**Chemical composition and magnetic property modifications of Na₂Ti₂Sb₂O using
PTFE as an alkali-metal ion extraction reagent**

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Abstract: Na^+ extraction from $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ has been attempted using polytetrafluoroethylene (PTFE; empirical formula CF_2) as the extraction reagent. Systematic increase in both lattice parameters a along the intralayer direction and c along the interlayer direction was observed with respect to the reacted PTFE amounts, suggesting the successful deintercalation of the interlayer Na^+ . In addition, ferromagnet-like behavior, which is rare for systems consisting of ions with low magnetic moments, such as $\text{Ti}^{3+}(\text{d}^1)$, was observed in the Na^+ -deintercalated $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$. This result suggests that the method of *Alkali-metal ion Extraction using Polytetrafluoroethylene as an extraction reagent* (AEP) can be utilized in order to induce interesting and important properties in compounds including highly air- and solvent-sensitive mixed-anion compounds such as $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$.

KEYWORDS: deintercalation, PTFE, AEP, superconductivity, ferromagnetism, CDW, SDW, layered compound

1. Introduction

The discovery of superconductivity in Fe-based layered compounds [1-3] has generated renewed and intense interest in layered transition metal oxypnictides and led to the discovery of another class of layered oxypnictide superconductors based on Ti whose structure consists of $\text{Ti}_2\text{Pn}_2\text{O}^{2-}$ (Pn = pnictogen) layers interspersed with cations [4-7]. Such superconductivity in the $\text{Ti}_2\text{Pn}_2\text{O}^{2-}$ layer containing compounds was expected in $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ [8, 9] several years before the first experimental observation of the superconductivity in $\text{BaTi}_2\text{Sb}_2\text{O}$ and its K^+ -doped phases [4, 5]. The crystal structure of $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ consists of $\text{Ti}_2\text{Sb}_2\text{O}^{2-}$ layers interspersed with double layers of Na^+ where the $\text{Ti}_2\text{Sb}_2\text{O}^{2-}$ layer unit consists of a square net of Ti^{3+} and O^{2-} capped with Sb^{3-} above and below the center of the Ti-O square net [8, 10, 11].

$\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ has been studied for many years because it exhibits a charge-density-wave (CDW)/spin-density-wave (SDW)-like anomaly at around 120 K in its electrical and magnetic properties, and it was expected that superconductivity might be induced if charge carriers were increased in order to annihilate the CDW/SDW state [8-14]. In the case of $\text{BaTi}_2\text{Sb}_2\text{O}$, such an increase in the charge carriers was possible through partial replacement of the interlayer Ba^{2+} with Na^+ . An analogous way to increase hole carriers in $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ would be through partial deintercalation of the interlayer Na^+ . However, such Na^+ deintercalation from $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ has not been successful because of its extremely high air and solvent sensitivity. In our previous study of $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$, we observed instantaneous decomposition of $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ upon its exposure to air and its contact with both aqueous and organic solvents [8]. Therefore, conventional deintercalation approaches, such as soft-chemical and electro-chemical reactions requiring liquid phase, have not been successful.

Recently, we have developed a totally new method of *Alkali-metal ion Extraction using Polytetrafluoroethylene as an extraction reagent* (AEP) [15-17]. PTFE (*Polytetrafluoroethylene*) is usually considered as an inert material. However, we found that it reacts rather well with some of alkali-metal ion containing compounds; thus, it can possibly be used as an alkali-metal ion extraction reagent. The AEP reaction can be performed in an inert atmosphere or under vacuum without involving any liquid phase. Therefore, we attempted Na^+ deintercalation from $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ by the AEP reaction in order to clarify the unique applicability of AEP to air and liquid sensitive compounds and to study the characteristics of the Na^+ -deintercalated $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$.

2. Experimental section

2.1 Material Synthesis. $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ was synthesized by solid-state reaction of Na_2O , Ti and Sb in a sealed Ta tube as described elsewhere [8]. Extraction of Na^+ from $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ was attempted at 350 °C at various ratios of F to Na that is CF_2 (empirical formula of PTFE) to $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ under vacuum for 12 h in a sealed fused silica ampoule.

2.2 Measurements and Analysis. Powder X-ray diffraction (XRD) profiles of $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ and that reacted with PTFE were obtained using $\text{Cu } K_\alpha$ radiation on a Rigaku RINT2200V/PC diffractometer. The diffraction peaks were indexed, and the lattice parameters were refined using APPLEMAN software [18]. Magnetic properties of $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ and its PTFE-reacted samples were measured using a Quantum Design MPMS system.

3. Results and discussion

The deintercalation of Na^+ from $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ to dope hole carriers was attempted based on the following nominal reaction scheme:

Figure 1 shows the powder XRD profiles of $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ and its reaction products. The values of x are all nominal in the following descriptions. For $x \geq 0.25$, the intensity from TiSb_2 secondary phase increased significantly. This suggests that deintercalation of Na^+ proceeded with decomposition of $\text{Na}_{2-x}\square_x\text{Ti}_2\text{Sb}_2\text{O}$ in that range with the larger amounts of PTFE. This expectation is also consistent with the refined lattice parameters as functions of x as shown in Figure 2. Both a along the intralayer direction and c along the interlayer direction increase as the reacted PTFE amount, which is proportional to x , increases, but no significant change was observed for $x > 0.25$, indicating that the maximum deintercalation amount of Na^+ is around $x = 0.25$.

Figure 1. (a) Selected powder XRD profiles of $\text{Na}_{2-x}\square_x\text{Ti}_2\text{Sb}_2\text{O}$ ($x = 0$) and its deintercalated products reacted with various PTFE amounts at 350 °C for 12 h under vacuum. (b) Magnified XRD profiles for $x = 0, 0.15, 0.25$ and 1.00, clarifying the increase in the intensity from 200 reflection of NaF for $x > 0$.

Figure 2. Refined lattice parameters a (red) along the intralayer direction and c (blue) along the interlayer direction as functions of x in $\text{Na}_{2-x}\square_x\text{Ti}_2\text{Sb}_2\text{O}$.

The increase in c along the interlayer direction is similar to the case for the partial K^+ deintercalation from $\text{K}_{0.8}(\text{Li}_{0.27}\text{Ti}_{1.73})\text{O}_4$ by the AEP reaction [17]. It is attributed to the decrease in the net attraction between the $\text{Ti}_2\text{Sb}_2\text{O}_6^-$ layers and the interlayer Na^+ whose number was decreased by the reaction. On the other hand, the increase in a along the intralayer direction is likely due to the increased repulsion between the adjacent apical Sb^{3-} within the layers, again because of the partial loss of the four nearest neighbor interlayer Na^+ by the reaction, exceeding the ionic size decrease effect of Ti^{3+} oxidized into Ti^{4+} . These systematic changes in the lattice parameters and the formation of NaF (Figure 1b) as in the expected chemical equation 1 with respect to the increased amount of the reacted PTFE are indicative of successful extraction of Na^+ from $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ [17].

In order to understand the effect of Na^+ extraction on the physical properties of $\text{Na}_{2-x}\square_x\text{Ti}_2\text{Sb}_2\text{O}$, we have measured the temperature dependence of χ_g (mass magnetic susceptibility), focusing on $x \leq 0.25$ samples, and the result is shown in Figure 3. The nominal deintercalation amount x in $\text{Na}_{2-x}\square_x\text{Ti}_2\text{Sb}_2\text{O}$ is used for the description of the samples reacted with the different amounts of PTFE in the following discussion for

simplicity. The result indicates that χ_g values of $x = 0.05$ and 0.15 samples were close, but χ_g values, in general, increased as x increased. Ti in the pristine $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ is all in a relatively unstable $3+$ state; Ti in Ti^{3+} containing compounds tends to be oxidized into stable Ti^{4+} and hole carriers are doped by their cation deintercalation. For example, electro-chemical Na^+ deintercalation from a layered Ti-based bronze Na_xTiO_2 oxidizes its Ti^{3+} into Ti^{4+} rather than inducing the O^{2-} -site deficiency in order to charge compensate the deintercalated system [19]. Therefore, it is likely that Na^+ deintercalation from $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ predominantly oxidizes Ti^{3+} into Ti^{4+} minimizing the O^{2-} -site deficiency or replacement of O^{2-} with F^- .

Figure 3. Temperature dependence of zero-field-cooled χ_g of $\text{Na}_{2-x}\square_x\text{Ti}_2\text{Sb}_2\text{O}$.

When Na^+ is deintercalated and Ti^{3+} is oxidized into Ti^{4+} , hole carriers are doped into $\text{Na}_{2-x}\square_x\text{Ti}_2\text{Sb}_2\text{O}$. Such an increase in the carrier concentrations changes the density of state at the Fermi level; thus, the Pauli paramagnetic component of the susceptibility should also be affected systematically as in the observed data in Figure 3. In addition, the sharp increase in χ_g below 40 K is attributed to the impurity Curie component [20]. No superconducting transition was observed for any x down to 2 K even when χ_g was measured at a low applied magnetic field of $H = 50$ Oe, and no change in the on-set $T_{\text{CDW/SDW}}$ (CDW/SDW transition temperature) at around 120 K was observed. The lack

of $T_{\text{CDW/SDW}}$ change in $\text{Na}_{2-x}\square_x\text{Ti}_2\text{Sb}_2\text{O}$ is not as yet understood. However, considering the multiple-band behavior of $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$, indicated by its negative Hall coefficient and positive Seebeck coefficient in the study of Liu et al.,[14] an increase in the electron rather than hole carrier concentration might be necessary in order to annihilate the CDW/SDW state.

H dependence of M_g (mass magnetization) of $\text{Na}_{2-x}\square_x\text{Ti}_2\text{Sb}_2\text{O}$ at 290 K is shown in Figure 4. The pristine $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ ($x = 0$) exhibits a linear relation between M_g and H for the entire H range consistent with paramagnetism [8]. On the other hand, the curved increase in M_g , which is reminiscent of ferromagnetism, up to around 4000 Oe was observed for all the other products reacted with PTFE ($x > 0$). Above 4000 Oe, M_g and H have a linear relationship for all x , attributed to paramagnetism. These results suggest that the observed M_g consists of the combination of paramagnetic and ferromagnet-like magnetization components.

Figure 4. H dependence of M_g of $\text{Na}_{2-x}\square_x\text{Ti}_2\text{Sb}_2\text{O}$ at 290 K.

In order to quantify those two components, the M_g data were re-plotted using the following relation:

$$M_g = M_{g0} + (dM_g / dH) H$$

where M_{g0} is extrapolated zero-field M_g and dM_g / dH was approximated using $[(M_g \text{ at } 20000 \text{ Oe}) - (M_g \text{ at } 10000 \text{ Oe})] / (20000 \text{ Oe} - 10000 \text{ Oe})$. M_{g0} and dM_g / dH as functions of x are shown in Figure 5. dM_g / dH is a component of M_g that has linear dependence on H . Therefore, it could be considered as the paramagnetic component. It increases as the hole carrier doping amount x increases, consistent with the general trend in the temperature dependence of χ_g (Figure 3). The saturation in dM_g / dH occurs at roughly the same x as that in the lattice parameter trend (Figure 2). This behavior further suggests that Na^+ was successfully extracted by reacting $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ with PTFE, and hole carriers were doped into $\text{Na}_{2-x}\square_x\text{Ti}_2\text{Sb}_2\text{O}$, increasing its magnitude of Pauli paramagnetic susceptibility.

Figure 5. M_0 and dM / dH as functions of x in $\text{Na}_{2-x}\square_x\text{Ti}_2\text{Sb}_2\text{O}$ at 290 K.

On the other hand, M_0 was zero for $x = 0$. It shows a small but finite increase gradually up to $x = 0.15$, and it increases significantly thereafter. x around 0.15 must therefore be a critical Na^+ extraction amount in terms of the magnetization behavior of $\text{Na}_{2-x}\square_x\text{Ti}_2\text{Sb}_2\text{O}$ system. M_0 is related to spontaneous magnetism because it is a component of M_g extrapolated to $H = 0$. $\text{Na}_{2-x}\square_x\text{Ti}_2\text{Sb}_2\text{O}$ for all x , except for $x = 0$, exhibits finite value of M_0 , and its increase with respect to x suggests the induction of

ferromagnet-like magnetization by Na^+ extraction. However, no hysteresis was observed in the M_g versus H measurements (Figure 4). Therefore, if it is truly ferromagnetic, it must be very soft.

In addition, we have measured the H dependence of M_g of the PTFE heated at 350 °C under vacuum, and it was diamagnetic (linear M_g / H slope of $-1.76(4) \text{ emu g}^{-1} \text{ Oe}^{-1}$). This result confirmed that PTFE powder used in our experiment is not ferromagnetically contaminated and it does not transform into a ferromagnetic organic radical compound [21] by heating under vacuum. The appearance of a ferromagnetic state in compounds with a small number of spin or magnetic moment, such as d^1 and d^9 systems, is very rare. There are only a few cases where ferromagnetic behavior has been observed in compounds consisting of $\text{Ti}^{3+}(d^1)$ magnetic ions [22, 23]. Therefore, this result suggests that the deintercalation of Na^+ from $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ led to the induction of such an exotic property. The co-existence of the ferromagnetic and CDW/SDW-like behaviors observed in $\text{Na}_{2-x}\square_x\text{Ti}_2\text{Sb}_2\text{O}$ for $x > 0$ is a rare phenomenon. However, a similar ferromagnetic CDW behavior in VSe_2 nanosheet has also been reported [24]. Such an example suggests possible interplay between ferromagnetic and CDW/SDW behaviors; thus, it also suggests that the ferromagnetic behavior observed in our reaction products originates from the Na^+ -extracted $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ rather than from other ferromagnetic impurities.

In conclusion, the systematic changes in the lattice parameters and formation of NaF byproduct with respect to the reacted PTFE amounts were observed for $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ reacted with PTFE, indicating the successful extraction of Na^+ . Previously, AEP reactions have been applied only for fully oxidized compounds. The results from this study clarified that the AEP method can also be applied to mixed-anion compounds, such as oxypnictides. Furthermore, they indicated that the AEP method can uniquely be used for highly air- and solvent-sensitive compounds. These unique features of the AEP

method enable deintercalation of alkali-metal ions from compounds that cannot be deintercalated by conventional reaction approaches. Furthermore, the ferromagnet-like behavior, which is very rare for Ti^{3+} system, was observed in the Na^+ -extracted $\text{Na}_2\text{Ti}_2\text{Sb}_2\text{O}$ samples produced by the AEP reaction. Therefore, the results of this study also suggest that the AEP method can be utilized in order to induce interesting and important properties in deintercalated compounds, and this approach to modifying chemical compositions and physical properties of various compounds should provide a new route for materials design.

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