

Full Length Article

Synthesis of rutile-type solid solution $\text{Ni}_{1-x}\text{Co}_x\text{Ti}(\text{Nb}_{1-y}\text{Ta}_y)_2\text{O}_8$ ($0 \leq x \leq 1$, $0 \leq y \leq 1$) and its optical propertyNobuhiro Kumada^{a,*}, Narumi Koike^a, Kousuke Nakanome^a, Sayaka Yanagida^a,
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ABSTRACT

Rutile-type solid solutions; $\text{Ni}_{1-x}\text{Co}_x\text{Ti}(\text{Nb}_{1-y}\text{Ta}_y)_2\text{O}_8$ ($0 \leq x \leq 1$, $0 \leq y \leq 1$) were prepared by high temperature solid state reaction. The solid solutions of niobates ($y=0$) had a rutile-type structure and those of tantalates ($y=1.0$) had a trirutile-type one. The trirutile-type structure appeared in the composition of $y \geq 0.4$. The crystal structures of these solid solutions for niobates and tantalates were refined by using synchrotron X-ray powder diffraction data and the R-factors were $R_{\text{wp}} = 1.76\text{--}1.92\%$ and $R_p = 1.13\text{--}1.19\%$ for niobates and $R_{\text{wp}} = 10.3\text{--}12.2\%$ and $R_p = 6.78\text{--}9.14\%$ for tantalates. Their lattice parameters for niobates ranges from $a = 4.69413(2)$ to $4.70411(2)$ Å and $c = 3.02187(1)$ to $3.03242(1)$ Å and those for tantalates ranges from $a = 4.6946(2)$ to $4.7065(2)$ Å and $c = 9.0829(3)$ to $9.1164(4)$ Å. The optical band gap for these solid solutions ranged from 1.63 to 2.50 eV and only $\text{NiTiTa}_2\text{O}_8$ exhibited photocatalytic activity for phenol decomposition under UV light irradiation. The dielectric constants for four end members, $\text{NiTiNb}_2\text{O}_8$, $\text{CoTiNb}_2\text{O}_8$, $\text{NiTiTa}_2\text{O}_8$ and $\text{CoTiTa}_2\text{O}_8$ were 25–75 in the temperature range from room temperature to 300 °C.

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1. Introduction

The mineral name, rutile is one of three polymorphs for a titanium oxide, TiO_2 . The crystal structure is formed by edge-sharing of one-dimensional chains composed of edge-shared TiO_6 octahedra running along the c -axis. Some tetravalent metal oxides such as SnO_2 [1], GeO_2 [1] and MnO_2 [2] etc. adopt this crystal structure. As well as the simple binary metal oxides, $\text{MM}'\text{O}_4$ and $\text{MTiM}'\text{O}_6$ ($M = \text{Cr, Fe, Ga}$; $M' = \text{Nb, Ta, Sb}$) [3] have the rutile-type structure in which two or three metals in the octahedral site is disordering at ambient temperature. These rutile-type compounds have been paid attention for their dielectric property, particular FeTiTaO_6 [4,5] and FeTiNbO_6 [6] showed interesting relaxor-like behavior and the dielectric behavior of $\text{NiTiNb}_2\text{O}_8$ [7] was reported to be a candidate for a microwave capacitor. There has been no report for dielectric property of multi-component rutile-type oxides except the above oxides.

The trirutile-type structure has three times c -axis of the rutile-type one by ordering the octahedral cations along the c -axis, and some of tantalates [8–10], antimonates [10] and bismuthates [11] adopt this structural type. The magnetic ordering and property of trirutile-type tantalates and antimonates had been investigated [8–11]. Also the rutile- and trirutile-type oxides have possibility of application to an electrode of a lithium secondary battery [13,14], because both structure-types have an octahedral tunnel along the c -axis which can be inserted by lithium ions, and the theoretical calculations showed Li insertion into the octahedral site by 0.7 eV/Li [15]. To our knowledge, there has been no report for investigation on photocatalytic property with multi-component rutile- or trirutile-type oxides, though these compounds have been paid attention to dielectric and electrochemical properties.

On the other hand, in the solid solution systems $\text{M}^{2+}/\text{Ti}^{4+}/\text{M}^{5+}/\text{O}$ ($\text{M}^{2+} = \text{Mg, Zn}$; $\text{M}^{5+} = \text{Nb, Ta}$) a variety of crystal structure types had been reported as follows; $\text{Mg}_{0.167}\text{Nb}_{0.333}\text{Ti}_{0.5}\text{O}_2$ with the rutile-type structure [16], $(\text{Mg}_{0.857}\text{Ti}_{0.143})(\text{Nb}_{0.857}\text{Ti}_{0.143})_2\text{O}_6$, with the columbite-type structure [17], $\text{ZnTiNb}_2\text{O}_8$ with the α - PbO_2 -type structure [18], $(\text{Zn}_{0.15}\text{Nb}_{0.3}\text{Ti}_{0.55})\text{O}_2$ with the rutile-type structure [19], Zn/Ti/Ta/O system with the spinel-type structure [20,21]. However, the crystal structure and some properties of the solid

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Table 1**Q7** Crystal data and structural parameters for the solid solution, $\text{Ni}_{1-x}\text{Co}_x\text{Ti}(\text{Nb}_{1-y}\text{Ta}_y)_2\text{O}_8$ ($0 \leq x \leq 1$).

x	R_{WP}	R_p	Lattice parameters		$M(\text{Ni}_{1/4-x/4}\text{Co}_{x/4}\text{Ti}_{1/4}\text{Nb}_{1/2})$	O	
	%	%	a (Å)	c (Å)		Site: $4f\ x=y, z=0$	Site: $4f\ x=y, z=0$
					U (Å ²)	x	U (Å ²)
0.0	1.83	1.13	4.69413(2)	3.02187(1)	0.0108(1)	0.3031(2)	0.0053(4)
0.2	1.89	1.17	4.69708(2)	3.02426(2)	0.0106(1)	0.3031(2)	0.0043(4)
0.4	1.87	1.16	4.69859(2)	3.02607(1)	0.0106(1)	0.3034(2)	0.0046(4)
0.6	1.92	1.15	4.70025(2)	3.02806(2)	0.0102(1)	0.3031(2)	0.0047(4)
0.8	1.76	1.13	4.70240(2)	3.03052(1)	0.0099(1)	0.3021(2)	0.0043(4)
1.0	1.86	1.19	4.70411(2)	3.03242(1)	0.0096(1)	0.3020(2)	0.0049(4)

solution, $\text{Ni}_{1-x}\text{Co}_x\text{Ti}(\text{Nb}_{1-y}\text{Ta}_y)_2\text{O}_8$ ($0 \leq x \leq 1$, $0 \leq y \leq 1$) have not been clarified except one end member, $\text{NiTiNb}_2\text{O}_8$ [7]. It is worthwhile to investigate the crystal structure and property in the solid solution, $\text{Ni}_{1-x}\text{Co}_x\text{Ti}(\text{Nb}_{1-y}\text{Ta}_y)_2\text{O}_8$ ($0 \leq x \leq 1$, $0 \leq y \leq 1$).

In this paper we will describe preparation, phase transition, crystal structure refinement and photocatalytic activity of the solid solution, $\text{Ni}_{1-x}\text{Co}_x\text{Ti}(\text{Nb}_{1-y}\text{Ta}_y)_2\text{O}_8$ ($0 \leq x \leq 1$, $0 \leq y \leq 1$).

2. Experimental

The solid solutions, $\text{Ni}_{1-x}\text{Co}_x\text{Ti}(\text{Nb}_{1-y}\text{Ta}_y)_2\text{O}_8$ ($0 \leq x \leq 1$, $0 \leq y \leq 1$) were prepared by solid state high temperature reaction as follows. Commercial reagents (purity > 99.9%), NiO , CoO , and rutile-type TiO_2 , Nb_2O_5 and Ta_2O_5 were used as starting compounds and the stoichiometric mixtures were mixed by ball-milling with zirconia ball in 2-propanol for 6 h. The mixtures were heated at 1200 °C for 3 h two times in air for the niobates and the reaction temperature raised up to 1400 °C for the tantalates. The products were identified by X-ray powder diffraction pattern using monochromated $\text{CuK}\alpha$ radiation. Synchrotron X-ray powder diffraction (SXRD) measurements were performed using beam line BL02B2 at the SPring-8 facility. The data were collected with a constant wavelength ($\lambda = 0.413653$ and 0.413287 Å) at room temperature. RIETAN-FP [22] was used for crystal structure refinement and crystal structure was drawn by using VESTA [23].

Diffuse reflectance spectra were measured with a JASCO V-550 spectrometer. The photocatalytic activity was checked by the decomposition of phenol (20 ppm solution) under UV-light and visible light with a cut-off wavelength of 420 nm. Time dependence of phenol concentration was checked by liquid chromatography (Prominence LC-20AT, Shimadzu).

The powder sample was added 1 wt% PVA aqueous solution and pressed under uniaxially at 10 kN and the pellets were sintered at 1200–1400 °C for 2 h. The surfaces of the sintered body were polished with emery paper and the electrode was formed using silver paste. Temperature dependence of dielectric constant was measured at frequency of 1.0 kHz by using a Hioki-4277A LCZ meter.

3. Results and discussion

The X-ray powder diffraction patterns for the solid solution, $\text{Ni}_{1-x}\text{Co}_x\text{TiNb}_2\text{O}_8$ ($0 \leq x \leq 1$) could be indexed completely with the tetragonal cell of the rutile-type structure (the space group, $P4_2/mnm$ (#136)) and no impurity phase was observed in the whole composition. The Rietveld crystal structure refinement using synchrotron powder X-ray diffraction (SXRD) data led to the R values ($R_{\text{WP}} = 1.76$ – 1.92% and $R_p = 1.13$ – 1.19%). Fig. 1 shows the Rietveld refinement patterns of SXRD for the end members, $\text{NiTiNb}_2\text{O}_8$ and $\text{CoTiNb}_2\text{O}_8$. The details of structure refinement and the structure parameters are summarized in Table 1 and selected interatomic distances are listed in Table 2. Their lattice parameters ranges from $a = 4.69413(2)$ to $4.70411(2)$ Å and $c = 3.02187(1)$ to $3.03242(1)$ Å, linearly depending on the value of x as shown in Fig. 2. The mag-

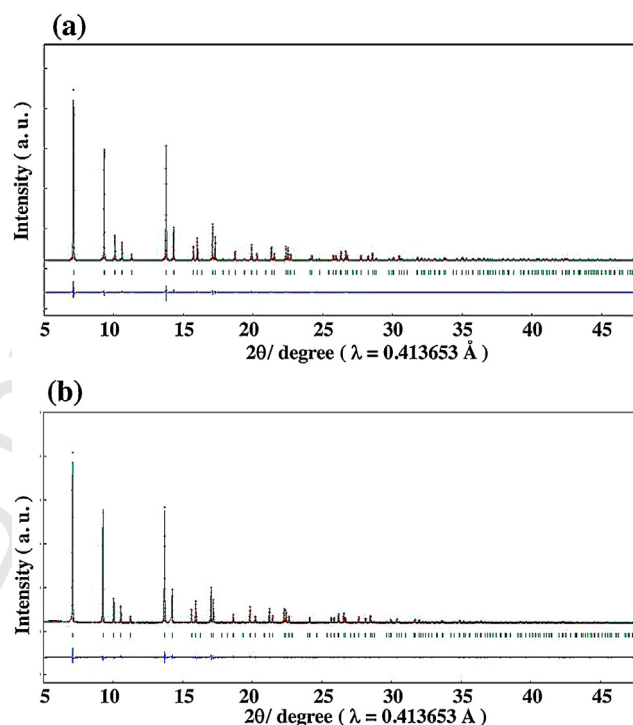


Fig. 1. Rietveld refinement patterns of SXRD for $\text{NiTiNb}_2\text{O}_8$ (a) and $\text{CoTiNb}_2\text{O}_8$ (b). In the upper portion, observed and calculated intensities are drawn by dots and lines, respectively. In the middle portion, the short vertical lines denote the positions of possible Bragg reflections. In the lower portion, the difference between the observed and calculated intensities is shown.

Table 2Selected interatomic distances (Å) for the solid solution, $\text{Ni}_{1-x}\text{Co}_x\text{TiNb}_2\text{O}_8$ ($0 \leq x \leq 1$).

x	M–O (x 2)	M–O (x 4)	Mean
0.0	2.0121(8)	1.9979(5)	2.0026
0.2	2.0133(8)	1.9994(5)	2.0040
0.4	2.0158(8)	1.9991(5)	2.0045
0.6	2.0110(8)	2.0038(6)	2.0062
0.8	2.0093(8)	2.0068(6)	2.0076
1.0	2.0090(9)	2.0086(6)	2.0087

nitude of the errors for the lattice parameters and bond distance is too small to represent the error bars in Figs. 2, 5 and 7. Fig. 3 shows the crystal structure of $\text{NiTiNb}_2\text{O}_8$. The rutile-type structure has only one crystallographic site of metal atom surrounded octahedrally by six oxygen atoms and in this solid solution four types of metal atoms occupy at this octahedral site. The mean metal–oxygen distances in the octahedral site increase linearly depending on the value of x as shown in Fig. 2. This linear increase comes from the difference of the ionic radii between Co^{2+} and Ni^{2+} . Shannon ionic radius (0.745 Å) of Co^{2+} with a high spin state is larger than that (0.690 Å) of Ni^{2+} for the six coordination [24].

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