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Intercalation of Water in a Layered Perovskite Compound, $NaEuTiO_4$

Kenji Toda,* Yutaka Kameo,† Satoru Kurita,† and Mineo Sato†

Department of Active Material Chemistry, Graduate School of Science and Technology, Niigata University,
8050 Ikarashi 2-nocho, Niigata 950-21

†Department of Chemistry and Chemical Engineering, Faculty of Engineering, Niigata University,
8050 Ikarashi 2-nocho, Niigata 950-21

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Intercalation of water was observed in a layered perovskite compound, $NaEuTiO_4$, leading to its hydrated derivatives. There are some metastable intermediates in the hydrated derivatives. The hydration process includes several steps that are topotactic. The crystal structure of the hydrated derivatives was identified by Rietveld analysis for the powder X-ray diffraction pattern. It is confirmed that the water molecules are inserted into the sodium layer of $NaEuTiO_4$.

Since the discovery of layered perovskite compounds, $NaLnTiO_4$ (Ln=rare earth), two research groups have been investigating the luminescence properties.[1,2] However, they did not identify the refined atomic positions. We have clarified the crystal structure of $NaLnTiO_4$.[3,4] The structural model for $NaEuTiO_4$ is illustrated in Fig. 1. In the course of the study, we found that an intercalation of water is possible for $NaLnTiO_4$, leading to hydrated derivatives.

It is interesting to study the nature of water species in the intercalated layers. Domen et al. reported that some layered compounds showed a noticeable photocatalytic activity.[5,6] Titanates such as TiO_2 and $SrTiO_3$ are most popular materials for use in photoelectrolysis cells because of their small electron affinity and low flat band potential.[7,8] Inoue et al. reported that the distortions of the host framework influence the photocatalytic activity.[9] $NaLnTiO_4$ has a two-dimensional framework formed by the distorted corner-sharing TiO_6 octahedra. Therefore, the hydrated derivatives of $NaLnTiO_4$ are thought to be candidates for new heterogeneous catalysts.

Studies on hydration in layered perovskite compounds have been little reported.[10—14] To the best of our knowledge, there is a single one on structural characterization of a hydrated K_2NiF_4-type compound.[15] The layered perovskite compound $NaLnTiO_4$ is of particular interest because it is the only $AA'BO_4$ compound that contains ordered A-site cations. In this structure the perovskite sheets follow each other with two types of interlayer; one (sodium layer) can be exchanged by various cations while the other (rare earth layer) can induce an absorption in the visible region. Modification of the interlayer can be controlled by the ion exchange of sodium ions and substitution of rare earth ions. Therefore, we expected that layered perovskite compounds, $NaLnTiO_4$ (Ln=rare earth), have a potential to act as a "two-dimensional" photocatalyst. We report in this paper the crystal structure of intermediates observed during its hydration.

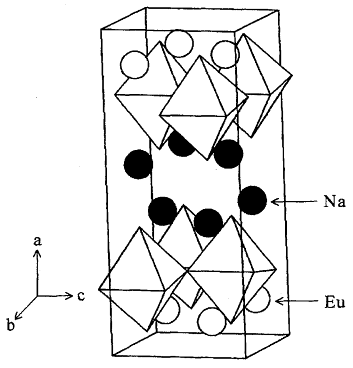


Fig. 1. Structural model of layered perovskite, $NaEuTiO_4$.

Experimental

The parent compound, $NaEuTiO_4$, was prepared by a conventional solid-state reaction. The starting materials were a mixture of sodium carbonate, europium oxide, and titanium oxide, An excess of sodium carbonate (30 mol%) was added to compensate for the loss due to the evaporation of the sodium component. The mixture was fired for 30 min at 900—1000 °C in air. The product was washed with distilled water. Then the product was immersed into water for 1 h—1 week and air-dried in a conditioned atmosphere (temperature 25 °C, relative humidity 60%) for 1 d. It is confirmed by flame reaction that there is no indication for the extraction of the sodium component. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku RAD-rA diffractometer, using Cu $K\alpha$ radiation, which was monochromatized by a curved crystal of graphite. The indexing of the powder XRD pattern for these compounds was examined with the aid of the computer program CELL.[16] Data analysis was done by the Rietveld method, using the RIETAN profile refinement program.[17] Thermogravimetric analysis (TGA) was done using a Mac Science thermal analyzer system 001 at a heating rate of 5 °C min^{-1} in air.

Results and Discussion

Water intercalation is characterized by crystallographic and thermal analysis. The intercalation of water into the interlayer of $NaEuTiO_4$ can be roughly classified into three stages, hereafter called α-phase, β-phase, and γ-phase. Figure 2 shows schematic representation of the stages in the transformation of $NaEuTiO_4$ to hydrated derivatives.

In a short immersion time ($t < 30$ min) α-phase was initially formed. It is difficult to isolate a single-phase of α-phase during the hydration process because the β-phase is much more stable on hydration in water than α-phase. The XRD patterns indicate that the samples contain a certain amount of β-phase. The β-phase could be isolated during the hydration process with a limited range of reaction time (30 min $< t <$ 1 h). The β-phase transforms into the γ-phase by further hydration. The γ-phase is unstable in the air at room temperature and stable in the water only. Its diffraction pattern, though similar to that of β-phase, shows a slight peak shift to the lower side of the diffraction angle compared to the β-phase. The γ-phase transforms into the α-phase when exposed to air. Since the transformation of α-phase in the air occurs rather rapidly, the structure of γ-phase has not been identified as an accurate crystal structure but is related to that of β-phase. The α-phase could be isolated by dehydration of the γ-phase. Exposing the α-phase to saturation vapor rehydrates it to the β-phase. The hydration–dehydration behavior was found to be reversible.

The XRD pattern (Fig. 3) obtained after immersion of the sample in water shows that diffraction peaks corresponding to the d-spacings along the stacking direction of the perovskite layer shift to the lower side of the diffraction angle during hydration. This obviously indicates that the water molecules can be easily inserted into the interlayer space of $NaEuTiO_4$. Since the insertion of water molecules was took place discontinuously step by step, the inserted water molecules seem to have some kind of zeolitic character.

Figure 4 show TGA data for the dehydration of α- and β-phase. TGA of the α-phase showed that 0.5 mole of water was lost up to 100 °C. TGA of the β-phase showed that 0.3 mole of water was lost up to 50 °C. Furthermore, TGA of the β-phase showed an additional step corresponding to the weight loss equivalent to that of 0.5 mole of water between 50—100 °C. On the basis of XRD patterns of various temperatures, the weight loss of the first step is attributed to the transformation from β- to α-phase. The total weight loss of α- and β-phase corresponds to 0.5 and 0.8 mole of water compared to the anhydrous, giving an initial composition of $NaEuTiO_4 \cdot 0.5H_2O$ and $NaEuTiO_4 \cdot 0.8H_2O$, respectively.

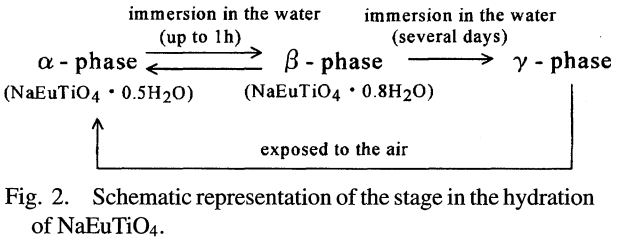


Fig. 2. Schematic representation of the stage in the hydration of $NaEuTiO_4$.

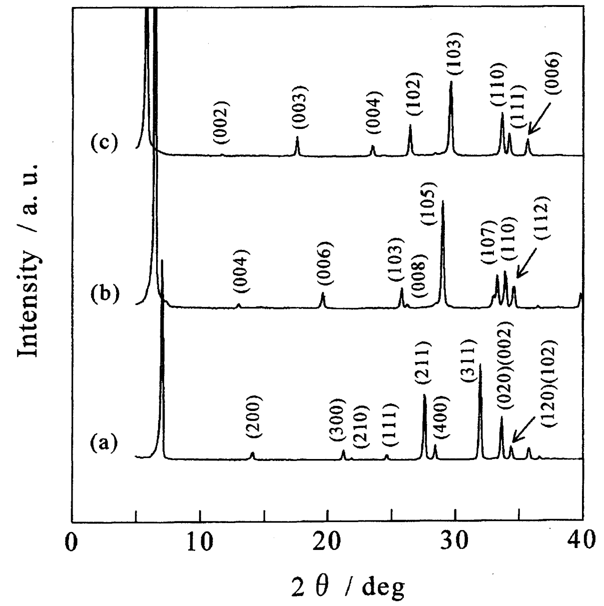


Fig. 3. Powder X-ray diffraction patterns for (a) $NaEuTiO_4$, (b) $NaEuTiO_4 \cdot 0.5H_2O$ [α-phase] and (c) $NaEuTiO_4 \cdot 0.8H_2O$ [β-phase].

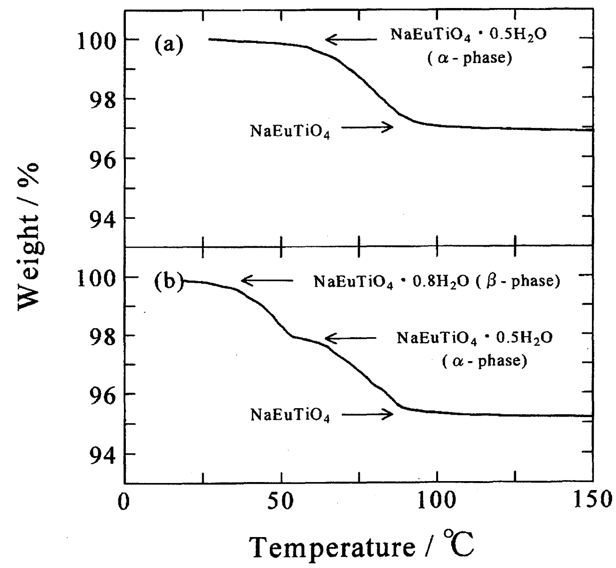
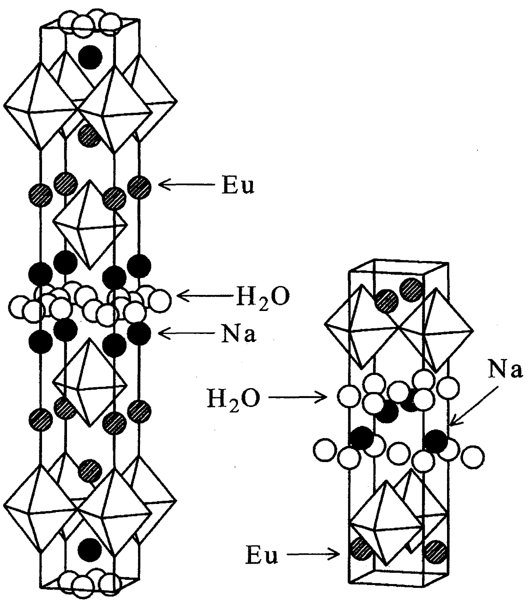


Fig. 4. TGA curve for (a) $NaEuTiO_4 \cdot 0.5H_2O$ [α-phase] and (b) $NaEuTiO_4 \cdot 0.8H_2O$ [β-phase].

We have proposed structural models for these compounds. The crystal structure found by the powder X-ray diffraction pattern using the Rietveld method, due to a lack of a single crystal. According to XRD data, the symmetry of α-phase is tetragonal with $a \approx 0.38$ nm and $c \approx 2.72$ nm. The reflection condition found was $h+k+l=2n$ for hkl reflections. This condition leds to eight possible space groups $I4$, $I\bar{4}$, $I4/m$, $I422$, $I4mm$, $I\bar{4}m2$, $I\bar{4}2m$, and $I4/mmm$. This result suggests that the structural unit of α-phase consists of an intergrowth of staggered perovskite layers with [EuO] rock salt layer and registered perovskite layers with $[(NaO)(H_2O)]$ layer. Refinement of the powder XRD data proceeded in several steps. The Rietveld refinement was done for all of the space groups in the early refinement stages. The perovskite layer and europium ions only were first refined. A difference Fourier map was then generated from the observed and calculated structure factors. It was confirmed that the water intercalates into the Na–O bilayer. Finally, the *I4/mmm* space group gave the most satisfactory fitting to the powder X-ray diffraction pattern. On the other hand, the XRD study of $NaEuTiO_4$ showed a tetragonal symmetry with only one systematic absence of $h+k=2n+1$ for $hk0$ reflections, indicating the possible space groups of *P4/n* or *P4/nmm* with $a \approx 0.38$ nm and $c \approx 1.51$ nm. Initial atomic positions were calculated by shifting the coordinates of the parent compound, $NaEuTiO_4$. The water molecules are statistically distributed in the site, forming a square-planar coordination around sodium atom. The structural models for α- and β-phase refined are shown in Fig. 5. The crystallographic data finally obtained from the Rietveld refinement are listed in Table 1.

These results definitely confirm that the hydration processes of $NaEuTiO_4$ have a topotactic character. Nevertheless, it must be pointed out that the positions of light atoms remain rather doubtful. In both phases, the isotropic thermal parameters of sodium atom and water molecule are fairly large. This may be due to a disorder of sodium and water positions. The water molecule is likely to be distributed across several sites. We considered the possibility of distributing them statistically in additional sites. However, such a refinement does not improve the agreement between observed and calculated XRD patterns. It is difficult to identify accurately the positions of sodium atoms and oxygen atoms belonging to a water molecule in between the perovskite layers, owing to the fact that these elements have a smaller contribution to the structure factors obtained in X-ray diffraction because of their small and almost the same atomic scattering factors. Therefore, it is evident that the results obtained here on the atomic positions may be considered as a structural model rather than an accurate structure.

The water molecules in both hydrates have been found to intercalate into the sodium layer, leading to a large expansion of their distance. These hydration steps are accompanied by significant structural rearrangement. The structural changes are caused by increase of hydrated water molecules in the interlayer spaces. It is interesting to compare the hydration behavior of $NaEuTiO_4$ with that of $Na_2Eu_2Ti_3O_{10}$. The layered perovskite compound $Na_2Eu_2Ti_3O_{10}$, with a triple perovskite layer, does not exist in any hydrous form even when the compounds are washed with distilled water.[3,18] This result suggests that the thickness of the perovskite layer is fairly important for the hydration behavior of layered titanate compounds. These differences can be explained by a weak interaction between the perovskite layer and interlayer



(a) $NaEuTiO_4 \cdot 0.5H_2O$ (α-phase)   (b) $NaEuTiO_4 \cdot 0.8H_2O$ (β-phase)

Fig. 5. Structural model of (a) $NaEuTiO_4 \cdot 0.5H_2O$ [α-phase] and (b) $NaEuTiO_4 \cdot 0.8H_2O$ [β-phase]. It should be noted that the results in the present structural determination express an averaged structure for $NaEuTiO_4 \cdot xH_2O$ because the water molecule is likely distributed across several sites.

Table 1. Crystallographic Data for $NaEuTiO_4 \cdot 0.5H_2O$ (α-Phase) and $NaEuTiO_4 \cdot 0.8H_2O$ (β-Phase)

Sample	Atom	Site[a)]	g	x	y	z	B/nm^2
$NaEuTiO_4 \cdot 0.5H_2O$	Na	4e	1.0	0.0	0.0	0.44(1)	0.5(1)
I4/mmm (No. 139)	Eu	4e	1.0	0.0	0.0	0.3001(2)	0.008(2)
$a=0.37347(2)$ nm	Ti	4e	1.0	0.0	0.0	0.1257(6)	0.003(4)
$c=2.7135(1)$ nm	O(1)	4e	1.0	0.0	0.0	0.061(2)	0.01(2)
$R_{wp}=14.69\%$	O(2)	8g	1.0	0.0	0.5	0.142(1)	0.02(1)
$R_F=3.20\%$	O(3)	4e	1.0	0.0	0.0	0.220(2)	0.02(2)
	Ow	8j	0.25	0.22(3)	0.5	0.0	0.2(1)
$NaEuTiO_4 \cdot 0.8H_2O$	Na	2c	1.0	0.0	0.5	0.556(5)	0.14(3)
P4/nmm (No. 129)	Eu	2c	1.0	0.0	0.5	0.9099(4)	0.006(2)
$a=0.37571(2)$ nm	Ti	2c	1.0	0.0	0.5	0.218(1)	0.012(5)
$c=1.50956(9)$ nm	O(1)	4f	1.0	0.0	0.0	0.192(2)	0.002(2)
$R_{wp}=14.59\%$	O(2)	2c	1.0	0.0	0.5	0.062(4)	0.03(2)
$R_F=3.12\%$	O(3)	2c	1.0	0.0	0.5	0.332(4)	0.04(2)
	Ow	4f	0.4	0.0	0.0	0.40(1)	0.11(6)

a) Multiplicity and Wyckoff notation.

sodium ions in NaEuTiO$_4$. Although the interlayer cations in the NaEuTiO$_4$ and Na$_2$Eu$_2$Ti$_3$O$_{10}$ have the same rock-salt type coordination, there is a large difference for the interaction between the perovskite layer and interlayer cations in both compounds. The perovskite layers of Na$_2$Eu$_2$Ti$_3$O$_{10}$ are negatively charged and separated by interlayer sodium ions, leading to a strong interaction between perovskite slabs and interlayer sodium ions. On the other hand, the (EuO) layer in NaEuTiO$_4$ is positively charged and the (NaO) layer is negatively charged. Since the perovskite layer is thought to be electrically neutral, the interaction between the perovskite layer and interlayer cation is weak. Therefore, the intercalation of water is possible for NaEuTiO$_4$, leading to its hydrated derivatives.

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References

1) G. Blasse, *J. Inorg. Nucl. Chem.*, **30**, 656 (1968).

2) C. Linares and M. Blanchard, *C. R. Acad. Sci. Paris, Ser. B*, **286**, 387 (1978).

3) K. Toda, Y. Kameo, M. Ohta, and M. Sato, *J. Alloys Comp.*, **218**, 228 (1995).

4) K. Toda, Y. Kameo, S. Kurita, and M. Sato, *J. Alloys Comp.*, in press.

5) K. Domen, J. Yoshimura, T. Sekine, A. Tanaka, and T. Onishi, *Catal. Lett.*, **4**, 339 (1990).

6) K. Domen, Y. Ebina, and J. Kondo, *Res. Chem. Intermed.*, **20**, 895 (1994).

7) G. Campet, M. Jakani, J. P. Doumerc, J. Claverie, and P. Hagenmuller, *Solid State Commun.*, **42**, 93 (1982).

8) G. Bin-Daar, M. P. Dare-Edwards, J. B. Goodenough, and A. Hamnett, *J. Chem. Soc., Faraday Trans. 1*, **79**, 1129 (1983).

9) Y. Inoue, T. Kubokawa, and K. Sato, *J. Phys. Chem.*, **95**, 4059 (1991).

10) J. Gopalakrishnan and V. Bhat, *Inorg. Chem.*, **26**, 4299 (1987).

11) M. Sato, J. Abo, and T. Jin, *Solid State Ionics*, **57**, 285 (1992).

12) M. Sato, J. Abo, T. Jin, and M. Ohta, *J. Alloys Comp.*, **192**, 81 (1993).

13) M. Sato, K. Toda, J. Watanabe, and K. Uematsu, *Nippon Kagaku Kaishi*, **1993**, 640.

14) M. Richard, L. Brohan, and M. Tournoux, *J. Solid State Chem.*, **112**, 345 (1994).

15) R. V. Shpanchenko, E. V. Antipov, and L. M. Kovba, *Mater. Sci. Forum*, **133—136**, 639 (1993).

16) Y. Takaki, T. Taniguchi, H. Yamaguchi, and T. Ogura, *J. Ceram. Soc., Jpn. Int. Ed.*, **95**, 565 (1987).

17) F. Izumi, *Nippon Kesshou Gakkaishi*, **27**, 23 (1985).

18) K. Toda, Y. Kameo, M. Fujimoto, and M. Sato, *J. Ceram. Soc. Jpn.*, **102**, 737 (1994).