Thermogravimetry study of ion exchange and hydration in layered oxide materials

Oleg Silyukov · Mikhail Chislov · Alena Burovikhina · Tatyana Utkina · Irina Zvereva

Abstract The behavior in aqueous solutions of the two types of layered perovskite-like structures, $NaLnTiO_4$ titanates (Ln = Nd, La) belonging to the family of Ruddlesden–Popper phases and $ANdTa_2O_7$ tantalates (A = Na, Cs, H) belonging to the family of Dion–Jacobson phases, has been studied by means of thermogravimetric analysis and powder X-ray diffraction. In the case of $NaLnTiO_4$ compounds, the substitution of protons for sodium cations and the water intercalation into the interlayer space of the crystal structure were observed and proton-containing layered oxides with general formula $H_xNa_{1-x}LnTiO_4 \cdot yH_2O$ ($0.63 < x < 1$, $0 < y < 0.74$) have been obtained. Investigation on the hydration in layered tantalates $ANdTa_2O_7$ (A = H, Na, Cs) showed that $NaNdTa_2O_7$ and $HNdTa_2O_7$ form compounds intercalated by water molecules. Two steps of water intercalation were observed for $NaNdTa_2O_7$ and $HNdTa_2O_7$. Stable hydrated compounds $HNdTa_2O_7 \cdot 0.84H_2O$, $NaNdTa_2O_7 \cdot 0.60H_2O$, and $NaNdTa_2O_7 \cdot 1.35H_2O$ were synthesized.

Introduction

Complex oxides with perovskite-like crystal structures are of great interest due to their unique properties: high-temperature superconductivity, colossal magnetoresistance [1, 2], photocatalytic activity in water decomposition by UV irradiation [3, 4], ionic conductivity [5, 6], ion-exchange properties, ability to the intercalation and interlayer modification [7], etc. Especially, interesting are layered oxides belonging to the Ruddlesden–Popper and Dion–Jacobson phases. These materials are promising catalysts for photoinduced processes of water splitting and degradation of toxic organic compounds in water [8]. Their physico-chemical properties are sensitive to the content and structure of the interlayer space that could be easily modified by the ion-exchange and intercalation reactions.

In contact with water, the interlayer space of alkali-containing layered oxides can intercalate water molecules. The other possibility is the exchange of metal cations in the interlayer space for protons [9, 10]. Protonated forms of layered perovskite-like oxides appear to be solid acids associated with a number of unique physical and chemical properties. They can also be used as precursors for low temperature ion-exchange reactions [11].

The complex oxides $NaLnTiO_4$ (Ln = Nd, La) belong to the Ruddlesden–Popper phases. Their structure can be described as stacking of the perovskite-like blocks made up from TiO_6 octahedra and rock salt layers containing Nd^{3+} and Na^+ ions. There is a complete ordering of Na^+ and Nd^{3+} cations inside the rock salt layers owing to essential differences in charge (Fig. 1). The Na^+ cations in the structure of $NaLnTiO_4$ are bound to the perovskite layers weaker than Nd^{3+} and have a substantial mobility that results in high ionic conductivity and ion-exchange activity of $NaLnTiO_4$ [12, 13]. The protonated and hydrated Ruddlesden–Popper phases $H_xNa_{1-x}LaTiO_4 \cdot yH_2O$ formed by ion-exchange and intercalation reaction have been reported [14]. On the other hand, only a few data were

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Fig. 1 Schematic structure representation of layered perovskite-like oxides under study

NaNdTiO$_4$ HNdTa$_2$O$_7$ NaNdTa$_2$O$_7$ CsNdTa$_2$O$_7$
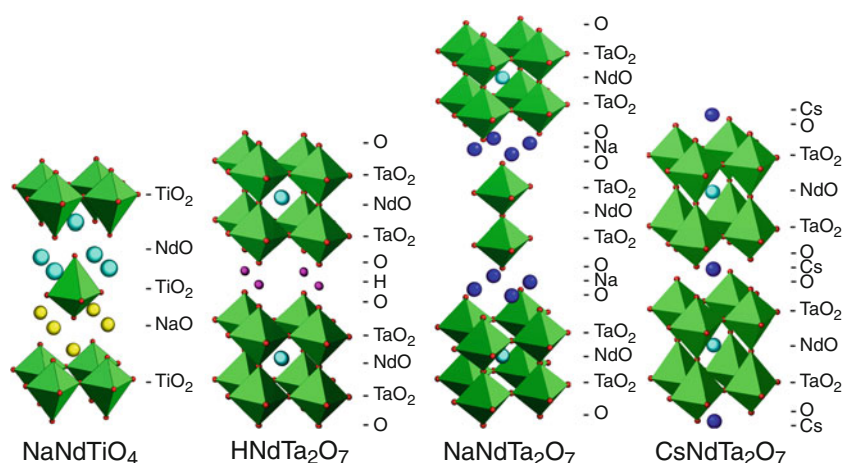
obtained on the hydration of NaNdTiO$_4$ oxide with the same tetragonal structure as NaLaTiO$_4$.

The series of the layered perovskite-like oxides ANdTa$_2$O$_7$ belong to the Dion–Jacobson phases. Their structure could be described as double layered perovskite-like blocks made up from TaO$_6$ octahedra with 12-coordinated Nd^{3+} ions between the octahedra and A$^+$ ions in the interlayer space. Na$^+$, Cs$^+$, and H$^+$ cations have different ionic radii leading to different stacking shift of perovskite blocks as shown in Fig. 1. The hydration process was investigated for tantalates [3] in connection with their photocatalytic activity. The highest activity was found for Nd-containing compounds but the water intercalation was not described in details as a multistage process similar to the one found for NaLaTa$_2$O$_7$ [15] and NaLaNb$_2$O$_7$ [16, 17].

In this article, we describe the behavior of the perovskite-like complex titanates NaLnTiO$_4$ (Ln = Nd, La) and tantalates ANdTa$_2$O$_7$ (A = Na, Cs, H) in aqueous solutions. The importance of this study is due, first, to the prospects of using layered oxides as catalysts of processes in aqueous medium, as the stability of a catalyst is an important characteristic that determines the possibility of its application to a particular catalytic system, and second, to the possibility of using protonated forms as precursors to obtain new compounds by soft-chemical reactions. The investigation of the intercalation was carried out using thermogravimetry (TG) of water desorption as main method for the mass analysis of intercalated compounds [18–20].

Experimental

Layered oxides NaLnTiO$_4$ (Ln = Nd, La) and CsNdTa$_2$O$_7$ were prepared by conventional solid state reaction in air at atmospheric pressure using as reagents carbonates (Na$_2$CO$_3$ and Cs$_2$CO$_3$, 99.9%), and oxides (La$_2$O$_3$, Nd$_2$O$_3$, TiO$_2$, and Ta$_2$O$_5$, 99.95%) of the corresponding metals. Stoichiometric amounts of oxides with 40% excess of sodium carbonate and 50% excess of cesium carbonate (both evaporate at the high temperature of synthesis) were ground in an agate mortar, pelletized by pressure 100 kg/cm^2 and heated in an alumina crucible. For the NaLnTiO$_4$ series heating was carried out at 850 °C for 10 h according to the results of the investigation of the formation and thermal stability of NaNdTiO$_4$ [20, 21]. CsNdTa$_2$O$_7$ was obtained by heating at 850 °C for 10 h followed by regrinding and heating at 1,100 °C for additional 10 h.

NaNdTa$_2$O$_7$ was prepared by the ion-exchange reaction of CsNdTa$_2$O$_7$ with NaNO$_3$. Ground CsNdTa$_2$O$_7$ powder was added to molten NaNO$_3$ (reagents ratio was 1:50) and stirred up with magnetic stirrer at 360 °C for 10 h. The solid mixture obtained after cooling was washed with distilled water. Protonated compounds HNdTa$_2$O$_7$ and HLnTiO$_4$ were prepared by ion exchange with excess of 0.1H HCl solution. For this purpose, initial Na-containing oxides were ground, suspended in HCl solution, and stirred up at 25 °C for 24 h, then the as-prepared H-containing phases were filtered, washed with distilled water, and dried at room temperature under CaCl$_2$.

To achieve a complete intercalation/ion exchange each prepared complex oxide (1 g) was ground and dispersed in 100 mL of distilled water by a magnetic stirrer for 7 days. In the case of NaLnTiO$_4$ samples, various amounts of hydrochloric acid were added to investigate the behavior of the oxide exposed in solutions with different pH values.

Combination of TG and powder X-ray diffraction analysis (XRD) was used for the investigation of hydration and ion-exchange phenomena. TG analysis was made using a NETZSCH TG209 F1 Iris microbalance with heating rate 2–10 K min^{-1}. Differential thermal analysis was performed using a Thermoscan-1 Analytpribor with the same

program of recording. The amount of water intercalated and the degree of ion exchange were estimated using the procedure previously described [22]. The pH value and Na^+ ion concentration were determined using IPL-103 ion-meter. The crystal structure was identified with a powder ARL X'TRA diffractometer (Cu Kα radiation, 35 mA–45 kV). Parameters of the unit cells have been calculated using the GSAS software. Scanning electron microscopy (SEM) was performed on a Carl Zeiss EVO 40EP microscope.

Results and discussion

$NaLnTiO_4$ (Ln = Nd, La)

The $NaLnTiO_4$ water suspensions were found to have an alkaline reaction, which corresponds to nearly 50% substitution of H^+ for Na^+ ions resulting in the formation of $H_xNa_{1-x}LnTiO_4 \cdot yH_2O$ solid solutions. The degree of proton substitution for sodium cations was determined with a higher accuracy using the results of TG (Figs. 2a, 3a). For

Fig. 2 TG curves and XRD patterns of $NaLaTiO_4$ derivatives
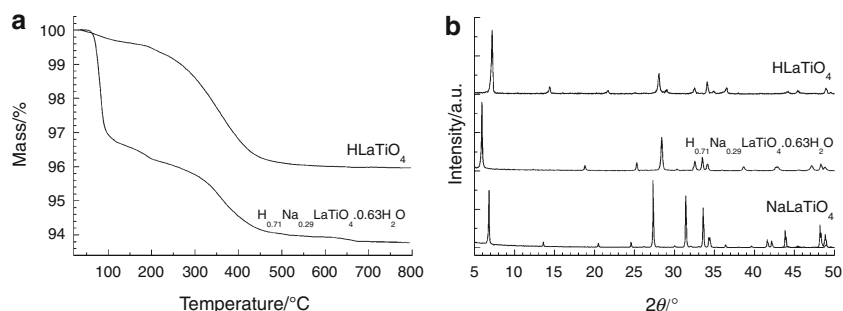
Fig. 3 TG curves and XRD patterns of $NaNdTiO_4$ derivatives

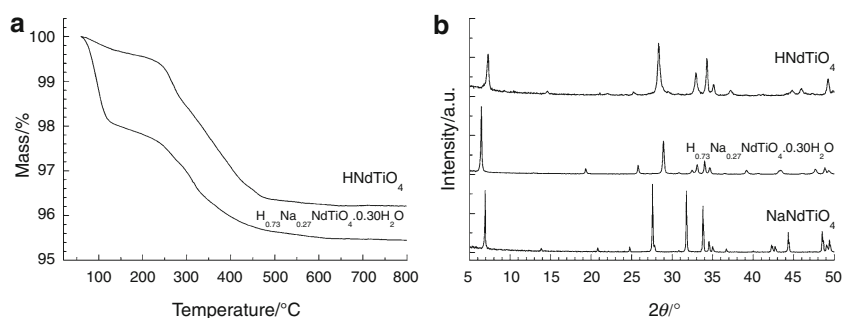**Table 1** $H_xNa_{1-x}LnTiO_4 \cdot yH_2O$ samples composition and unit cells parameters

HCl equivalents added	Solution pH	Chemical composition	Space group	a/Å	c/Å
		$HLaTiO_4$	$P4/nmm$	3.72	12.29
1	5.5	$H_{0.99}Na_{0.01}LaTiO_4 \cdot 0.06H_2O$	$P4/nmm$	3.72	12.35
0.8	6.4	$H_{0.97}Na_{0.03}LaTiO_4 \cdot 0.32H_2O$	$P4/nmm$	3.74	12.93
0.6	9.5	$H_{0.71}Na_{0.29}LaTiO_4 \cdot 0.69H_2O$	$I4/mmm$	3.75	28.12
0.4	11.4	$H_{0.77}Na_{0.23}LaTiO_4 \cdot 0.62H_2O$	$I4/mmm$	3.75	28.12
0.2	11.5	$H_{0.63}Na_{0.37}LaTiO_4 \cdot 0.74H_2O$	$I4/mmm$	3.76	28.14
0	11.9	$H_{0.71}Na_{0.29}LaTiO_4 \cdot 0.63H_2O$	$I4/mmm$	3.75	28.13
–	–	$NaLaTiO_4$	$P4/nmm$	3.74	12.94
2		$HNdTiO_4$	$P4/nmm$	3.70	12.26
1	5.6	$H_{0.99}Na_{0.01}NdTiO_4 \cdot 0.06H_2O$	$P4/nmm$	3.71	12.53
0.8	6.3	$H_{0.85}Na_{0.15}NdTiO_4 \cdot 0.21H_2O$	$P4/nmm$	3.72	12.96
0.6	9.7	$H_{0.66}Na_{0.34}NdTiO_4 \cdot 0.43H_2O$	$I4/mmm$	3.74	27.81
0.4	11.2	$H_{0.70}Na_{0.30}NdTiO_4 \cdot 0.47H_2O$	$I4/mmm$	3.74	27.82
0.2	11.5	$H_{0.64}Na_{0.36}NdTiO_4 \cdot 0.43H_2O$	$I4/mmm$	3.74	27.81
0	11.8	$H_{0.73}Na_{0.27}NdTiO_4 \cdot 0.30H_2O$	$I4/mmm$	3.74	27.68
–	–	$NaNdTiO_4$	$P4/nmm$	3.78	13.01

both La- and Nd-containing substances the weight loss occurs in two steps. We ascribed the weight loss in the 70–130 °C range to the release of the intercalated water in the interlayer space of the $NaLnTiO_4$ oxide crystal structure. The second weight loss at temperatures higher than 200 °C corresponds to the decomposition of the substituted compound, as this temperature range coincides with the decomposition temperature of the completely protonated $HLnTiO_4$ oxides (Figs. 2a, 3a). Accordingly, differential thermal analysis shows an exothermic effect at the beginning of second mass loss step that is generally typical for the decomposition processes.

x, the degree of substitution and y the amount of intercalated water, as calculated from the TG data for $H_xNa_{1-x}LnTiO_4 \cdot yH_2O$ exposed in water and acid solutions are presented in Table 1.

The analysis of the substitution degree values and the amount of intercalated water in $NaLnTiO_4$ (Table 1) indicates that on adding not more than 0.6 equivalent of HCl to
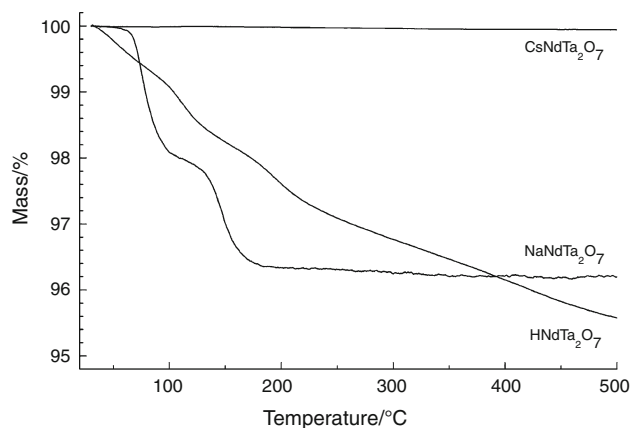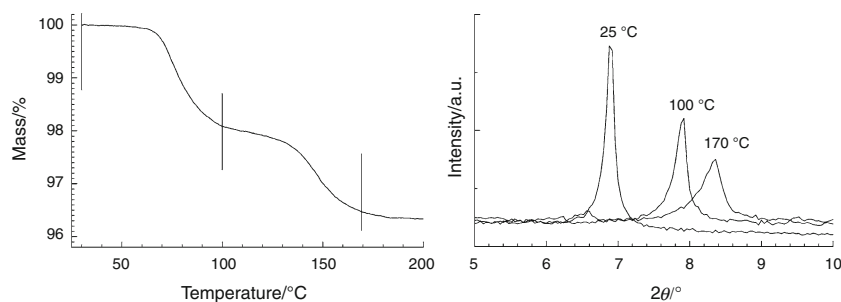

Fig. 4 TG curves of $ANdTa_2O_7$ (A = H, Na, Cs)

a suspension (pH > 9.5) the amount of intercalated water and the degree of substitution in $H_xNa_{1-x}LnTiO_4 \cdot yH_2O$ are almost the same. In more acidic solutions, a significant decrease in the amount of intercalated water is observed simultaneously with an increase of the substitution degree.

The (XRD) data show (Figs. 2b, 3b) the identity of the X-ray patterns of samples obtained on adding 0–0.6 equivalent of HCl to the $NaLnTiO_4$ suspension. All hydrated compounds with $0.43 < y < 0.74$ crystallize in the $I4/mmm$ space group (Table 1). The increase of the c parameter in $H_xNa_{1-x}LnTiO_4 \cdot yH_2O$ as compared to the starting $NaLnTiO_4$ points to a widening of the interlayer space due to the intercalation of water molecules. This assumption was checked by preparing $H_xNa_{1-x}LnTiO_4$ dehydrated samples by heating the $H_xNa_{1-x}LnTiO_4 \cdot yH_2O$ hydrated ones at 150 °C for 1.5 h. Resulting c parameters are close to that of the initial $NaLnTiO_4$.

As to the samples obtained in more acidic solutions (0.8–1 equivalents of HCl added, pH < 9) the $H_xNa_{1-x}LnTiO_4 \cdot yH_2O$ phases crystallize in $P4/nmm$ space group. The unit cell parameter c decreases indicating a compression of the interlayer space as the degree of H^+ substitution for Na^+ increases. The X-ray pattern of the sample in the most acidic solution under study (equivalent amounts of acid and oxide) almost completely coincides with the X-ray pattern of the fully substituted anhydrous $HLnTiO_4$. Therefore, in the acid medium a fully substituted $HNdTiO_4$ compound is nearly completely free from intercalated water that is proved by the evidence of no weight loss along the heating up to 250 °C.

SEM had demonstrated that the ion exchange of H^+ for Na^+ and the intercalation processes do not result in a change of the particles size and morphology.

Table 2 Unit cell parameters of oxides exposed in water

Oxide	Space group	a/Å	c/Å
$HNdTa_2O_7 \cdot xH_2O$	$P4/m$	3.87	11.71
$NaNdTa_2O_7 \cdot xH_2O$	$I4/m\ 2/m\ 2/m$	3.86	25.64
$CsNdTa_2O_7$	$P4/mmm$	3.90	11.29

Table 3 Temperature range of existence, composition, and unit cells parameters of $NaNdTa_2O_7 \cdot xH_2O$

Temperature/°C	Composition	a/Å	c/Å
<65	$NaNdTa_2O_7 \cdot 1.35H_2O$	3.86	25.64
105–125	$NaNdTa_2O_7 \cdot 0.60H_2O$	3.85	22.37
>165	$NaNdTa_2O_7$	3.87	21.02

Fig. 5 TG curve and XRD patterns of $NaNdTa_2O_7 \cdot 1.35H_2O$

Fig. 6 TG/DTG curves and XRD patterns of HNdTa$_2$O$_7\cdot$0.84H$_2$O
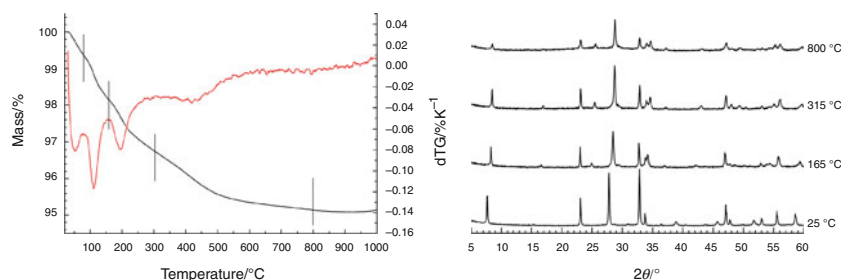
ANdTa$_2$O$_7$ (A = H, Na, Cs)

TG curves of complex oxides ANdTa$_2$O$_7$ exposed in water are presented in the Fig. 4. One can see that CsNdTa$_2$O$_7$ is stable upon heating; NaNdTa$_2$O$_7$ and HNdTa$_2$O$_7$ lose mass during the heating. Parameters of the ANdTa$_2$O$_7$ unit cells (M = H, Na, Cs) exposed in water are presented in Table 2. The increase of distance between the layers in the row Na > H > Cs which is strongly connected with the c parameter for HNdTa$_2$O$_7$ and CsNdTa$_2$O$_7$ (1/2c for NaNdTa$_2$O$_7$) could be affected by the intercalation of water molecules in the interlayer space.

TG curve of NaNdTa$_2$O$_7$ has two steps of weight loss (Fig. 5). It was found that NaNdTa$_2$O$_7$ intercalates 1.35 mol of water per mole of the anhydrous compound. The partially intercalated sample has a composition that could be described by the formula NaNdTa$_2$O$_7\cdot$0.6H$_2$O. A multistage weight loss during TG was reported earlier for the isostructural oxides NaLaNb$_2$O$_7\cdot$1.6H$_2$O [15, 16] and NaLaTa$_2$O$_7\cdot$1.9H$_2$O [17] but intermediate compounds have never been isolated and characterized.

For the detailed investigation of multistage processes XRD analysis was performed following the end of each step of weight loss on the TG curve. XRD patterns of intercalated NaNdTa$_2$O$_7\cdot x$H$_2$O heated to the temperatures 100, 170 °C are presented in the Fig. 4; cell parameters of the stable forms and their chemical composition are presented in Table 3.

Weight loss of HNdTa$_2$O$_7$ is divided into four stages (Fig. 6). First of them (30–75 °C) refers to the dehydration of surface water. Three steps of weight loss could be observed in the temperature interval 75–515 °C. The weight loss in the temperature interval 300–515 °C is well described by the following reaction:

HNdTa$_2$O$_7 \rightarrow$ NdTa$_2$O$_{6.5}$ + 0.5H$_2$O.

The other two steps on TG curve are related to the deintercalation of water molecules from the interlayer space. Parameters of the unit cell and chemical composition of intermediate compounds are given in the Table 4. XRD patterns for the initial proton-containing compound HNdTa$_2$O$_7$ and its decomposition product NdTa$_2$O$_{6.5}$ are nearly the same (Fig. 6). A similar result was obtained previously for the isostructural oxide HLaNb$_2$O$_7$ [5, 23].

Both NaNdTa$_2$O$_7\cdot$1.35H$_2$O and HNdTa$_2$O$_7\cdot$0.84H$_2$O have two temperature intervals of intercalated water elimination. It was found that regarding the exchange of H$^+$ for the alkali cation when exposed in water, CsNdTa$_2$O$_7$ and NaNdTa$_2$O$_7$ are stable. Similarly to titanates, SEM data demonstrated that ion exchange and intercalation/deintercalation processes do not result in change of the particle size and morphology.

Conclusions

Instability of the layered NaLnTiO$_4$ (Ln = Nd, La) oxides in aqueous solutions was found. Due to ion exchange of protons for sodium cations in the crystal structure of NaLnTiO$_4$, layered proton-containing oxides HLnTiO$_4$ form in the acidic medium, while a series of H$_x$Na$_{1-x}$LnTiO$_4\cdot y$H$_2$O compounds are formed in the neutral and alkali medium. The dehydration process of partially substituted compounds H$_x$Na$_{1-x}$LnTiO$_4\cdot$H$_2$O occurs in two stages. The first one in the 70–130 °C range is the release of the water intercalated in the interlayer space, and the second one at temperatures higher than 200 °C is the decomposition of the protonated compounds.

NaNdTa$_2$O$_7$ and HNdTa$_2$O$_7$ intercalate water into the interlayer space. Molecular formulae of fully intercalated compounds are NaNdTa$_2$O$_7\cdot$1.35H$_2$O and HNdTa$_2$O$_7\cdot$0.84H$_2$O. Deintercalation process takes place during heating and has two steps in the different temperature intervals for both compounds.

The two types of layered perovskite-like structures under study show a different behavior during the water exposure. While Ruddlesden–Popper phases NaLnTiO$_4$

Table 4 Temperature range of existence, composition, and unit cells parameters of HNdTa$_2$O$_7\cdot x$H$_2$O

Temperature/°C	Composition	a/Å	c/Å
<75	HNdTa$_2$O$_7\cdot$0.84H$_2$O	3.87	11.71
160	HNdTa$_2$O$_7\cdot$0.40H$_2$O	3.87	10.69
315	HNdTa$_2$O$_7$	3.86	10.48

(Ln = Nd, La) oxides undergo an ion exchange of H^+ for Na^+ conjugated with water intercalation, the Dion–Jacobson phase $NaNdTa_2O_7$ is stable to ion exchange and form only water intercalates with formulae $NaNdTa_2O_7 \cdot 0.6H_2O$ and $NaNdTa_2O_7 \cdot 1.35H_2O$.

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