$ compounds are unstable in water media and $Na_2Nd_2Ti_3O_{10}$, even in air.

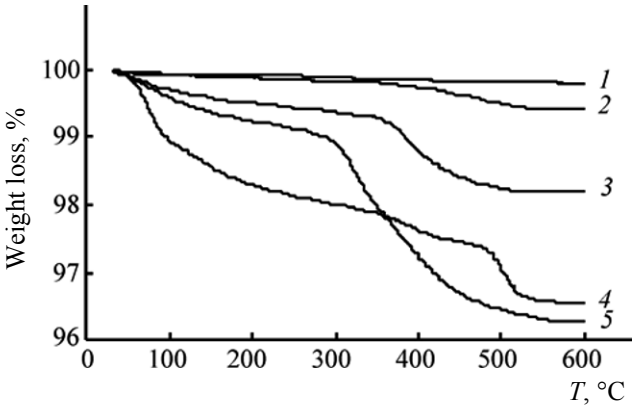

Fig. 3. Thermogravimetric curves of $A_2Ln_2Ti_3O_{10}$ samples treated by water. (*1*) $Li_2Nd_2Ti_3O_{10}$, (*2*) $Na_2La_2Ti_3O_{10}$, (*3*) $Na_2Nd_2Ti_3O_{10}$, (*4*) $K_2Nd_2Ti_3O_{10}$, (*5*) $H_2Nd_2Ti_3O_{10}$.

An ionic exchange during treatment of $K_2Ln_2Ti_3O_{10}$ compounds by water is also observed, which is confirmed by both TGA and XRD. In this case partially hydrogen-substituted phases $H_xK_{2-x}Nd_2Ti_3O_{10y}\cdot H_2O$ ($x \approx 1$, $y \approx 0.7$), which are capable of intercalating water due to potassium ions remained in the interlayer space, are formed.

Thus, layered titanates $K_2Ln_2Ti_3O_{10}$ undergo in water both intercalation and ion exchange, $Na_2Ln_2Ti_3O_{10}$ only ion exchange, and $Li_2Ln_2Ti_3O_{10}$ compounds are stable in water.

Diffuse scattering spectra of the compounds under study and the band gap width E_g estimated on their basis are presented in Fig. 4. The band gap width of $A_2Ln_2Ti_3O_{10}$ oxides decreases in the series A = Li > Na > K and also increases approximately by 0.1 eV on passing from lanthanum-containing oxides to neodymium-containing oxides. Thus, the band gap width is in inverse dependence on ionic radii of elements entering into the composition of complex oxides.

The photocatalytic activity of $A_2Ln_2Ti_3O_{10}$ samples was estimated by measuring the rate of hydrogen evolution from their aqueous suspensions containing 0.1% of isopropyl alcohol under UV light irradiation.

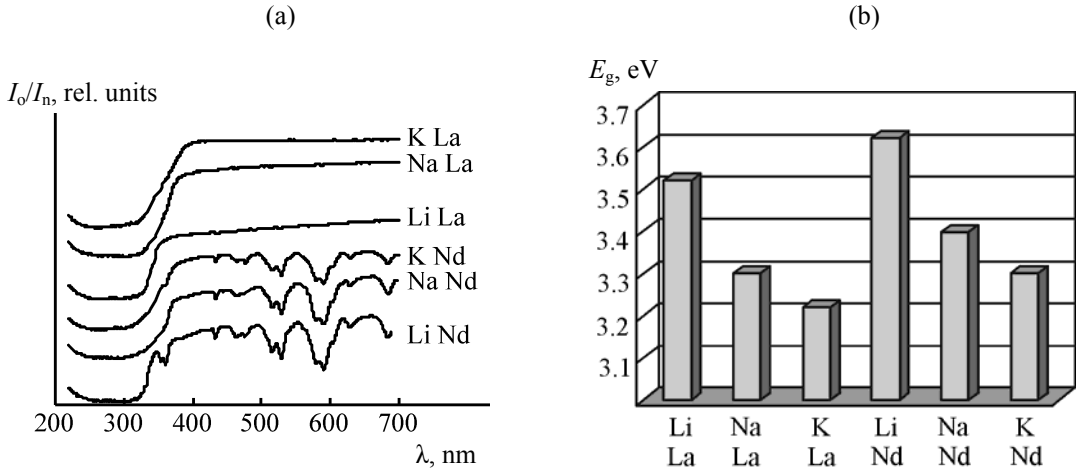

Fig. 4. (a) Diffuse scattering spectra and (b) calculated values of the band gap width of samples $A_2Ln_2Ti_3O_{10}$. A = Li, Na, K; Ln = La, Nd.

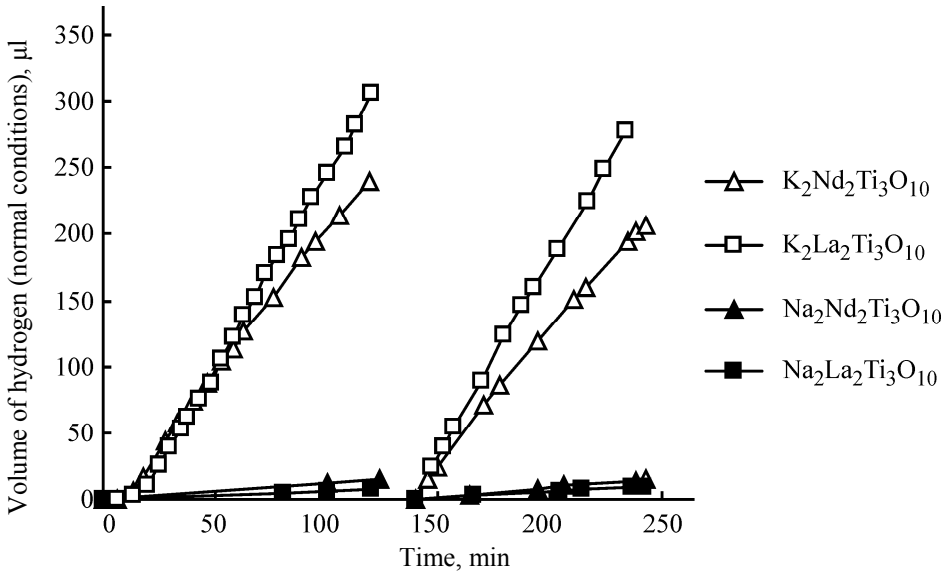

Fig. 5. Dependence of the volume of evolved hydrogen on time of UV irradiation of $A_2Ln_2Ti_3O_{10}$ suspensions in 0.1% isopropyl alcohol.

Kinetic curves obtained in the course of these experiments are presented in Fig. 5.

Experiments on the kinetics of photoinduced hydrogen evolution were carried out on a custom-made installation we designed (Fig. 6).

The highest rate of hydrogen evolution is observed in the $K_2La_2Ti_3O_{10}$ (175 μl/h) and $K_2Nd_2Ti_3O_{10}$ (113 μl/h) suspensions. The rate of hydrogen evolution in the case of Na-containing phases is essentially lower: 5 μl/h for $Na_2Ln_2Ti_3O_{10}$ and 9 μl/h for $Na_2Nd_2Ti_3O_{10}$. In the experiments with Li-containing samples trace amounts of hydrogen (~1 μl/h) were evolved. Thus, the photocatalytic activity decreases in the series $K_2La_2Ti_3O_{10}$ > $K_2Nd_2Ti_3O_{10}$ >> $Na_2Nd_2Ti_3O_{10}$ > $Na_2Ln_2Ti_3O_{10}$ > $Li_2Ln_2Ti_3O_{10}$.

The essential diference between the photocatalytic activity of $K_2Ln_2Ti_3O_{10}$ and $Na_2Ln_2Ti_3O_{10}$ is attributable to the ability of K-containing phases to intercalate water into interlayer space, which is absent in the case of Na-containing analogs. These latter also have a slightly greater band gap width (for identical lanthanides), however in this case it is not the deciding factor, as E_g values for $Na_2La_2Ti_3O_{10}$ and $K_2Nd_2Ti_3O_{10}$ practically coincide, whereas their photocatalytic activities differ more than by a factor of 20.

The change in the photocatalytic activity of $A_2Ln_2Ti_3O_{10}$ on passing from $A_2La_2Ti_3O_{10}$ to

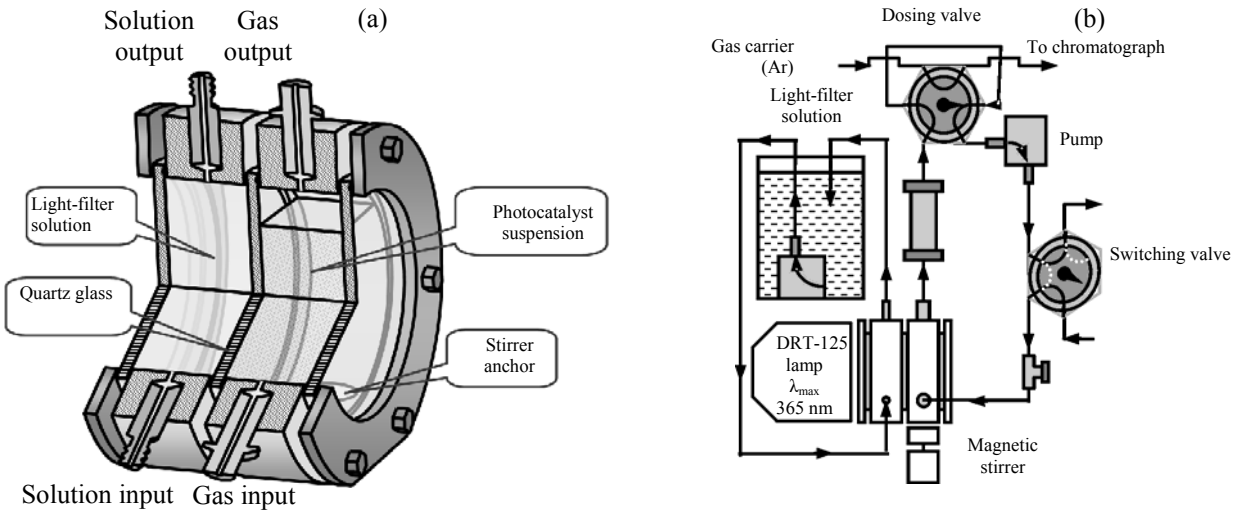

Fig. 6. Experimental installation for studying kinetics of photoinduced hydrogen evolution from a photocatalyst suspension. (a) external irradiation cell, (b) general scheme of the installation.

$A_2Nd_2Ti_3O_{10}$ should be caused not only by a change in zone structure, but also by ion-exchange processes, which occur more intensively in the case of the neodymium-containing oxide. Hydrogen-substituted compounds formed in this case are capable of the intercalation of water into the interlayer space, but to a lesser degree than $K_2Ln_2Ti_3O_{10}$. Therefore the ion exchange reduces the photocatalytic activity of $K_2Ln_2Ti_3O_{10}$, whereas the activity of $Na_2Ln_2Ti_3O_{10}$, on the contrary, increases. It is apparently the reason which is responsible for the observed experimental dependence of the photocatalytic activity on the layered oxide composition. For Li-containing layered oxides neither intercalation nor ion exchange occur in water, therefore these compounds possess the minimal photocatalytic activity. It is also necessary to note that the band of the fundamental absorption of these compounds lies in the region of shorter waves as compared with the most intensive line of the mercury lamp radiation (365 nm), therefore the power of light accessible to absorption was less for these compounds than for the others.

Thus the decrease in the photocatalytic activity in the series of layered titanates $K_2La_2Ti_3O_{10}$ > $K_2Nd_2Ti_3O_{10}$ >> $Na_2Nd_2Ti_3O_{10}$ > $Na_2La_2Ti_3O_{10}$ > $Li_2Ln_2Ti_3O_{10}$ fully correlates with the ability of these compounds to intercalation of water into interlayer space and their ion-exchange properties. The intercalation of water into interlayer space essentially influences the rate of the photoinduced hydrogen evolution and is a defining factor leading to a high photocatalytic activity.

EXPERIMENTAL

Layered perovskite-type titanates $A_2Ln_2Ti_3O_{10}$ were synthesized by a solid-phase technique from the corresponding simple oxides and carbonates Ln_2O_3 (99.9%), TiO_2 (99.9%), and A_2CO_3 (99.9%). Before the synthesis all the reagents were annealed to remove traces of moisture. Amounts of the reagents were taken in accordance with the stoichiometry of the reaction

$$Ln_2O_3 + 3TiO_2 + A_2CO_3 \rightarrow A_2Ln_2Ti_3O_{10} + CO_2\uparrow.$$

Carbonates of alkali metals were taken in excess of 40% to compensate their losses on heating. The reagents in the sum of 1 g were weighed to within 1×10^{-4} g, mixed, and carefully ground in an agate mortar within 30 min. The resulting charges were pressed in 0.5 g tablets, which were placed in a corundum crucible and calcinated in a Silit furnace at 900°C over 6 h. According to the X-ray phase analysis, all synthesized substances were single-phase without noticeable impurities.

Phase compositions of the obtained samples and the changes in structure during hydration/dehydration were monitored by means of an ARL X'TRA powder diffractometer (CuK_α radiation).

Diffuse scattering spectra of the complex oxide were measured on a Specord-M40 spectrophotometer. The optical width of the energy gap was determined by constructing the Kubelka-Munk function in the coordinates $(K\cdot h\nu)^{1/2} = f(h\nu)$ and finding a crossing point of linear portions.

Thermogravimetric analysis was carried out on a Netzsch TG 209 F1 Iris thermal microbalance accurate to 10^{-7} g.

To prepare reaction suspension, 70 mg of a photocatalyst was carefully ground in an agate mortar, 70 ml of 0.1% aqueous solution of isopropyl alcohol was added, shaken, and left for a day to reach an equilibrium between the photocatalyst and the solution. To degas the photocatalyst particles, directly before the experiment each suspension was exposed to an ultrasonic treatment within 10 min (a "SAPFIR" ultrasound bath of power 55 W).

The reaction suspension of 55 ml by volume was placed in an external irradiation cell supplied with a powerful magnetic stirrer (Fig. 6a). Gas circulating in a closed contour of a total volume 80 ml was bubbled through the suspension. To remove air from the system, the contour was flushed by argon for 15 min at the beginning of the experiment, then the contour was closed, the lamp was switched on, and the time of the experiment start was recorded. Hydrogen evolved during the photocatalytic reaction was collected in the gas phase, the composition of which was determined by gas chromatography method at certain time intervals (a Tsvet-800 chromatograph with a heat conductivity detector and a column of 2 m in length packed with molecular sieves). To prevent moisture condensation in certain subsystems, the gas contour, including the circulating pump and valves, was thermostated at 80°C.

A DRT-125 mercury lamp served as the radiation source. Light reached a reaction cell after passing through a 22 mm layer of a light-filter KCl+NaBr solution maintained at 15°C, which served for cutting off IR and short-wave UV ($\lambda < 220$ nm) radiation. The necessity of using the light filter is caused by the fact that the spectrum of the DRT-125 mercury lamp contains a short-wave radiation causing a direct (non-catalytic) photolysis of isopropyl alcohol with hydrogen evolution, which is undesirable when studying the photocatalysis.

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