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Possibility of Superconductivity in New Reduced Tantalate and Titanate with the Layered Perovskite Structure

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Abstract

New reduced tantalate, $Na_2Ca_2Ta_3O_{10}$, and titanate, $Na_{1.0}Ca_{0.95}La_2Ti_3O_{10}$, were synthesized by intercalation reaction from the parent Dion–Jacobson and Ruddlesden–Popper type layered perovskite compounds. The crystal structure of the tantalate was determined by the Rietveld analysis of the powder X-ray diffraction pattern. The intercalation compound, $Na_2Ca_2Ta_3O_{10}$, is the first example of reduced tantalate with the Ruddlesden–Popper type structure. In some of reduced tantalate and titanate compounds, the diamagnetic signals have been observed below 7 K. Therefore, these compounds are thought to be good candidates for new oxide superconductors. © *1999 Elsevier Science Limited. All rights reserved*

Keywords: X-ray methods, magnetic properties, superconductivity, oxide superconductors, perovskites.

1 Introduction

The discovery of high temperature superconductor in the La–Ba–Cu–O system by Bednorz and Muller in 1986 have stimulated considerable interest in this research field.[1] The transport properties of the transition metal oxides depend mainly on two factors: (a) the interaction between the transition metal *d*-oxygen *s*/*p* orbital and (b) the dimensionality of crystal structure. For example, while $SrVO_3$ having a cubic perovskite structure is metallic, two-dimensional Sr_2VO_4 with a K_2NiF_4 structure is semiconducting.[2] The superconductivity and charge-density-wave instability are two most attractive physical properties in the low-dimensional transition-metal compounds with mixed d^1–d^0 configurations. The presence of such phenomena are considered to be caused by strong electron–phonon coupling.[3] Both strong on-site Coulomb repulsion and electron-phonon interaction are taken into account to study the high-T_c superconductors in many theoretical models. From such a standpoint, numerous experimental and theoretical studies have been performed extensively on many layered perovskite compounds.

In a recent paper, Maeno *et al.*[4] reported the superconductivity of the layered perovskite compound Sr_2RuO_4 which is a 4d transition metal oxide. This is a first example of non-cuprate superconductor with a same topology of the corner-sharing octahedra observed in the high temperature superconductor, $La_{2-x}Ba_xCuO_4$. Although the ruthenium strontium oxide superconductor, Sr_2RuO_4, has a number of similarities (strong Coulomb correlation and large anisotropy) to those of cuprate superconductor, there are some dissimilarities such as the electron configuration ($4d^4$) or spin state (low-spin state with spin 1).

Our strategies for search of new non-cuprate superconductors were the electron doping for the insulating d^0 system with a layered perovskite structure. The triple layered perovskite compounds, $NaCa_2Ta_3O_{10}$ and $Na_2La_2Ti_3O_{10}$, are thought to be good candidates for the insulating parent compounds.[5–7] The Ta^{4+} ($5d^1$) and Ti^{3+} ($3d^1$) valences are mutually complementary to the Cu^{2+} ($3d^9$) with a spin 1/2.

In this paper, we report the synthesis of new reduced tantalate, $Na_2Ca_2Ta_3O_{10}$, and titanate, $Na_{1.0}Ca_{0.95}La_2Ti_3O_{10}$, with a layered perovskite structure. These reduced compounds were synthesized by the soft chemical route such as the

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ion-exchange and intercalation reactions. The result of preliminary magnetic susceptibility measurements are also reported. They yield the information on the possibility of superconductivity in these reduced tantalate and titanate.

2 Experimental

RbCa$_2$Ta$_3$O$_{10}$ was prepared as previously described.[5] Sodium ion-exchanged compound, NaCa$_2$Ta$_3$O$_{10}$, was prepared by ion-exchange reaction of the rubidium compound.[6] The ion-exchange was carried out by reacting the RbCa$_2$Ta$_3$O$_{10}$ with molten NaNO$_3$ at 673 K for 24 h. After the reaction, the ion-exchanged product was collected, washed with distilled water and air-dried at room temperature. The completion of the ion-exchange reaction for sodium ion-exchanged compound, NaCa$_2$Ta$_3$O$_{10}$, was confirmed by XRD and X-ray fluorescence analyses. Sodium intercalation was carried out by reacting the sample NaCa$_2$Ta$_3$O$_{10}$ with sodium azide NaN$_3$ in an evacuated quartz tube at 673 K for 20 min. After the decomposition of the azide was completed, the tube was sealed off.

The compound Na$_2$La$_2$Ti$_3$O$_{10}$ was prepared as described in Ref.7. Layered perovskite Na$_{2(1\text{-}x)}$Ca$_x$La$_2$Ti$_3$O$_{10}$ ($x = 0{\cdot}95$) with the interlayer vacancy was prepared by the ion-exchange reaction with the multivalent cation.[8,9] The ion exchange was carried out by reacting the parent compounds with molten Ca(NO$_3$)$_2$ at 623 K for 72 h in an evacuated Pyrex tube. After the reaction, the precipitate of the product was collected, washed with distilled water and air-dried at room temperature. The preparation of reduced compound was performed by reacting the sample Na$_{0{\cdot}1}$Ca$_{0{\cdot}95}$La$_2$Ti$_3$O$_{10}$ with the sodium azide in an evacuated quartz tube at 673 K for 20 min. The chemical composition of the products were determined by the induction coupled plasma (ICP).

Both intercalation compounds were stored in the evacuated quartz ampoules because of the high unstability in the air. The products were characterized with X-ray powder diffraction and magnetic susceptibility measurements. Powder XRD patterns were recorded on a Rigaku RAD-rA diffractometer equipped with a hand made attachment for nitrogen gas flow. The data were collected by a step-scanning mode in the 2θ range of 20–100° with a step width 0·02° and a step time 4 s. The powder XRD patterns obtained were indexed with the aid of the computer program CELL.[10] The structure refinement was carried out by the Rietveld method, using the RIETAN94 profile refinement program.[11]

Temperature dependence of the magnetic susceptibility was measured for powder samples in the quartz ampoules using a Quantum Design MPMS-5S SQUID magnetometer (temperature range: 4·2–300 K; applied field: 50 G). The calibration was also made on a blank quartz ampoule under the same conditions as in the case of containing the samples.

3 Results and Discussion

Figure 1 shows the crystal structures of parent compounds, NaCa$_2$Ta$_3$O$_{10}$ and Na$_2$La$_2$Ti$_3$O$_{10}$. The compounds NaCa$_2$Ta$_3$O$_{10}$ is the layered perovskite materials with the partially occupied interlayer site. Since the interlayer sites of Na$_2$La$_2$Ti$_3$O$_{10}$ are fully occupied, the intercalation reaction never occur in this compound. Therefore, the ion-exchange reaction with the divalent cations was used to open the interlayer space. On alkali metal intercalation, the color of three sample powders changed from a white to dark blue color. Clearly, the reaction of parent compounds with the sodium azide results in the insertion of additional sodium metal. The intercalation compounds can easily be reoxidized when exposed to air at room temperature.

Powder XRD patterns of parent tantalate, NaCa$_2$Ta$_3$O$_{10}$, and intercalation compound, Na$_2$Ca$_2$Ta$_3$O$_{10}$, are given in Figs 2 and 3. The XRD pattern obtained after intercalation reaction of the sample shows that diffraction peaks corresponding to the d-spacings along the stacking direction of the perovskite layer shift to the higher side of the diffraction angle during intercalation. The reflection peaks of NaCa$_2$Ta$_3$O$_{10}$ and Na$_2$Ca$_2$Ta$_3$O$_{10}$ were indexed with a tetragonal symmetry. The reflection condition found was $h + k + l = 2n$ for hkl

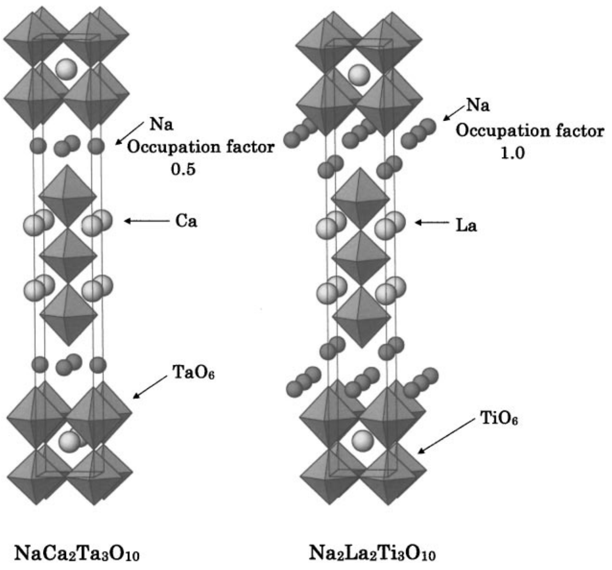

Fig. 1. Structural model of tantalate, NaCa$_2$Ta$_3$O$_{10}$, and titanate, Na$_2$La$_2$Ti$_3$O$_{10}$.

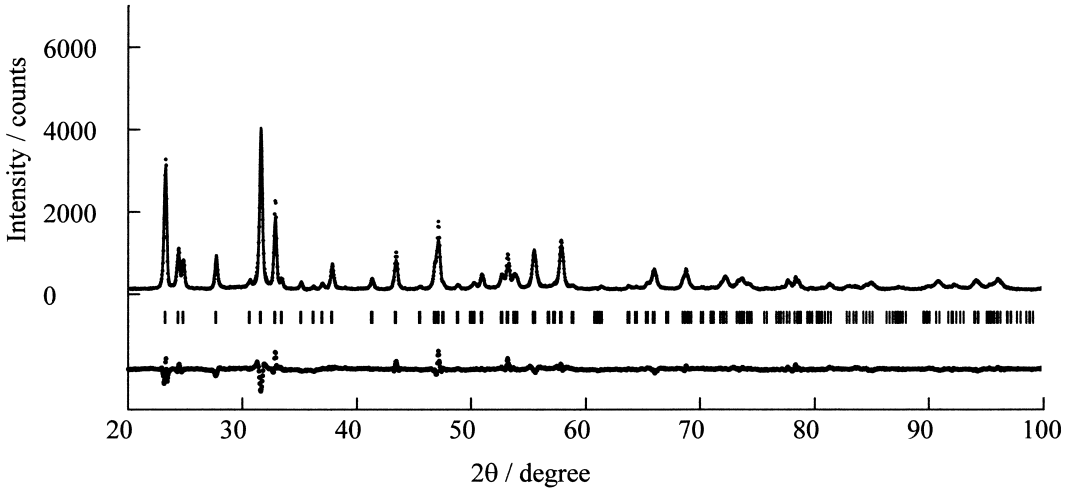

Fig. 2. X-ray powder pattern fitting for $NaCa_2Ta_3O_{10}$. The calculated and observed patterns are shown on the top by the solid line and the dots, respectively. The vertical marks in the middle show the positions calculated for Bragg reflections. The trace on the bottom is a plot of the difference between the calculated and the observed intensities.

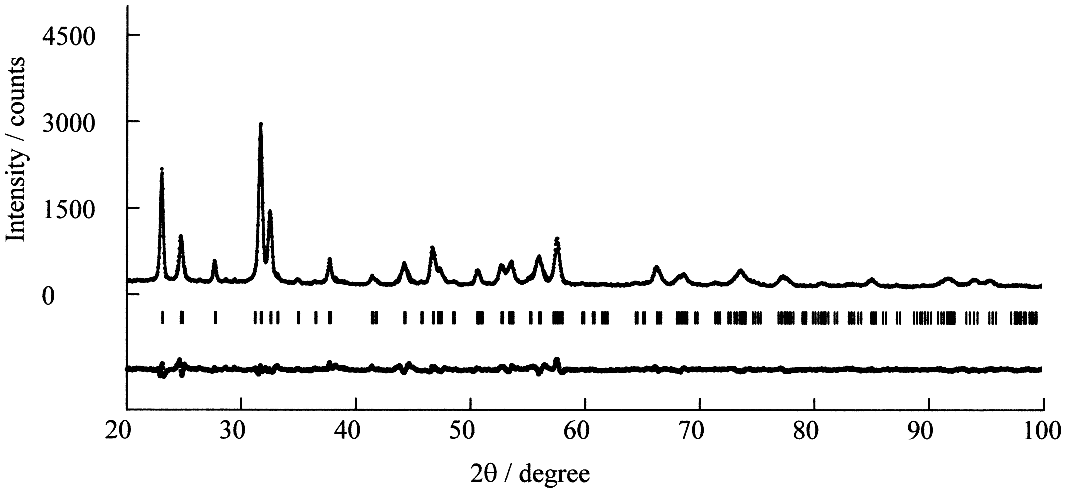

Fig. 3. X-ray powder pattern fitting for $Na_2Ca_2Ta_3O_{10}$.

reflections, leading to possible space groups with I-type lattice. In the early refinement stage, the site assignment for sodium ions was not included. In the final refinement stage, the location of the sodium ion site was estimated using difference Fourier maps. While the sodium ions in parent compound occupy the tetrahedral coordination sites between the perovskite layers, the coordination of Na–O observed in intercalation compound is a rock-salt type. The most reliable solution with physically meaningful crystallographic parameters was finally achieved when adopting I4/mmm space group for both compounds. The crystallographic data of $NaCa_2Ta_3O_{10}$ and $Na_2Ca_2Ta_3O_{10}$ are listed in Table 1. As shown in Fig. 4, the structure of intercalation compound, $Na_2Ca_2Ta_3O_{10}$, is composed of a triple layered perovskite unit and a rock-salt unit of sodium ion stacked alternately along the *c*-axis. Therefore, this compound is the first example of reduced tantalate with Ruddlesden-Popper type structure.

Figure 5 shows the powder XRD patterns of $Na_2La_2Ti_3O_{10}$, $Na_{0.1}Ca_{0.95}La_2Ti_3O_{10}$ and the intercalation compound $Na_{1.0}Ca_{0.95}La_2Ti_3O_{10}$. The *c*-axis lattice constant becomes smaller after the ion-exchange process. This shrinkage is due to the smaller ionic radius of calcium ion. The ion-exchanged compound, $Na_{0.1}Ca_{0.95}La_2Ti_3O_{10}$, originally white, exhibit deep blue color upon intercalation. The increased interlayer charge density of the sodium ion in the intercalation compound leads to a large contraction along the stacking direction of perovskite layers. This behavior is approximately consistent with the reductive intercalation of the Dion–Jacobson series member.[12]

Finally, we mention the result of preliminary magnetic susceptibilities measurements for reduced tantalate, $Na_2Ca_2Ta_3O_{10}$ and titanate, $Na_{1.0}Ca_{0.95}$ $La_2Ti_3O_{10}$. Due to the electrical neutrality in the intercalation compounds, the average formal oxidation states of the tantalum in $Na_2Ca_2Ta_3O_{10}$ and the titanium in $Na_{1.0}Ca_{0.95}La_2Ti_3O_{10}$ are $+4{\cdot}67$

Table 1. The crystallographic data of $NaCa_2Ta_3O_{10}$ and $Na_2Ca_2Ta_3O_{10}$

Sample	*Atom*	*Site*[a]	g[b]	x	y	z
$NaCa_2Ta_3O_{10}$	Na	4d	0·5	0·0	0·5	0·25
I4/mmm (no. 139)	Ca	e4	1·0	0·0	0·0	0·426(1)
$a = 0{\cdot}38607(3)$ nm	Ta(1)	2a	1·0	0·0	0·0	0·0
$c = 2{\cdot}9216(2)$ nm	Ta(2)	4e	1·0	0·0	0·0	0·1452(2)
	O(1)	4c	1·0	0·0	0·5	0·0
	O(2)	4e	1·0	0·0	0·0	0·064(2)
	O(3)	8g	1·0	0·0	0·0	0·135(2)
	O(4)	4e	1·0	0·0	0·0	0·207(3)
	Overall isotropic thermal parameter $Q = 0{\cdot}004(2)$ nm^2					
	R-factors					
	$R_{wp} = 10{\cdot}52\%$, $R_p = 8{\cdot}40\%$, $R_I = 7{\cdot}04\%$, $R_F = 4{\cdot}31\%$					
$Na_2Ca_2Ta_3O_{10}$	Na	4e	1·0	0·0	0·0	0·282(2)
I4/mmm (no. 139)	Ca	4e	1·0	0·0	0·0	0·420(1)
$a = 0{\cdot}38872(5)$ nm	Ta(1)	2a	1·0	0·0	0·0	0·0
$c = 2{\cdot}8655(4)$ nm	Ta(2)	4e	1·0	0·0	0·0	0·1452(2)
	O(1)	4c	1·0	1·0	0·5	0·0
	O(2)	4e	1·0	0·0	0·0	0·067(3)
	O(3)	8g	1·0	0·0	0·0	0·122(2)
	O(4)	4e	1·0	0·0	0·0	0·202(2)
	Overall isotropic thermal parameter $Q = 0{\cdot}001(1)$ nm^2					
	R-factors					
	$R_{wp} = 7{\cdot}85\%$, $R_p = 6{\cdot}07\%$, $R_I = 4{\cdot}65\%$, $R_F = 2{\cdot}69\%$					

[a] Multiplicity and Wyckoff notation.
[b] Occupancy.

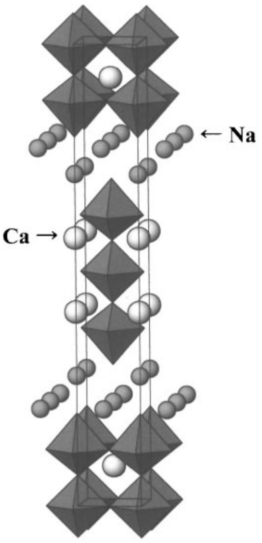

Fig. 4. Crystal structure of intercalation compound, $Na_2Ca_2Ta_3O_{10}$.

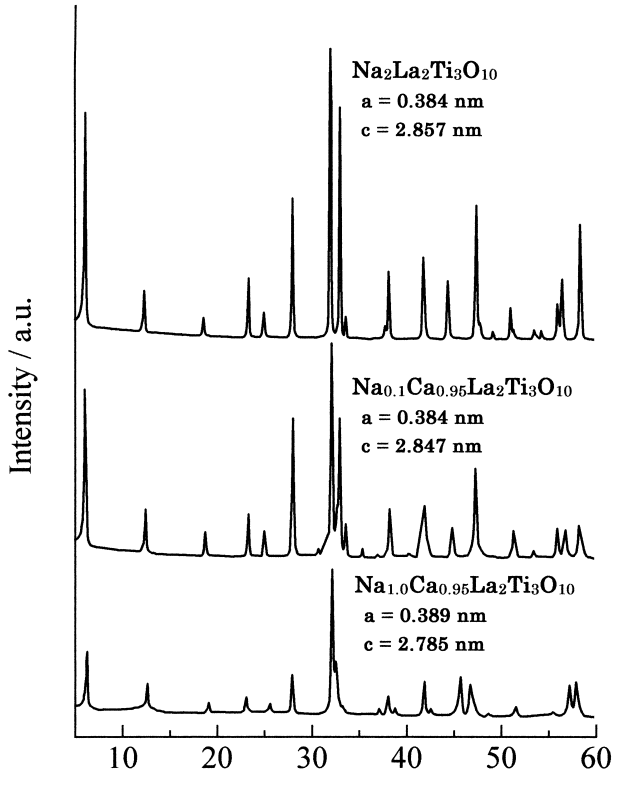

Fig. 5. The XRD patterns of parent compound $Na_2La_2Ti_3O_{10}$, ion-exchanged compound $Na_{1\cdot0}Ca_{0\cdot95}La_2Ti_3O_{10}$ and intercalation compound $Na_{1\cdot0}Ca_{0\cdot95}Ti_3O_{10}$.

and +3·7, respectively. The electronic structure of reduced tantalate is expected to be similar to that of niobate.[13] The reduced niobate $Li_xKCa_2Nb_3O_{10}$ is reported to indicate the superconductivity below ca 6 K.[14] These electron-doped layered perovskites are interesting as the example of one-electron analogues of the one-hole superconducting copper oxides with a two-dimensional character. These intercalation compounds show deep blue color suggesting a possible delocalization of the doped d-electros. The present reduced perovskites show Pauli paramagnetism down to 10 K, indicating the metallic behavior. Their magnetic susceptibilities are almost constant from room temperature to 10 K. Figure 6 shows the temperature dependence of the magnetic susceptibility for the tantalate, $Na_2Ca_2Ta_3O_{10}$.

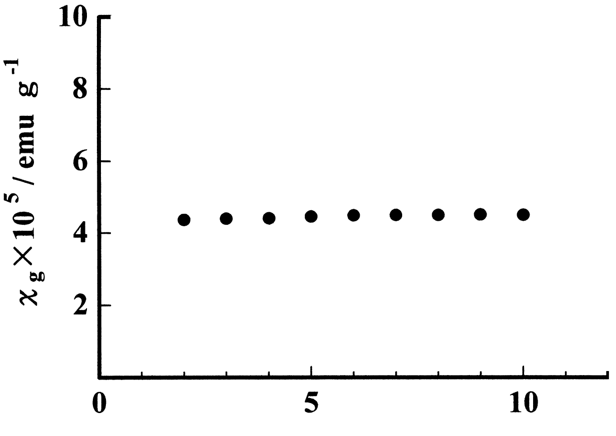

Fig. 6. Temperature dependence of the magnetic susceptibility for the Ruddlesden–Popper type $Na_2Ca_2Ta_3O_{10}$.

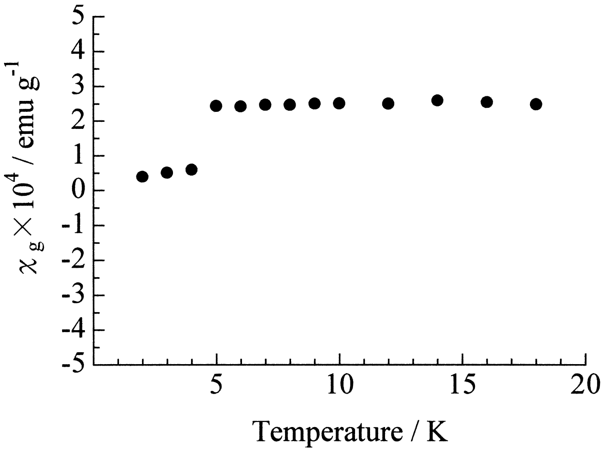

Fig. 7. Temperature dependence of the magnetic susceptibility for the reduced titanate, $Na_{1.0}Ca_{0.95}Ti_3O_{10}$.

In several samples, a sharp drop in the magnetic susceptibilities were observed below 7 K. As an example, Fig. 7 shows the magnetic susceptibility of the titanate, $Na_{1.0}Ca_{0.95}La_2Ti_3O_{10}$. This behavior may occur from the diamagnetic impurity, short-range magnetic ordering or the change of two Pauli paramagnetic states with a structural transition. A more credible hypothesis is the one that the superconductive transition caused the diamagnetic signals in these samples. However, these diamagnetic signals are too small to identify the bulk superconductivity. To realize the layered perovskite materials with a high superconducting volume fraction, a knowledge of the phase diagram as a function of electron doping is an essential prerequisite to optimize the doping process. The systematic exploration are in progress and the results will be reported in forthcoming papers. Though still far from perfect, our investigation will support to clarify the mechanism of high Tc superconductors.

4 Conclusion

New reduced transition metal oxides, $Na_2Ca_2Ta_3O_{10}$ and $Na_{1.0}Ca_{0.95}La_2Ti_3O_{10}$, with the layered perovskite structure were synthesized by the soft chemical route such as the ion-exchange and intercalation reactions. Preliminary magnetic susceptibilities measurements indicate the possibility of the superconductivity in these intercalation compounds.

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