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Synthesis, Crystal Structures and Magnetic Properties of Fluorite-related Compounds

$\text{Ce}_3\text{MO}_7 \ (M = \text{Nb, Ta})$

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Key-words: Cerium; Niobium, Tantalum, Oxides; Crystal structure; Magnetic properties.
Abstract

Ternary oxides Ce$_3$NbO$_7$ and Ce$_3$TaO$_7$ were successfully synthesized by the solid state reaction under flowing hydrogen atmosphere. The structures were determined by the powder X-ray diffraction. Both the compounds were crystallized in the orthorhombic space groups $Pnma$ (for Ce$_3$NbO$_7$) and $Cmcm$ (for Ce$_3$TaO$_7$).

Both the structures have similar features: two kinds of infinite chains formed by corner-sharing NbO$_6$ (TaO$_6$) octahedra and edge-sharing Ce(1)O$_8$ cubes, the slabs consisting of alternate chains, and 7-coordinated Ce(2) ions existing between the slabs. In the structure of Ce$_3$NbO$_7$, the NbO$_6$ octahedra running along the $a$-axis are titled towards the 0 0 1 direction, while in the Ce$_3$TaO$_7$ structure, the TaO$_6$ octahedra running along the $c$-axis are titled towards the 0 1 0 direction.

Magnetic susceptibility measurements for Ce$_3$NbO$_7$ and Ce$_3$TaO$_7$ show that both compounds are paramagnetic down to 1.8 K, and confirm that the Ce ion is in the trivalent state. From specific heat ($C_p$) measurements, a rapid increase of $C_p/T$ has been observed below 3 K for both the compounds, indicating the onset of magnetic ordering between Ce$^{3+}$ ions at further lower temperatures.
1. Introduction

It is well known that oxides containing rare earth elements show a variety of magnetic properties due to the behavior of unpaired 4f electrons. When the rare ions are arrayed in a structurally characteristic manner, interesting magnetic behavior has been often found.

Here, we focus our attention on compounds with the general formula $Ln_3MO_7$, where $Ln$ is a rare earth and $M$ is the 4d or 5d transition metal. Rossell determined first the parent structure of this family of compounds, La$_3$NbO$_7$ [1]. These compound have a characteristic defect-fluorite structure. The relationship to the fluorite structure is as follows. The fluorite unit cell for oxides has the composition $M^{4+}_4$O$_8$. If the four tetravalent metal ions are replaced by three trivalent ions ($Ln$) and one pentavalent ion ($M$), one oxide vacancy is formed per fluorite cell. Due to significant differences in radii between the $Ln^{3+}$ and $M^{5+}$ ions, cation ordering occurs on the metal sites and the oxide-vacancy orders on the anion sites. The $M^{5+}$ ion is coordinated with six oxygen ions, forming an $MO_6$ octahedron. These octahedra share corners forming one-dimensional chains which are oriented along the $c$-axis. One-third of the $Ln$ ions are coordinated by eight oxygen ions and the $LnO_8$ cubes also form a one-dimensional chain through edge-sharing.

Many studies have been performed, due to this unique crystal structure and possible related magnetic properties for $Ln_3MO_7$ compounds ($M$ = Mo [2-4], Ru [5-20], Re [21-24], Os [14, 25-27], and Ir [28-31]). Since the trivalent state is a stable oxidation state common to all rare earth ions, it is expected to form $Ln_3MO_7$ compounds from $Ln$ = La to Lu. However, a
molybdate CeMoO$_7$ is the only cerium-containing compound [32]. One reason for this is that in addition to the trivalent state, the tetravalent state is also stable for cerium ions.

In this study, we challenged to obtain cerium-containing $Ln_3MO_7$ compounds for $M = \text{Nb}, \text{Ta}$, and have prepared Ce$_3\text{NbO}_7$ and Ce$_3\text{TaO}_7$ for the first time. Through X-ray diffraction measurements, their structures were determined, and magnetic susceptibility and specific heat measurements were performed from 1.8 to 300 K to study their magnetic properties.

2. Experimental

2.1. Sample Preparation

Two Ce$_3MO_7$ compounds ($M = \text{Nb}, \text{Ta}$) could be prepared by the solid state reaction in flowing hydrogen atmosphere. As starting materials, cerium dioxide CeO$_2$, niobium oxide Nb$_2$O$_5$ and tantalum oxide Ta$_2$O$_5$ were used. They were weighed in an appropriate metal ratio and the mixtures were ground in an agate mortar. The mixtures were pressed into pellets and then heated in a flow of H$_2$ gas at 1300 °C for 12 h. After cooling to room temperature, the pellets were crushed, re-pressed into pellets, and reheated in the same conditions. These procedures were repeated three times.

2.2. X-ray Diffraction Analysis

Powder X-ray diffraction profiles were measured using a Rigaku Multi-Flex diffractometer with Cu-K$\alpha$ radiation ($\lambda = 1.5406$ Å) equipped with a curved graphite monochromator. The data were collected by step-scanning in the angle range of $10^\circ \leq 2\theta \leq 120^\circ$ at a $2\theta$ step-size of 0.02°.
The X-ray diffraction data were analyzed by the Rietveld technique, using the programs RIETAN-FP [33], and the crystal structure was drawn by using the VESTA program [34].

2.3. TG-DTA Measurements

To check the thermal stability of the specimens, thermogravimetric and differential thermal analysis (TG-DTA) measurements were performed with a TG-DTA 2000S (Mac Science) over the temperature range of 300-800 K with a heating rate of 5 K min$^{-1}$ in a flow of oxygen gas. In this measurement, $\alpha$-Al$_2$O$_3$ was used as a standard material.

2.4. Magnetic Susceptibility Measurements

The temperature-dependence of the magnetic susceptibility was measured in an applied field of 0.1T over the temperature range of 1.8K $\leq T$ $\leq$ 300K, using a SQUID magnetometer (Quantum Design, MPMS5S). The susceptibility measurements were performed under both zero-field-cooled (ZFC) and field-cooled (FC) conditions. The former was measured upon heating the sample to 300 K under the applied magnetic field of 0.1 T after zero-field cooling to 1.8 K. The latter was measured upon cooling the sample from 300 to 1.8 K at 0.1 T.

2.5. Specific Heat Measurements

The specific heat measurements were carried out using a relaxation technique with a commercial physical property measurement system (Quantum Design, PPMS) in the temperature range of 1.8K $\leq T$ $\leq$ 300K. The pelletized sample (~10 mg) was mounted on a thin alumina plate with Apiezon N-grease for better thermal contact.
3. Results and Discussion

3.1. Synthesis and crystal structure

In this study, we have synthesized, for the first time, two compounds Ce$_3$NbO$_7$ and Ce$_3$TaO$_7$ under heating conditions in a flow of H$_2$ gas. For compounds containing $M$ = Ru, Ir, Os, Re, it will be difficult to obtain Ce$_3$MO$_7$ compounds in the same preparation conditions, because these transition metals are more easily reduced than cerium. Figure 1 (a) shows the X-ray diffraction profile of Ce$_3$TaO$_7$. Crystal structures for La$_3$TaO$_7$ and Pr$_3$TaO$_7$ have been reported to be well described in the orthorhombic space group Cmcm [35]. The diffraction patterns are similar to that for the fluorite structure and all reflections appeared to be consistent with the C-centered conditions, $h + k = 2n$, and $h 0 l$ reflections with odd $l$ are absent. We have analyzed the X-ray diffraction profiles with the same space group Cmcm. All the reflections observed could be successfully indexed. The crystallographic data determined for Ce$_3$TaO$_7$ are listed in Table 1.

Figure 1 (b) shows the X-ray diffraction profile of Ce$_3$NbO$_7$. We tried to analyze the X-ray diffraction data with the Cmcm model, but some reflection peaks cannot be explained from the extinction conditions (for example, the peak at $2\theta \sim 27.5^\circ$ which is indexed to be $1 1 2$). Previously, La$_3$NbO$_7$, Pr$_3$NbO$_7$ and Nd$_3$NbO$_7$ were reported to be crystallized in the orthorhombic space group Pnma [36]. Then, we performed Rietveld analysis for the X-ray diffraction data on Ce$_3$NbO$_7$ with the Pnma model. All the reflections observed of Ce$_3$NbO$_7$ could be successfully indexed with the same space group. The structural parameters determined for Ce$_3$NbO$_7$ are listed in Table 2.
The crystal structures for Ce$_3$TaO$_7$ (Cmcm) and Ce$_3$NbO$_7$ (Pnma) are illustrated in Fig. 2. Both the structures have similar features: two kinds of infinite chains formed by corner-sharing TaO$_6$ (NbO$_6$) octahedra and edge-sharing Ce(1)O$_8$ cubes, the slabs consisting of alternate chains, and 7-coordinated Ce(2) ions existing between the slabs. As depicted in Fig. 3, the TaO$_6$ octahedra running along the $c$-axis are tilted towards the 0 1 0 direction in the structure of Ce$_3$TaO$_7$ and the Ta-O-Ta angle is 160.4°, while in the Ce$_3$NbO$_7$ structure, the NbO$_6$ octahedra running along the $a$-axis are tilted towards the 0 0 1 direction and the Nb-O-Nb angle is 153.9°.

Figures 4(a) and (b) show the variation of lattice parameters for Ln$_3$TaO$_7$ (Ln = La – Nd) and Ln$_3$NbO$_7$ (Ln = La – Nd) against the ionic radii of the 8-coordinate Ln$^{3+}$ ions [37], respectively. The lattice parameter data for Ln$_3$TaO$_7$ (Ln = La, Pr, Nd) and Ln$_3$NbO$_7$ (Ln = La, Pr, Nd) were obtained from references [35, 36]. The unit cell is orthorhombic with dimensions $a \sim 2a_f$, $b \sim \sqrt{2}a_f$, $c \sim \sqrt{2}a_f$ for Ln$_3$TaO$_7$, and $a \sim \sqrt{2}a_f$, $b \sim 2a_f$, $c \sim \sqrt{2}a_f$ for Ln$_3$NbO$_7$ ($a_f$ : the unit cell of the fluorite structure). For comparison, all the data are converted to $\sqrt{2}a_f$. The lattice parameters tend to increase smoothly with the ionic radius of Ln$^{3+}$ ions. This result also indicates that all the rare earth ions are in the trivalent state.

3.2. Thermal stability

In order to investigate the thermal stability of Ce$_3$MO$_7$ (M = Nb and Ta), the TG-DTA measurements were performed in a flow of O$_2$ gas (Fig. 5). In both data, the sample weight begins to increase at ~450 K and reaches a constant value (+3.5 % for M = Nb and +3.1 % for Ta) at 600 K. The DTA curve also shows a broad exothermic peak between these temperatures.
The increments are close to 3.8 and 3.4 %, respectively, which are calculated by assuming that all the trivalent Ce ions are oxidized to the tetravalent state. In the XRD patterns for the samples after TG-DTA measurements, the Ce₃MO₇ phase was not detected and the two kinds of fluorite-like phases were observed. These facts suggest that the Ce₃MO₇ compounds are easily oxidized and decomposed by heating in an O₂ atmosphere.

3.3. Magnetic properties

Figure 6 depicts the temperature dependence of the magnetic susceptibility for Ce₃TaO₇ in the temperature range between 1.8 and 300 K. Since the electronic configuration of Ce³⁺ ion is [Xe]⁴f¹ ([Xe]: xenon electronic core), magnetic interactions between Ce³⁺ ions are expected. However, no magnetic ordering has been observed down to 1.8 K. The reciprocal magnetic susceptibility vs. temperature curve has been also shown in the same figure. In the high temperature region, the Curie-Weiss law fitting was applied to the temperature dependence of the susceptibility. The effective magnetic moment and the Weiss constant for Ce₃TaO₇ were obtained to be 2.95 μₜ and -12.6 K, respectively. Since Ta⁵⁺ ions do not contribute to the paramagnetic behavior of Ce₃TaO₇, the effective magnetic moment per mole of Ce³⁺ ions is calculated to be 1.71 μₜ. Since the ground state of Ce³⁺ is ²F₅/₂, the effective magnetic moment for the free Ce³⁺ ion is 2.54 μₜ, i.e., the experimental magnetic moment is smaller than the free ion value. This result means that the smaller effective magnetic moment of Ce³⁺ ion is due to the effect of crystal field [38]. The same results have been reported for Pr⁴⁺-containing compounds [39]. The electronic configuration of Pr⁴⁺ is the same as that of Ce³⁺.

For Ce₃NbO₇, its temperature dependence of the magnetic susceptibility and the reciprocal
magnetic susceptibility is shown in Fig. 7. No magnetic ordering has been observed down to 1.8 K. By applying the Curie-Weiss law to the reciprocal susceptibility vs. temperature curve, the effective magnetic moment and the Weiss constant for Ce$_3$NbO$_7$ were determined to be 3.06 $\mu_B$ and -13.6 K. Nb$^{5+}$ ions are also diamagnetic, and they do not contribute to the magnetic behavior of Ce$_3$NbO$_7$. Therefore, the effective magnetic moment per mole of Ce$^{3+}$ ions is calculated to be 1.77 $\mu_B$. Smaller effective magnetic moment of Ce$^{3+}$ ion compared with the free ion value is due to the crystal field effect on the Ce$^{3+}$ ions.

In order to clarify the possibility of magnetic ordering of Ce$^{3+}$ magnetic moments at low temperatures, the specific heat ($C_p$) measurements were performed. Figures 8 (a) and (b) depict the temperature dependence of $C_p/T$ for Ce$_3$NbO$_7$ and Ce$_3$TaO$_7$, respectively. Both the compounds show a rapid increasing of $C_p/T$ below 3 K, indicating the onset of magnetic ordering at further lower temperatures. It may be antiferromagnetic, because the Weiss constants are negative.

**Summary**

Ternary oxides Ce$_3$NbO$_7$ and Ce$_3$TaO$_7$ were synthesized by the solid state reaction. Both the compounds were crystallized in the orthorhombic space groups $Pnma$ (for Ce$_3$NbO$_7$) and $Cmcm$ (for Ce$_3$TaO$_7$). Magnetic susceptibility measurements for Ce$_3$NbO$_7$ and Ce$_3$TaO$_7$ confirm that the Ce ions are in the trivalent state.

**References**


Figure captions

Fig. 1  Powder x-ray diffraction profiles for (a) Ce$_3$TaO$_7$ and (b) Ce$_3$NbO$_7$. The calculated and observed profiles are shown on the top solid line and cross markers, respectively. The vertical marks in the middle show positions calculated for Bragg reflections. The lower trace is a plot of the difference between calculated and observed intensities. The inset of (b) shows the comparison between two structural models; the solid line on the top represents the calculated profile for the $Pnma$ model. An arrow shows the diffraction line which can be explained only by the $Pnma$ model.

Fig. 2. a: Crystal structure for Ce$_3$TaO$_7$ (space group: $Cmcm$) and b: that for Ce$_3$NbO$_7$ (space group: $Pnma$).

Fig. 3. a: Structure for Ce$_3$TaO$_7$ viewed from the [1 0 0] direction and b: that for Ce$_3$NbO$_7$ viewed from the [0 1 0] direction.

Fig. 4. Variation of lattice parameters for (a) Ln$_3$TaO$_7$ and (b) Ln$_3$NbO$_7$ compounds with ionic radii of 8-coordinated Ln$^{3+}$ ions.

Fig. 5. Temperature dependence of the TG (black line) and DTA (red line) for (a) Ce$_3$NbO$_7$ and (b) Ce$_3$TaO$_7$.

Fig. 6. Temperature dependences of magnetic susceptibility and reciprocal magnetic susceptibility for Ce$_3$TaO$_7$ in the temperature range between 1.8 and 300 K. The solid line is the Curie-Weiss fitting.

Fig. 7. Temperature dependences of magnetic susceptibility and reciprocal magnetic susceptibility for Ce$_3$NbO$_7$ in the temperature range between 1.8 and 300 K. The solid
line is the Curie-Weiss fitting.

Fig. 8. Temperature dependence of specific heat divided by temperature ($C_p/T$) for (a) $\text{Ce}_3\text{NbO}_7$ and (b) $\text{Ce}_3\text{TaO}_7$. 
Table 1  Structural parameters for Ce$_3$TaO$_7$.

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<tr>
<td>Ce(2)</td>
<td>8g</td>
<td>0.228(3)</td>
<td>0.294(3)</td>
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<tr>
<td>Ta</td>
<td>4b</td>
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<td>1/2</td>
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<td>0.31(5)</td>
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<tr>
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<td>1/4</td>
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Note. Space group $Cmcm$ (No. 63); $a = 11.0514(8) \text{Å}, b = 7.5668(5) \text{Å}, c = 7.7153(4) \text{Å}, V = 645.19(5) \text{Å}^3$, $R_{wp} = 11.31\%$, $R_B = 2.41\%$, $R_e = 9.41\%$, where

\[
R_{wp} = \left[ \sum_i w_i \left( y_i - f_i(x) \right)^2 / \sum_i w_i y_i^2 \right]^{1/2}, \quad R_B = \frac{\sum_k |I_o(h_k) - I(h_k)|}{\sum_k I_o(h_k)}, \quad \text{and}
\]

\[
R_e = \left[ \frac{(N - P)}{\sum_i w_i y_i^2} \right]^{1/2}.
\]

a: For the same ions, $B$ values were fixed to be equal.
Table 2  Structural parameters for Ce$_3$NbO$_7$.

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<td>0.264(3)</td>
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Note. Space group $Pnma$ (No. 62); $a = 7.7123(9)$ Å, $b = 11.0413(1)$ Å, $c = 7.5510(5)$ Å, $V = 643.00(8)$ Å$^3$, $R_{wp} = 13.84\%$, $R_B = 2.36\%$, $R_e = 12.07\%$. 

a: For the same ions, B values were fixed to be equal.
Fig. 1(a)

Intensity

$2\theta/\degree$

$\text{Ce}_3\text{TaO}_7$
Fig. 1(b)
Ce(1)O$_8$  MO$_6$  Ce(2)

Fig. 2
Fig. 3
Fig. 4

**a**

![Graph a](image)

**b**

![Graph b](image)

Lattice parameters (Å)

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**Ln$_3$TaO$_7$**

- $a / \sqrt{2}$
- $b$
- $c$

**Ln$_3$NbO$_7$**

- $a$
- $b / \sqrt{2}$
- $c$
Fig. 7

$\chi / \text{emu mol}^{-1}$ vs $T / \text{K}$ for $\text{Ce}_3\text{NbO}_7$. The graph shows the temperature dependence of magnetic susceptibility.
Fig. 8

(a) $\text{Ce}_3\text{NbO}_7$

(b) $\text{Ce}_3\text{TaO}_7$