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# Soft-chemical reaction of layered perovskite $Na_2Nd_2Ti_3O_{10}$ and its microwave dielectric properties

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**Abstract**

The mechanism of soft-chemical reaction of $Na_2Nd_2Ti_3O_{10}$ has been investigated in terms of the structure and composition. The $Na_{0.21}Nd_{0.60}TiO_3$ was prepared by soft-chemical reaction using layered perovskite $Na_2Nd_2Ti_3O_{10}$ through protonated layered perovskite $H_{1.37}Na_{0.63}Nd_2Ti_3O_{10}$ with $HNO_3$ solution. The ion-exchange ratio of the $Na^+/Ti^{4+}$ in $Na_2Nd_2Ti_3O_{10}$ was estimated by using inductively coupled plasma spectrometry (ICP), and the weight loss of $H_2O$ were changed from 0.70 to 0.21. The products; the protonated $H_{1.37}Na_{0.63}Nd_2Ti_3O_{10}$ was transferred from layered perovskite to three-dimensional perovskite at around 400–600 °C as following topochemical condensation and dispersion the interlayer Na into Nd site. The crystal structure of $Na_{0.21}Nd_{0.60}TiO_3$ was assigned to a double perovskite structure with orthorhombic space group *Pmmm*. The dielectric properties of the specimen showed an $\varepsilon_r = 86$, a $Qf = 1500$ GHz and a $\tau_f = +270$ ppm/°C.

Also, the sintered ceramics containing $Na_{0.21}Nd_{0.60}TiO_3$ plate-like particles by spark plasma sintering (SPS) exhibited a $\{0\,0\,l\}$ orientation degree of 9.9%. The obtained samples showed anisotropy in the dielectric properties according to the different directions parallel and perpendicular to *c*-axis.


*Keyword:* Tungstenbronze-type compound; Impurities; Dielectric properties

## 1. Introduction

For several years, a titanates adopting the perovskite structure have been attracted as materials for applications in the electronic components industry. In particular, a solid solution based on $R_{2/3}TiO_3$ (R: rare earth element) with perovskite ceramics such as $La(Mg_{1/2}Ti_{1/2})O_3$–$La_{2/3}TiO_3$,[1] $NiTiO_3$–$La_{2/3}TiO_3$[2] and $La(Zn_{1/2}Ti_{1/2})O_3$[3] has been widely studied due to their exhibit useful dielectric properties. However, there are no reports for synthesis of pure $R_{2/3}TiO_3$ since it has an unstable structure due to one-third deficiency in R-site of its. On the other hand, a new technique; soft-chemical reaction can be easily converted crystal structure from one form to another through "soft" chemistry such as an intercalation, an ion-exchange, an exfoliation and a topochemical dehydration at low temperatures.[4] Also, these reactions are very versatile and can be used to synthesize compositions not attainable by conventional solid state method, thus we adopted it to synthesize unstable phase $Nd_{2/3}TiO_3$. For the synthesis $Nd_{2/3}TiO_3$, the layered perovskite $Na_2Nd_2Ti_3O_{10}$ was selected because it belongs to the Ruddresden–Popper phase exhibited easily ion exchange of the alkali metal or proton in aqueous or molten salt media.[5,6] Then we synthesized $Nd_{2/3}TiO_3$ as following two steps as shown in Fig. 1. The first step; the protonated oxides $H_2Nd_2Ti_3O_{10}$ were prepared by the ion-exchange, as show in Eq. (1). The second step; eliminate the $H_2O$ in interlayer proton and oxygen of perovskite layer with heating as show in Eq. (2):

$$Na_2Nd_2Ti_3O_{10} + 2HNO_3 \rightarrow H_2Nd_2Ti_3O_{10} + 2Na^+ + 2NO_3^- \quad (1)$$

$$H_2Nd_2Ti_3O_{10} \rightarrow Nd_2Ti_3O_9\,(Nd_{2/3}TiO_3) + H_2O \quad (2)$$

In this paper, we report the mechanism of soft-chemical reaction of $Na_2Nd_2Ti_3O_{10}$ with detail results of structure and composition. Also, the microwave dielectric properties of the products are presented.

## 2. Experimental

The layered perovskite $Na_2Nd_2Ti_3O_{10}$ as starting compound for soft-chemical reaction was prepared by the conventional

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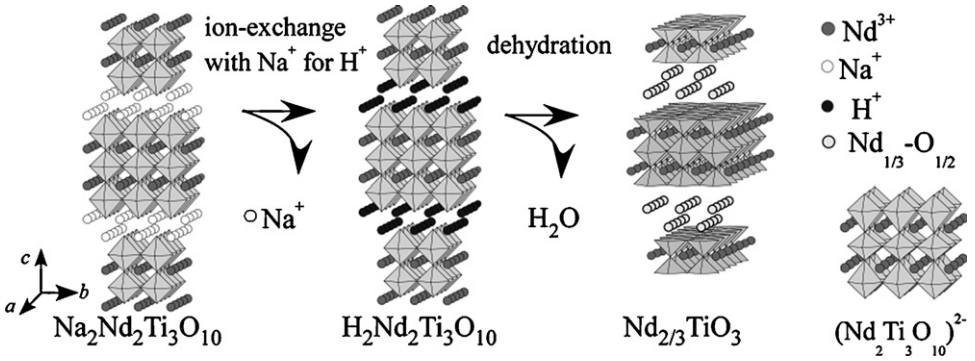


Fig. 1. Schematic representation of soft-chemical reaction with the layered perovskite $Na_2Nd_2Ti_3O_{10}$ (including dehydration and reduction).

solid state reaction method. Stoichiometric quantities of dried neodymium oxide; $Nd_2O_3$ (purity of 99.9%) preheated at 1000 °C, titanium oxide; $TiO_2$ (purity of 99.97%) and sodium carbonate; $Na_2CO_3$ (purity of 99.9%) were mixed with ethanol. After drying, the powder mixture was preheated at 1100 °C for 4 h in air. An excess amount of $Na_2CO_3$ (20 wt.%) was added to compensate for loss of alkali metal due to volatilization during heating. After the product grinding, the powder $Na_2Nd_2Ti_3O_{10}$ was continuously stirred by 300 rpm with 5 mol/dm$^3$ $HNO_3$ (100 cm$^3$ $HNO_3$ per gram $Na_2Nd_2Ti_3O_{10}$) for 96 h. The products were filtered out, and then washed with distilled water five times and dried at 120 °C for 3 h. The obtained products are calcined at 900 °C for 30 min, and then the powder was pressed into pellets and sintered at 1450 °C for 2 h, or consolidated by spark plasma sintering (SPS, SPS515S, SCM) process at 1250 °C for 5 min under 40 MPa, respectively.

The powder X-ray diffraction (XRD, X'pert MPD, Philips) using monochromatized Cu Kα radiation was performed for phase identification and determined the orientation degree of textured ceramics. The Rietveld refinement was carried out using a synchrotron radiation powder diffraction date obtained by a multiple two theta detector system (MDS) at BL-4B2 in Photon Factory of High Energy Accelerator Research Organization (PF-KEK), Thukuba, Japan. RIETAN-2000 program[7] was applied using approximately 29,002 intensity date collected in the two-theta range from 5° to 150°. Inductively coupled plasma spectrometry (ICP, ICPS-7000, Shimazu) was used for the ion-exchange ratio $Na^+/Ti^{4+}$. Microstructural observations were conducted using a scanning electron microscopy (SEM, JSM-5200, JEOL). Thermogravimetric analysis (TGA, TG8120, Rigaku) were performed to determinate the amount of eliminated $H_2O$. The density of the sintered ceramics was evaluated using Archimedes' method. Lotgering's method[8] was used to evaluate the orientation degree of samples. The orientation degree ($F$) was calculated from intensities of XRD peak using the formula, $F = (P - P_0)/(1 - P_0)$, where the $P$ is the ratio of the sum of oriented peak intensities to the sum of all peak intensities in the texture specimen pattern, and the $P_0$ is a similar ratio referring to the powder pattern with a random crystal orientation. The $F$ of the $\{0\,0\,l\}$ plane was calculated for the polished surfaces parallel and perpendicular to $c$-axis. Microwave dielectric properties were measured by using a Hakki and Coleman method[9] with a network analyzer (8720ES, Agilent) using the $TE_{0\,1\,1}$ mode. The temperature coefficient of resonant frequencies was measured in the temperature range between 20 and 80 °C. An impedance analyzer (HP-4294A, Agilent) was used for measurement of the temperature dependence of dielectric constant at 1 GHz. Prior to the measurement of the temperature dependence, silver electrodes were pasted on both side of the disk sample.

## 3. Results and discussion

### 3.1. Preparation of $Na_{0.21}Nd_{0.63}TiO_3$ particles

Fig. 2 shows the X-ray diffraction pattern of $Na_2Nd_2Ti_3O_{10}$ and the products treated with 5 mol/cm$^3$ $HNO_3$ solution at room temperature. The tetragonal diffraction peaks $\{0\,0\,l\}$ of all products were shifted to the high two-theta areas, and the intensity of these peaks was increased with increasing treating time. It sug-

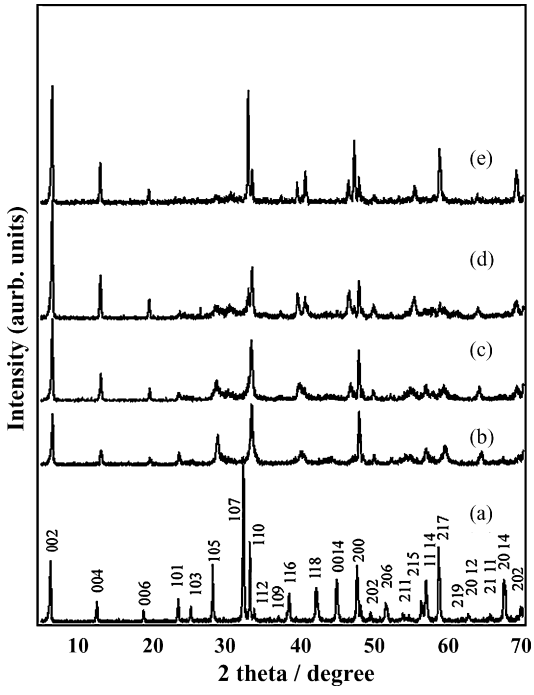


Fig. 2. XRD patterns of layered perovskite $Na_2Nd_2Ti_3O_{10}$ (a), and the products treated with $HNO_3$ for 12 h (b), 24 h (c), 48 h (d) and 96 h (e), respectively.

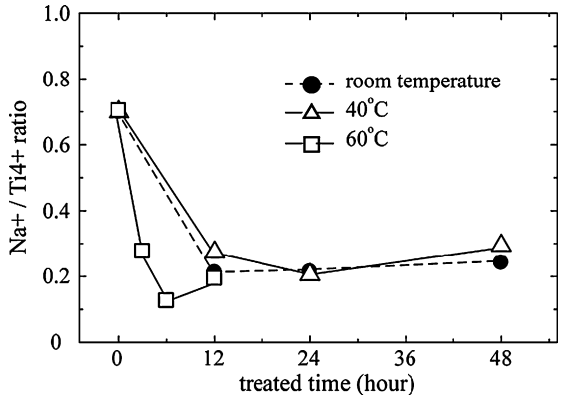


Fig. 3. The variation of $Na^+/Ti^{4+}$ ratios as a function of treated time for $Na_2Nd_2Ti_3O_{10}$.

gests that the exchange reaction shrinks the *c*-axis because the protons ($H^+$) with smaller than $Na^+$ ions occupy an interlayer spaces.

The ICP was carried out to estimate the ion-exchange ratio of the interlayer $Na^+$ ion versus $Ti^{4+}$ ion of perovskite-like slabs $(Nd_2Ti_3O_{10})^{2-}$ during the structural changing of $Na_2Nd_2Ti_3O_{10}$. The results are shown in Fig. 3. The $Na^+/Ti^{4+}$ ratio was decreased from 0.70 to 0.21 up to stirring time of 12 h at room temperature (RT). The products treated for 12 h were identified as a protonated oxide; $H_{1.37}Na_{0.63}Nd_2Ti_3O_{10}$. Treating time with longer than 12 h does not affect significantly the $Na^+/Ti^{4+}$ ratio. Also, large difference in the ion ratios was observed at the treated temperature of 40 and 60 °C, respectively.

Since the amount of the collected products was in inversely proportional to the increase of the reaction temperature, the products were almost not obtained in the case of treated at 60 °C. For this reason, we prepared the layered perovskite $H_{1.37}Na_{0.63}Nd_2Ti_3O_{10}$ by treated at RT for 12 h. The thermogravimetric analyses of the obtained $H_{1.37}Na_{0.63}Nd_2Ti_3O_{10}$ were performed to estimate the amounts of contents of loaded protons into the layers, because the exchanged proton into interlayer Na site could not estimate directly by ICP. Fig. 4 shows the temperature dependence of TG curve of the. $H_{1.37}Na_{0.63}Nd_2Ti_3O_{10}$. The weight loss of approximately 3% was observed in the range from 300 to 600 °C. The experimental weight loss results from elimination water produced by the

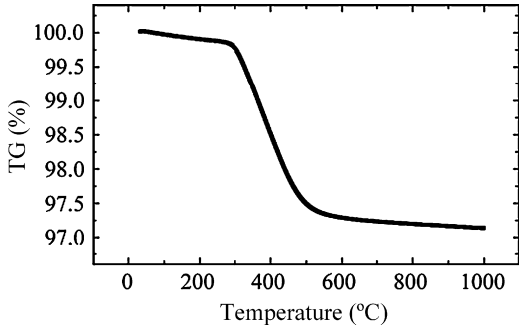


Fig. 4. Thermogravimetric analysis for protonated oxide; $H_{1.37}Na_{0.63}Nd_2Ti_3O_{10}$.

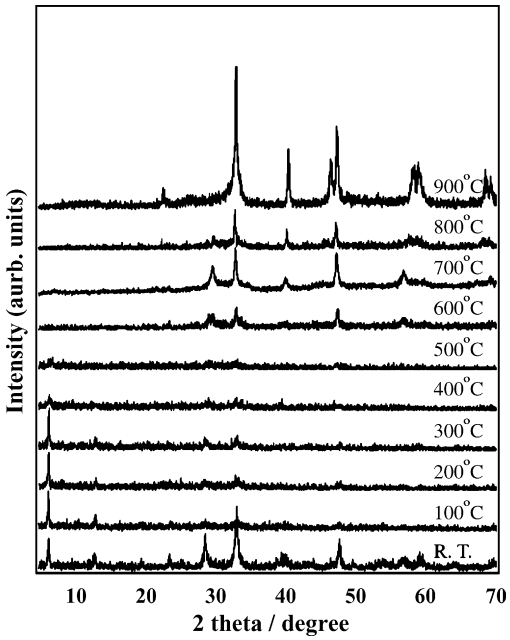


Fig. 5. Thermal evolution of protonated oxide; $H_{1.37}Na_{0.63}Nd_2Ti_3O_{10}$ in the range from RT to 900 °C.

interlayer proton and oxygen of perovskite layer. The weight loss is corresponded to the theoretical one estimated from the proton contents based on the analytical results.

The thermal structural evolutions of the $H_{1.37}Na_{0.63}Nd_2Ti_3O_{10}$ in the range from RT to 900 °C were shown in Fig. 5. Owing to the poor crystallization at high temperatures, a structure refinement was unsuccessful. The low-angle reflections represented layer-type structure, which observed up to 400 °C. Further more heating 600 °C, a protonated oxide phase showed three-dimensional perovskite phase after appearing the broad peaks in the range from 400 to 600 °C. The broad peaks may be due to the partial elimination of $H_2O$ produced by the interlayer protons and oxygen of perovskite, which causes the formation of the A-site defective three-dimensional perovskite. The $Na_{0.21}Nd_{0.60}TiO_3$ with three-dimensional structure was obtained at around 600 °C. The microstructure of particles obtained after heating at 900 °C was shown in Fig. 6. The particles exhibit plate-like shape with exfoliation of one-side direction.

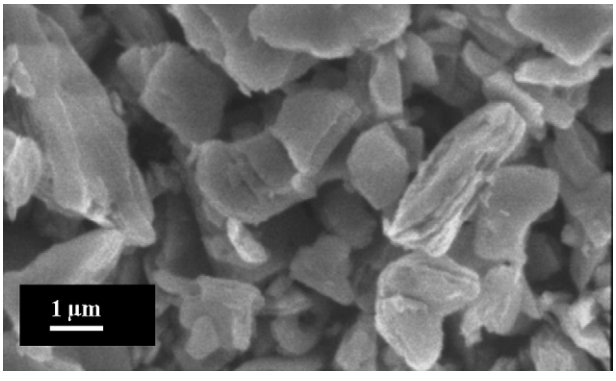


Fig. 6. SEM micrograph of $Na_{0.21}Nd_{0.60}TiO_3$ powder.

Table 1
Crystallographic data of $Na_{0.21}Nd_{0.60}TiO_3$

| Site | | Room temperature | | | | |
|---|---|---|---|---|---|---|
| | | *g* | *x* | *y* | *z* | *B* (Å$^2$) |
| Nd1 | 1c | 0.344(6) | 0 | 0 | 0.5 | 0.803(8) |
| Na1 | 1c | 0.21(4) | 0 | 0 | 0.5 | 0.81(2) |
| Nd2 | 1a | 0.856 | 0 | 0 | 0 | 0.636(9) |
| Na2 | 1a | 0.20 | 0 | 0 | 0 | 0.81(2) |
| Ti | 2t | 1 | 0.5 | 0.5 | 0.2611(1) | 2.41(8) |
| O1 | 1h | 1 | 0.5 | 0.5 | 0.5 | 1.2(1) |
| O2 | 2r | 1 | 0 | 0.5 | 0.2181(6) | 2.8(1) |
| O3 | 2s | 1 | 0.5 | 0 | 0.2691(7) | 1.9(1) |
| O4 | 1f | 1 | 0.5 | 0.5 | 0 | 0.636(9) |

*Note*: Orthorhombic, space group: *Pmmm* (no. 47). Occupancy for M atom *g*(M) is constrained as follows: $g(Nd1) = 1.20 - g(Nd2)$ and $g(Na1) = 0.42 - g(Na2)$. Thermal parameter *B* for Na is constrained as follows: $B(Na1) = B(Na2)$. $a = 3.83555(1)$ Å, $b = 3.83810(1)$ Å and $c = 7.73067(2)$ Å. $R_{wp} = 16.36\%$, $R_1 = 7.81\%$, $R_F = 5.31\%$ and $S = 1.38$.

### 3.2. Synthesis of the sintered sample $Na_{0.21}Nd_{0.60}TiO_3$ and its microwave dielectric properties

Table 1 lists the refined structure parameters of sintered sample $Na_{0.21}Nd_{0.60}TiO_3$ by Rietveld refinement. The reflections were confirmed a three-dimensional perovskite structure phase which has the alternative arrangement of the A-site cations (Na or Nd) along the *c*-axis assigned to the orthorhombic cell with $a(\sim a_p) \times b(\sim a_p) \times c(\sim 2a_p)$. The results indicate that the layered perovskite $H_{1.37}Na_{0.63}Nd_2Ti_3O_{10}$ was formed from the $Na_{0.21}Nd_{0.60}TiO_3$ by topochemical condensation and the diffusion of interlayer Na ions into Nd-site existed between $TiO_6$ octahedra of $Na_{0.21}Nd_{0.60}TiO_3$. The impurity phases; $Nd_2Ti_2O_7$ and $TiO_2$ were also confirmed. The dielectric properties of the specimen with density 4.48 g/cm$^3$ exhibited a $\varepsilon_r = 86$, a $Qf = 1{,}500$ GHz and a $\tau_f = +270$ ppm/°C.

### 3.3. Synthesis of the textured sintered sample $Na_{0.21}Nd_{0.60}TiO_3$ and its dielectric properties

We tried to synthesize textured ceramics by using SPS because the obtained $Na_{0.21}Nd_{0.60}TiO_3$ with plate-like particles (Fig. 6) is expected orientation by uniaxially pressure. The sintered ceramics showed the orientation aligned direction $\{0\,0\,l\}$, and its orientation degree *F* showed 9.9%. To investigate the effects of the orientation direction on dielectric properties, two samples with different direction parallel and perpendicular to *c*-axis were prepared as shown in Fig. 7. The temperature coefficient of dielectric constant ($\tau_\varepsilon$) of these samples; $Na_{0.21}Nd_{0.60}TiO_3$(//) and $Na_{0.21}Nd_{0.60}TiO_3$(⊥) were showed different values −391 ppm/°C and −349 ppm/°C.

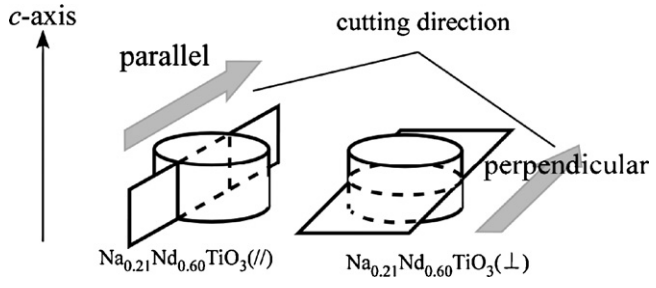


Fig. 7. Schematic illustrations of the samples cutting toward parallel and perpendicular to *c*-axis.

## 4. Conclusions

The soft-chemical reaction of layered perovskite $Na_2Nd_2Ti_3O_{10}$ results in the formation of three-dimensional perovskite $Na_{0.21}Nd_{0.60}TiO_3$ through the synthesis of protonated oxide of the $H_{1.37}Na_{0.63}Nd_2Ti_3O_{10}$ with layered perovskite structure. The $Na_{0.21}Nd_{0.60}TiO_3$ has the alternative arrangement of the A-site cations (Na or Nd) along the *c*-axis assigned to the orthorhombic cell with $a(\sim a_p) \times b(\sim a_p) \times c(\sim 2a_p)$. The dielectric properties of the sintered sample exhibited $\varepsilon_r = 86$, $Qf = 1500$ GHz and $\tau_f = +270$ ppm/°C.

The textured ceramics with the plate-like $Na_{0.21}Nd_{0.60}TiO_3$ particles showed orientation toward $\{0\,0\,l\}$ direction. The temperature coefficient of dielectric constant ($\tau_\varepsilon$) of the cutting samples with different directions. The $Na_{0.21}Nd_{0.60}TiO_3$(//) and $Na_{0.21}Nd_{0.60}TiO_3$(⊥) were showed different values −391 and −349 ppm/°C.

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