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Thermal Stability of Layered Perovskite-Like Oxides $NaNdTiO_4$ and $Na_2Nd_2Ti_3O_{10}$

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Abstract—Thermal stabilities of layered perovskite-like oxides $NaNdTiO_4$ and $Na_2Nd_2Ti_3O_{10}$ were studied in the temperature ranges from 780 to 1100°C and from 1100 to 1400°C, respectively. Chemical mechanism of their thermal decomposition was proposed. Higher thermal stability of $Na_2Nd_2Ti_3O_{10}$ was rationalized on the basis of crystallochemical data.

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A large number of layered perovskite-like compounds and solid solutions based thereon have been studied up to now. These compounds constitute one of the most promising classes of ceramic materials. Depending on their composition and structure, they possess a broad spectrum of technically important physicochemical properties, such as high ionic conductivity [1, 2], high-temperature superconductivity [3], giant magnetoresistance [4], and catalytic and photocatalytic activity [5–8]. However, a necessary condition for successful application of these materials in one or another branch of chemical industry, electronics, or energetics is knowledge of their thermal stability.

In the present article we report on two layered perovskite-like titanates belonging to the homologous series $(Na,Nd)_{n+1}Ti_nO_{3n+1}$, where n is number of perovskite layers; $NaNdTiO_4$ contains one perovskite layer, and $Na_2Nd_2Ti_3O_{10}$, three perovskite layers. The existence in this series of hypothetical two-layer oxide is impossible because of electroneutrality. Interest in these compounds originates from perspectives in their use as catalysts of photoinduced reactions, including decomposition of water with generation of hydrogen as alternative fuel and decomposition of toxic organic substances. The above oxides can also be used as precursors in mutual transformations of perovskite-like phases via ion exchange [9, 10].

The oxides $NaNdTiO_4$ and $Na_2Nd_2Ti_3O_{10}$ are representatives of the Ruddlesden–Popper phase [11]. Crystalline structures of these compounds resemble the structure of the complex oxides Sr_2TiO_4 and $Sr_4Ti_3O_{10}$, respectively: they belong to tetragonal crystal system, and the titanium atoms therein occur in octahedral environment (they are surrounded by oxygen atoms). The crystal structure of $Na_2Nd_2Ti_3O_{10}$ belongs to the same space symmetry group as strontium titanates, *I*4/*mmm* [12]. However, due to large difference in charges, sodium and neodymium cations are completely ordered by nonequivalent structural positions. As a result, sodium cations occupy nine-coordinate positions between perovskite structure type blocks, and they form with the nearest oxygen atoms rock salt structural fragments. Here, twelve-coordinate neodymium cations occupy positions inside perovskite block.

Unlike $Na_2Nd_2Ti_3O_{10}$, both sodium and neodymium atoms in $NaNdTiO_4$ are nine-coordinate. Ordering of the alkali and rare earth metal cations implies that one rock salt fragment is populated by only sodium cations, and the other, by only Nd ions. As s result, mirror symmetry plane passing through the centers of the octahedra orthogonally to the *c* axis is lacking, and *P*4/*nmm* space group appears [13–15].

It was interesting to elucidate the behavior of cation-ordered layered structures organized in a block mode at elevated temperature. Whether such structures are stable or they will undergo decomposition, for their structure already includes fragments (three- or two-dimensional) that may be precursors of the released phases. These problems were not studied so far.

In the present work we examined thermal stability of cation-ordered oxides $NaNdTiO_4$ and $Na_2Nd_2Ti_3O_{10}$

in the temperature ranges 780–1100 and 1100–1400°C, respectively. The lower limit of the temperature range was determined by the temperature of synthesis of the corresponding oxide [16, 17]. The study was performed by isothermal sintering followed by X-ray powder diffraction analysis of the sintered samples.

The results showed that $NaNdTiO_4$ is stable up to 900°C. The X-ray powder diffraction pattern of a sample of $NaNdTiO_4$ calcined at 900°C over a period of 6 h is the same as that of the pure substance with no traces of possible decomposition products. Heating of samples at 950, 1000, and 1050°C induced decomposition, and the degree of decomposition increased as the temperature rose. Apart from reflections typical of the initial compound ($NaNdTiO_4$), diffraction maxima belonging to three-layer $Na_2Nd_2Ti_3O_{10}$ oxide were present, and those corresponding to sodium-free phases were observed (Nd_2TiO_5 and $Nd_2Ti_3O_9$). The complete decomposition of $NaNdTiO_4$ occurred at 1100°C; the X-ray powder diffraction pattern of a sample calcined at that temperature showed the absence of traces of the initial compounds. Our results suggest that the decomposition of $NaNdTiO_4$ in the temperature range from 950 to 1100°C follows Eq. (1).

$$8\,NaNdTiO_4 \rightarrow Na_2Nd_2Ti_3O_{10} + 2\,Nd_2TiO_5 + Nd_2Ti_3O_9 + 3\,Na_2O. \qquad (1)$$

Figure 1 illustrates structural transformations corresponding to reaction (1).

At a temperature above 900°C, Na^+ and Nd^{+3} cations become disordered, so that rearrangement of atoms in the $NaNdTiO_4$ structure becomes possible. Perovskite layers in the –P–RS–P–RS– chain every two P layers are displaced by $(a + b)/2$ to produce structure $Na_2Nd_2Ti_3O_{10}$.

Apart from $Na_2Nd_2Ti_3O_{10}$, a compound with analogous structure ($Nd_2Ti_3O_9$) but containing no sodium atoms is formed. Unlike $Na_2Nd_2Ti_3O_{10}$, the oxide $Nd_2Ti_3O_9$ is characterized by a high density of oxygen vacancies localized in the interlayer space [18]. As a result, some titanium atoms residing in the vicinity of interlayer space are surrounded by only five oxygen atoms. One third of Nd^{3+} ions is transferred from the space in the perovskite layer block to the positions of oxygen vacancies, while two thirds remain in the layers. As a rough approximation, we can presume that a half of oxygen atoms occupying anionic positions in the interlayer space of the $Na_2Nd_2Ti_3O_{10}$ structure is replaced by irregularly distributed two thirds of Nd^{3+} cations and one third of O^{2-} anions.

The third product of decomposition of Nd_2TiO_5 belongs to the cuspidine structure type $Ca_4(Si_2O_7\Upsilon)\cdot(OH,F)_2$, where Υ stands for a vacancy [19]. By

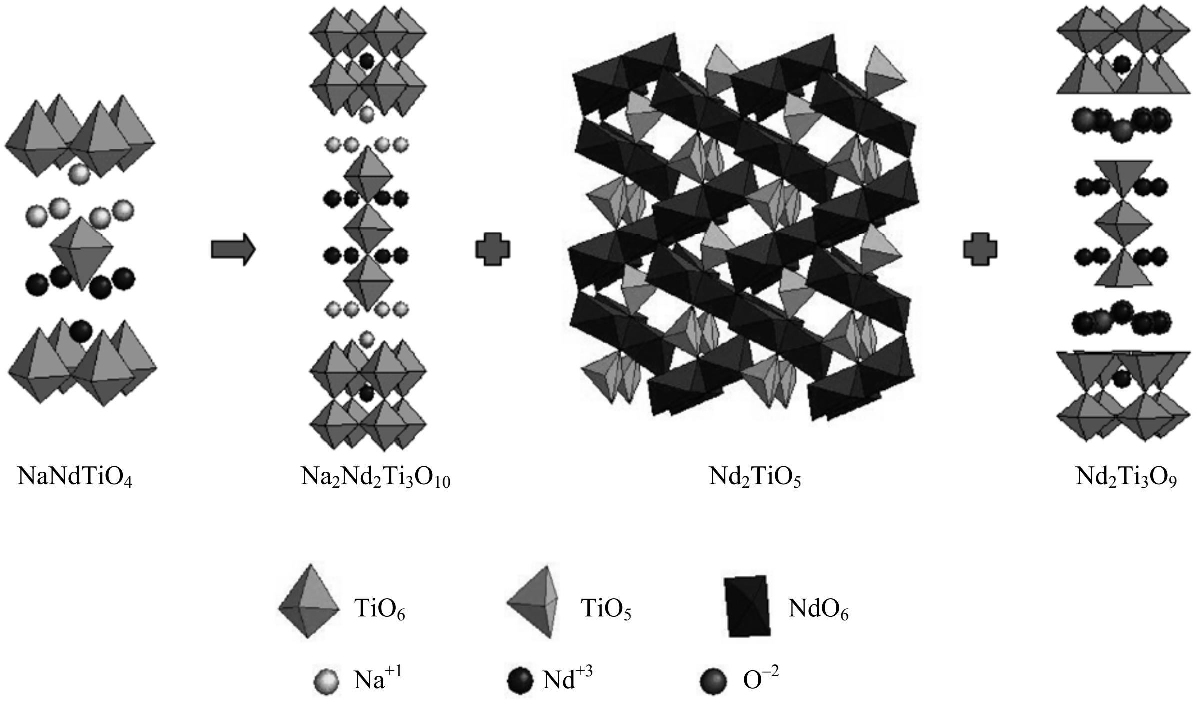

Fig. 1. Structural transformations in the thermal decomposition of $NaNdTiO_4$.

doubling the number of atoms in formula Nd_2TiO_5, this compound may be represented as $Nd_4(Ti_2O_8)O_2$. Instead of Si_2O_7 groups, the Nd_2TiO_5 structure includes isolated chains formed by vertex-joined TiO_5 trigonal bipyramids. The neodymium atoms coordinate oxygen atoms in the octahedral mode.

One product of reaction (1) should be Na_2O; however, this simple oxide was not detected by X-ray powder diffraction. A probable reason is that sodium oxide readily reacts with carbon dioxide on exposure to air with formation of sodium carbonate which cannot be distinguished from the other decomposition products due to relatively small reflection intensities. In addition, both sodium carbonate and sodium oxide are more volatile than the other components at high temperature.

The oxide $Na_2Nd_2Ti_3O_{10}$ was found to be stable up to 1100°C. The X-ray powder diffraction pattern of a sample of $Na_2Nd_2Ti_3O_{10}$ calcined at 1200°C displayed diffraction maxima corresponding to Nd_2TiO_5, $Nd_2Ti_3O_9$, and $Nd_{2/3}TiO_3$. The two latter phases are different crystalline modifications of a compound with the composition $Nd_2Ti_3O_9$: one of these has tetragonal structure, and the structure of the other phase is distorted to orthorhombic. After sintering at 1300°C, diffraction peaks of $Nd_2Ti_2O_7$ appear in addition to those of the above listed titanates. As the temperature approaches 1400°C, reflections corresponding to Nd_2TiO_5 and $Nd_2Ti_3O_9$ disappear, and $Nd_{2/3}TiO_3$, $Nd_2Ti_2O_7$, and traces of the initial oxide ($Na_2Nd_2Ti_3O_{10}$) remain in the sample. Prolonged calcination at 1400°C leads to complete decomposition of $Na_2Nd_2Ti_3O_{10}$, as follows from disappearance of the peak at a small angle ($2\theta = 6.32°$) typical of layered perovskite-like compounds.

Thus the results of X-ray powder diffraction analysis indicated that the products of decomposition of $Na_2Nd_2Ti_3O_{10}$ are Nd_2TiO_5 and $Nd_{2/3}TiO_3$. On the basis of stoichiometric considerations, the formation of TiO_2 (rutile modification) which is not detected by X-ray analysis may be presumed in addition to the above products. Presumably, at temperatures above 1100°C small TiO_2 particles with a large surface area are transformed from liquid-like state (generated at a temperature equal to 2/3 of the melting point [20]; mp 1870°C) to amorphous state. The thermal decomposition of $Na_2Nd_2Ti_3O_{10}$ can be described by Eq. (2):

$$2Na_2Nd_2Ti_3O_{10} \rightarrow 3Nd_{2/3}TiO_3 + Nd_2TiO_5 + 2TiO_2 + 2Na_2O. \quad (2)$$

No Nd_2TiO_5 phase was detected in the sample calcined at 1400°C, but reflections corresponding to $Nd_2Ti_2O_7$ were observed. Therefore, $Nd_2Ti_2O_7$ is unlikely to be formed directly from $Na_2Nd_2Ti_3O_{10}$ but is generated according to Eq. (3).

$$TiO_2 + Nd_2TiO_5 \rightarrow Nd_2Ti_2O_7. \quad (3)$$

Structural transformations accompanying reactions (2) and (3) are illustrated by Figs. 2a, 2b. Below 1300°C, $Nd_2Ti_3O_9$ is detected in the X-ray powder patterns together with $Nd_{2/3}TiO_3$, and only the latter is stable above that temperature. Thus $Nd_2Ti_3O_9$ is an intermediate in the transformation into three-dimensional cation-deficient compound $Nd_{2/3}TiO_3$ [reaction (4)]:

$$Nd_2Ti_3O_9 \rightarrow 3\,Nd_{2/3}TiO_3. \quad (4)$$

Layered perovskite-like structure is still retained in $Nd_2Ti_3O_9$, whereas $Nd_{2/3}TiO_3$ has a perovskite structure in which one third of Nd^{3+} positions are vacant [21].

As the temperature rises, the thermal decomposition of $Na_2Nd_2Ti_3O_{10}$ is characterized by degradation of phases with less distorted structure and stabilization of structures with lower symmetry. In the temperature range from 1300 to 1400°C Nd_2TiO_5 is converted into $Nd_2Ti_2O_7$ whose structure is represented by infinite layers of very strongly distorted TiO_6 octahedra [22].

The microphotographs of polycrystalline $NaNd\cdot TiO_4$ and $Na_2Nd_2Ti_3O_{10}$ samples (Figs. 3a, 3b) revealed different morphologies of their particles. Samples of $NaNdTiO_4$ consist of extended particles with a size not exceeding 1 µm, while $Na_2Nd_2Ti_3O_{10}$ particles have irregular shape with a size of 3.5 µm. The microphotographs of the decomposed compounds (Figs. 3c, 3d) show their multiphase structure: different shapes and sizes of particular polycrystals are obvious.

The stability of compounds having a layered structure may be rationalized by considering structural specificities of complex oxides. From the viewpoint of crystal chemistry, different thermal behaviors of layered oxides are determined by different degrees of anisotropy of their structure and chemical bonds. Phase transformations are accompanied by change of coordination environment of Nd^{3+} cations (the coordination numbers are equal to 9, 12, and 6) and Ti^{4+} (coordination numbers 6 and 5) and considerable distortion of the coordination polyhedra. The coordination numbers of Nd^{3+} and Ti^{4+} in the initial oxides and their decomposition products are given in table.

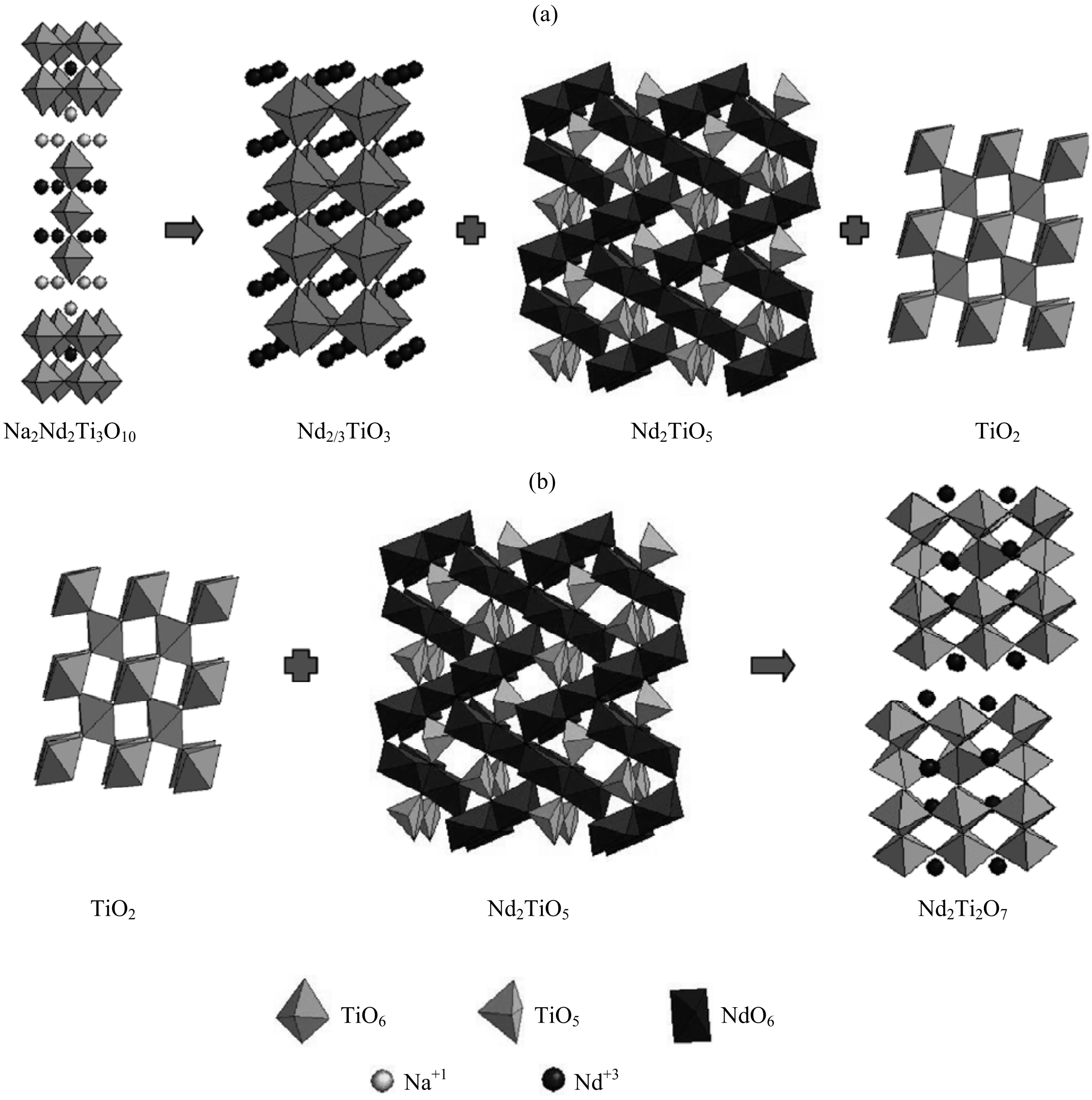

Fig. 2. Structural transformations in the (a) thermal decomposition of $Na_2Nd_2Ti_3O_{10}$ and (b) formation of $Nd_2Ti_2O_7$ from the decomposition products of $Na_2Nd_2Ti_3O_{10}$.

The formation of layered structures involves distortion of polyhedra through simultaneous extension and shortening of the axial (i.e., directed along the *c* axis) Ti–O bonds. For example, Ti^{4+} cations in $NaNdTiO_4$ are surrounded by oxygen anions in octahedral mode and are somewhat displace from the octahedron center along the *c* axis; the four equatorial Ti–O bonds have equal lengths, while one axial Ti–O is shortened (1.738 Å), and the other is strongly extended (2.541 Å). In the crystalline structure of $NaNdTiO_4$ one rock salt layer is populated by only sodium cations, and the other, by only neodymium ions. Insofar as the charge between perovskite layers is compensated incompletely due to ordering of Na and Nd cations, Ti^{4+} ions are displaced toward the sodium-containing layer, and just that factor is responsible for distortion of the titanium octahedra. Unlike one-layer structures, triple perovskite layers consisting of TiO_6 octahedra in the structure of $Na_2Nd_2Ti_3O_{10}$ are separated only by double NaO layer. Three octahedra

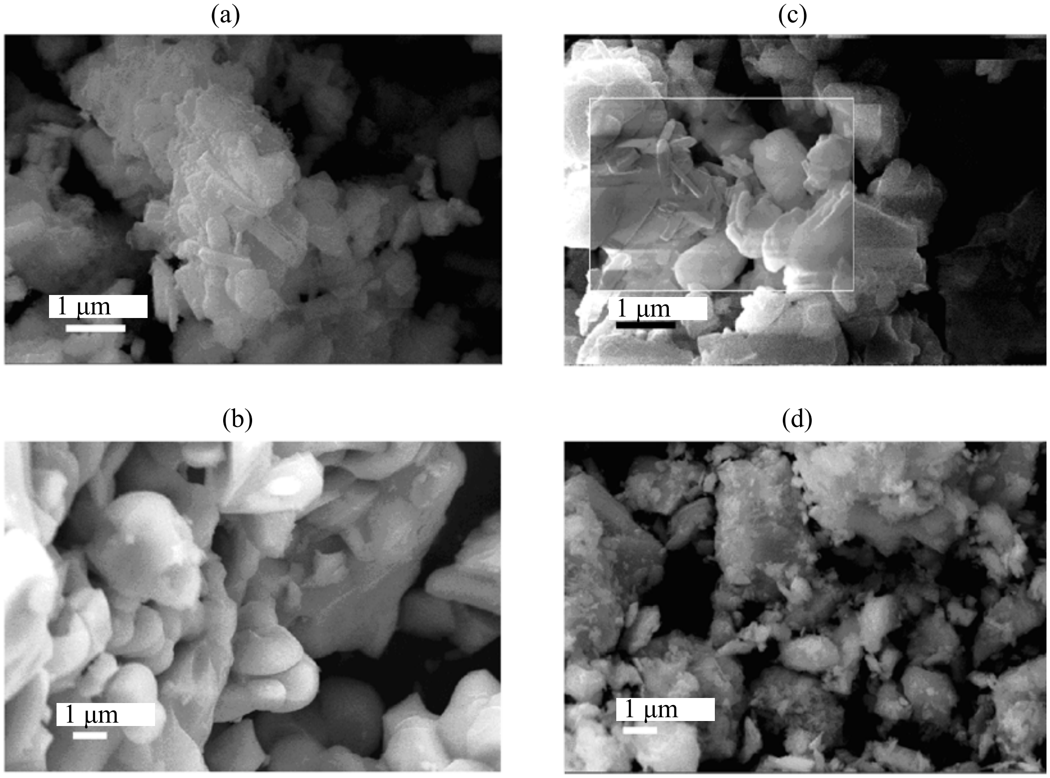

Fig. 3. Electron microphotographs of (a, b) initial and (c, d) decomposed samples of (a, c) $NaNdTiO_4$ and (b, d) $Na_2Nd_2Ti_3O_{10}$.

arranged along the *c* axis, which form the triple layer, are distorted to different extents. The character of distortion of the terminal octahedra is similar to that observed for one-layer compounds, whereas the central octahedron is distorted insignificantly; in combination with Nd cations it resembles a fragment of perovskite structure, which is a stable entity.

Titanium atoms in the layered structure retain their six-coordinate state, as in perovskite, while the environment of Nd atoms may change considerably; as a result, the structure is destabilized. The coordination number of Nd in $Na_2Nd_2Ti_3O_{10}$ with triple perovskite layer is equal to 12, which is more energetically favorable for large cations; the Nd atoms in $NaNdTiO_4$ are nine-coordinate.

Different lengths of the bridging Na–O bonds which connect different layers, the coordination environment of Na^+ cations (coordination number 9) in compounds with $n = 1$ and $n = 3$ being the same, are also responsible for the higher stability of the layered

Symmetry, unit cell parameters, and coordination numbers of cations in the initial oxides $NaNdTiO_4$ and $Na_2Nd_2Ti_3O_{10}$ and their decomposition products

Compound	Space group (crystal system)	Unit cell parameters, Å	Coordination number	
			Nd^{3+}	Ti^{4+}
$NaNdTiO_4$	*P*4/*nmm* (tetragonal)	*a* = *b* = 3.7506, *c* = 12.824	9	6
$Na_2Nd_2Ti_3O_{10}$	*I*4/*mmm* (tetragonal)	*a* = *b* = 3.8182, *c* = 28.369	12	6
Nd_2TiO_5	*Pnam* (orthorhombic)	*a* = 10.72, *b* = 11.361, *c* = 3.84	6	5
$Nd_2Ti_3O_9$	*I*4/*mmm* (tetragonal)	*a* = *b* = 3.8334, *c* = 24.363	12	6
$Nd_{2/3}TiO_3$	*Pmmm* (orthorhombic)	*a* = 3.8335, *b* = 3.852, *c* = 7.7413	12	6
$Nd_2Ti_2O_7$	*P*21 (monoclinic)	*a* = 7.677, *b* = 5.456, *c* = 26.013	12	6

structure of $Na_2Nd_2Ti_3O_{10}$ which is characterized by stronger interaction between perovskite layers and Na^+ cations in rock salt blocks. The Na–O bond length in $Na_2Nd_2Ti_3O_{10}$ is 2.28 Å against 2.33 Å in $NaNdTiO_4$ [23].

Our experimental data on the thermal stability of layered oxides $NaNdTiO_4$ and $Na_2Nd_2Ti_3O_{10}$ indicate that the structure of completely ordered compounds may become unstable under certain thermodynamic conditions and that it may undergo decomposition into structurally related phases. At elevated temperature, Ruddlesden–Popper one-layer phase ($NaNdTiO_4$) is converted into $Na_2Nd_2Ti_3O_{10}$ with triple perovskite layer, and further increase in temperature induces transformation of $Na_2Nd_2Ti_3O_{10}$ into deficient perovskite $Nd_{2/3}TiO_3$ structure type.

Thus, layered perovskite-like titanates $NaNdTiO_4$ (one perovskite layer) and $Na_2Nd_2Ti_3O_{10}$ (three perovskite layers) at high temperature tend to be converted into more stable structure, either perovskite or layered structure with a larger number of perovskite layers. These findings provide one more support to the fact that synthetic perovskite-like structures are less stable than the natural perovskite structure.

EXPERIMENTAL

The thermal stability of oxide samples was studied by isothermal sintering and annealing. Series of experiments were performed, starting from the temperature of synthesis of the examined compounds to the temperature of their complete decompositin. The initial temperature for $NaNdTiO_4$ was 900°C, taking into account that this temperature ensures preparation of the pure compound. Samples were heated to 1100°C through a step of 50 deg. The stability of $Na_2Nd_2Ti_3O_{10}$ was studied in the temperature range from 1100 to 1400°C through a step of 100 deg. Samples of $NaNdTiO_4$ were kept for 6 h. Decomposition of $Na_2Nd_2Ti_3O_{10}$ required a longer time. Samples were analyzed on a qualitative level by X-ray powder diffraction. Morphology of the initial particles and decomposition products was determined by electron microscopy.

The complex oxides $NaNdTiO_4$ and $Na_2Nd_2Ti_3O_{10}$ were synthesized according to ceramic technology. As starting compounds we used commercial (Johnson Mattey) neodymium oxide Nd_2O_3 (containing 99.99% of the main substance), finely dispersed titanium oxide TiO_2 (99.9%, anatase; preliminarily calcined for 3 h at 780°C to remove moisture), and sodium carbonate Na_2CO_3 (99.5%). The syntheses were carried out under atmospheric pressure on exposure to air according to reactions (5) and (6).

$$Na_2CO_3 + 2\,TiO_2 + Nd_2O_3 \rightarrow 2\,NaNdTiO_4 + CO_2, \quad (5)$$

$$Na_2CO_3 + 3\,TiO_2 + Nd_2O_3 \rightarrow Na_2Nd_2Ti_3O_{10} + CO_2. \quad (6)$$

The reactants were weighed with an accuracy of 10^{-4} g and thoroughly mixed in an agate mortar over a period of 40 min per gram of the initial mixture. The resulting mixture was pressed into 0.5-g pellets with a diameter of 0.7 cm. Samples were sintered in a silicon carbide furnace, and the temperature was monitored by a platinum–rhodium thermocouple. The isothermal mode was maintained with an accuracy of ±1°C using a TP 403 programmable regulator. The oxide $NaNdTiO_4$ was obtained at 780°C in 3 h, and its three-layer homolog $Na_2Nd_2Ti_3O_{10}$ was synthesized in two steps by sintering for 3 h at 600°C and for 3 h at 1100°C. The initial mixture for the synthesis of $Na_2Nd_2Ti_3O_{10}$ was prepared using 40% excess of sodium carbonate to compensate its loss during the process.

Qualitative X-ray powder diffraction analysis of the obtained samples was performed on an ARL X'TRA diffractometer (CuK_α irradiation; scan range 2θ = 5–50° for $NaNdTiO_4$ and 5–70° for $Na_2Nd_2Ti_3O_{10}$ with a step of 0.04°, scan period 4 s). The phase composition was determined with the aid of ICDD PDF-2 database. The microphotographs of the initial samples and decomposition products were obtained using a Carl Zeiss EVO 40EP scanning electron microscope.

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