

Phase relations in $\text{Na}_x\text{Cr}_x\text{Ti}_{8-x}\text{O}_{16}$ at 1350 °C and crystal structure of hollandite-like $\text{Na}_2\text{Cr}_2\text{Ti}_6\text{O}_{16}$

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Abstract

Phase relations of rutile, freudenbergite, and hollandite structures were examined in the pseudobinary system $\text{NaCrO}_2\text{--TiO}_2$ (i.e., $\text{Na}_x\text{Cr}_x\text{Ti}_{8-x}\text{O}_{16}$) at 1350 °C. The hollandite structure was obtained in the composition range $1.7 \leq x \leq 2.0$. The symmetry of the samples at room temperature was tetragonal for $x = 1.7$ and 1.75, and monoclinic for $x = 1.8$ and above. Single crystals of monoclinic hollandite $\text{Na}_2\text{Cr}_2\text{Ti}_6\text{O}_{16}$ were grown and the structure refinement has been carried out using an X-ray diffraction technique. The space group was $I2/m$ and cell parameters were $a = 10.2385(11)$, $b = 2.9559(9)$, $c = 9.9097(11)\text{Å}$, and $\beta = 90.545(9)^\circ$ with $Z = 1$. The Na ion distribution in the tunnel was markedly deformed from that in the tetragonal form. It was suggested that Cr/Ti ratios were different between the two framework metal sites.

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1. Introduction

TiO_2 -based hollandite-like compounds (i.e., priderites) are obtained in many pseudobinary systems $\text{AMoO}_2\text{--TiO}_2$, $A'M_2\text{O}_4\text{--TiO}_2$, $A_2M'O_2\text{--TiO}_2$, and $A'M'O_2\text{--TiO}_2$ ($A = \text{K}^+$, Rb^+ , Cs^+ ; $A' = \text{Ba}^{2+}$, $M = \text{Al}^{3+}$, Ga^{3+} , Ti^{3+} , Cr^{3+} , Fe^{3+} , etc.; $M' = \text{Mg}^{2+}$, Co^{2+} , Ni^{2+} , Zn^{2+} , etc.). The structure is characterized by a host framework containing one-dimensional (1d) tunnels constructed by infinite chains of pseudocuboctahedral cavities [1]. Alkali and alkali-earth cations are located in the 1d tunnel, and called tunnel cations. The host structure of hollandite was evaluated for immobilization of radioactive wastes [2]. On the other hand, K - and Rb -hollandites are known as 1d ionic conductors [3–5], in which the 1d tunnel is used as a conduction path of the tunnel cations.

The cavity in the hollandite tunnel, however, appears too large to stabilize the Na ion. Actually, compounds isostructural to freudenbergite [6], which contain small cavities accommodating the Na ion, are formed in systems $\text{NaMO}_2\text{--TiO}_2$ and $\text{Na}_2M'O_2\text{--TiO}_2$ [7]. Thus, it is generally

accepted that large cations such as K , Rb , Cs , and Ba are stabilized in the hollandite structure, while the freudenbergite structure is suitable for containing the Na ion. However, Bayer et al. [7] reported that the Na ion can be accommodated in the hollandite tunnel by taking Cr^{3+} as M . Single crystals of hollandite $\text{Na}_x\text{Cr}_x\text{Ti}_{8-x}\text{O}_{16}$ ($x \approx 1.7$) were obtained by the flux method [8]. One of the unique characters of this material is the delocalized distribution of the Na ion in the tunnel. Further, it was found that $\text{Na}_x\text{Cr}_x\text{Ti}_{8-x}\text{O}_{16}$ ($x \approx 1.7$) with a tetragonal form at room temperature transformed to the monoclinic phase at lower temperatures [9]. The variation of the Na ion distribution in the tunnel has been clarified by X-ray diffraction studies at 223 K (monoclinic) [9], 295 K (tetragonal) [8], and 773 K (tetragonal) [10], and its microscopic pictures were given by molecular dynamics simulations [11]. Ion conduction properties of the material were studied by impedance spectroscopy measurements, and the frequency-independent conduction was observed [12].

In this work, further synthetic studies in the pseudobinary system $\text{NaCrO}_2\text{--TiO}_2$ have been carried out to clarify phase relations between rutile, freudenbergite, and hollandite structures at 1350 °C. The hollandite structure was obtained in the composition range $1.7 \leq x \leq 2.0$, but the

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structure was a monoclinic form in the higher x region. Single crystals of hollandite $\text{Na}_2\text{Cr}_2\text{Ti}_6\text{O}_{16}$ were grown and an X-ray diffraction analysis has been carried out. It has been found that the Na ion distribution in this hollandite is different from those of $\text{Na}_x\text{Cr}_x\text{Ti}_{8-x}\text{O}_{16}$ ($x \approx 1.7$) in the tetragonal or monoclinic forms. Structural properties related to the tetragonal–monoclinic transformation of the hollandite structure were discussed.

2. Experimental

Phase relations in the system $\text{NaCrO}_2\text{–TiO}_2$ were examined by a quenching technique. Na_2CO_3 , Cr_2O_3 , and TiO_2 of an molar ratio of $x/2:x/2:8-x$, where x was varied from 1.0 to 2.0, were mixed, and heated at 900°C in a platinum crucible for 1 h. The mixture was ground and in a sealed platinum tube, heated at 1350°C for 20 h, and rapidly cooled to room temperature. The product was ground again and reheated at 1350°C in the same manner. Identification of products has been carried out by a powder X-ray diffraction technique.

Single crystals of $\text{Na}_2\text{Cr}_2\text{Ti}_6\text{O}_{16}$ were grown by an excess alkali method. Na_2CO_3 , Cr_2O_3 , and TiO_2 of an molar ratio of 1.2:1:6 were mixed and heated at 950°C for 30 min. The sample was put in a sealed platinum tube, then heated at 1350°C for 20 h. The product was taken out of the furnace, cooled to room temperature, and put into water to remove excess Na_2O . Needle-shaped deep-blue crystals were obtained. Chemical composition $\text{Na}_2\text{Cr}_2\text{Ti}_6\text{O}_{16}$ for the product was justified by the powder X-ray diffraction pattern which was essentially identical to that of the hollandite structure of $x = 2.0$ in the phase relation study mentioned above.

A single crystal of $\text{Na}_2\text{Cr}_2\text{Ti}_6\text{O}_{16}$ was mounted on a automated four-circle diffractometer (Rigaku AFC 7R). Crystallographic data and conditions for data collections and refinement are listed in Table 1. The framework structure (Ti, Cr, and O ions) of an initial model was taken from the previous study [9]. Positions of Na ions in the tunnel were determined by Fourier syntheses and difference Fourier syntheses. Occupation factors of Na ions were refined imposing constraint conditions so as to keep the amount of Na ions in a unit cell at 2.0. The Cr/Ti ratios at framework metal sites were refined imposing the constraint conditions so that the Cr/Ti ratio in a unit cell was 1/3, for which detailed explanations will be given in the following section. A program package JANA 2000 [13] was used for least-squares refinements and other calculations.

3. Results

3.1. Phase relations

Composition dependence of products is summarized in Table 2. A single phase of the freudenbergite structure was obtained only at $x = 1.4$, while the hollandite structure was found as a single phase in the range of $1.7 \leq x \leq 2.0$.

Table 1
Crystallographic data and conditions for data collection and refinement for $\text{Na}_2\text{Cr}_2\text{Ti}_6\text{O}_{16}$

<i>Mr</i>	693.2
Crystal system	Monoclinic
Space group	<i>I</i> 2/ <i>m</i>
<i>a</i> (Å)	10.2385(11)
<i>b</i>	2.9559(9)
<i>c</i>	9.9097(11)
β (deg)	90.545(9)
<i>V</i> (Å ³)	299.89(10)
<i>Z</i>	1
<i>D_x</i> (g/cm ³)	3.837(1)
μ (MoK α) (mm ^{−1})	5.69
Crystal size (mm)	0.03 × 0.03 × 0.07
Color	Dark blue
Radiation	MoK α (0.71069 Å) (graphite-monochromatized)
Refinement of cell parameters	24 reflections ($40^\circ \leq 2\theta \leq 42^\circ$)
Scan mode	ω – 2θ
2θ max.	80°
Range of <i>h, k, l</i>	−18 ≤ <i>h</i> ≤ 18, 0 ≤ <i>k</i> ≤ 5, −17 ≤ <i>l</i> ≤ 17
Standard reflections	3 every 200
Intensity decay	Less than 3%
Reflections measured	2136
Independent reflections	933
Observed reflections ($I_0 > 2\sigma(I_0)$)	804
<i>R</i> _{int}	0.0543
Absorption correction	Analytical
Transmission factor	0.727–0.855
Refinement on	<i>F</i> ²
<i>R</i> _{obs} (<i>F</i>), <i>wR</i> _{obs} (<i>F</i> ²), <i>S</i> _{obs}	0.0411, 0.0873, 1.43
<i>R</i> _{all} (<i>F</i>), <i>wR</i> _{all} (<i>F</i> ²), <i>S</i> _{all}	0.0526, 0.0895, 1.35
Weight factor	1/[$\sigma(I_0)^2 + 0.0004I_0^2$]
$\Delta\rho$ _{min} $\Delta\rho$ _{max}	−1.09 1.21 (e/Å ³)

Table 2
Composition dependence of products in the system $\text{NaCrO}_2\text{–TiO}_2$

<i>x</i>	Products
1.0	R, F
1.2	R, F
1.4	F
1.5	F, H(t)
1.6	F, H(t)
1.7	H(t)
1.75	H(t)
1.8	H(m)
1.85	H(m)
1.9	H(m)
2.0	H(m)

x: parameter in the chemical composition $\text{Na}_x\text{Cr}_x\text{Ti}_{8-x}\text{O}_{16}$.

R: rutile; F: freudenbergite structure; H(t): tetragonal hollandite structure; H(m): monoclinic hollandite structure.

Freudenbergite (Fig. 1) has a chemical composition $\text{NaFeTi}_3\text{O}_8$ [6], while isostructural compounds of Na-deficient compositions were also reported for $\text{Na}_x\text{Ti}_4\text{O}_8$ ($x \approx 0.8$) [14] and $\text{Na}_x\text{Ga}_x\text{Ti}_{4-x}\text{O}_8$ ($x \approx 0.81$) [15]. The symmetry of the hollandite structures after cooling to room temperature was tetragonal for $x = 1.7$ and 1.75, and monoclinic for $1.8 \leq x \leq 2.0$. It has been reported that

$\text{Na}_x\text{Cr}_x\text{Ti}_{8-x}\text{O}_{16}$ ($x \approx 1.7$), which has the tetragonal hollandite structure at room temperature, was the monoclinic form at -50°C [9]. Considering this fact, it is unclear whether the structure of hollandite $\text{Na}_x\text{Cr}_x\text{Ti}_{8-x}\text{O}_{16}$ for $1.8 \leq x \leq 2.0$ is the tetragonal form or the monoclinic at 1350°C . Namely, there are two possibilities explaining the results; (i) monoclinic structures are formed at 1350°C , or (ii) tetragonal forms are obtained at 1350°C , which transform to the monoclinic structure in the course of cooling the samples. Further discussion about this problem will be given in the following part. In any event, it has been confirmed from the present study that the stable phase in the composition range $1.7 \leq x \leq 2.0$ at 1350°C is hollandite.

3.2. Structure of $\text{Na}_2\text{Cr}_2\text{Ti}_6\text{O}_{16}$

Final structural parameters are listed in Table 3. Isotropic thermal parameters were used for Na2 and Na3 to avoid correlations between parameters. Selected intera-

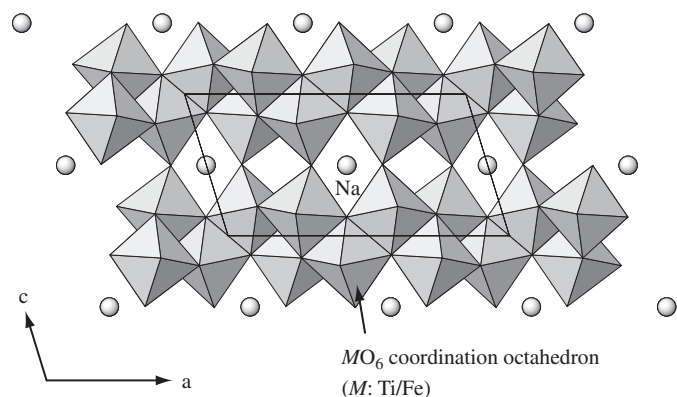


Fig. 1. Structure of freudenbergite projected along the b -axis.

tom distances are in Table 4. The framework structure is of a typical hollandite-type, but slightly distorted in conjunction with the monoclinic symmetry (Fig. 2). Loss of the four-fold axis in the symmetry of this hollandite is prominent in the distribution of the Na ions, which is demonstrated by seeing a difference Fourier map (Fig. 3) at $y = 0.5$ of a structure model at a stage that includes Ti, Cr, and O ions for a framework structure but no Na ions in the tunnel. Coordination environments of Na sites are shown in Fig. 4. Rather irregular coordinations are seen according to the deviation of the Na positions from the cavity center (0, 0.5, 0). As a unique character of Na-hollandite, a part of Na ions are found at the so-called *bottleneck* position (Na3), that is, the center of a small pseudosquare of oxygen ions.

There are two independent metal sites, $M1$ and $M2$, in the monoclinic hollandite structure. The Cr/Ti ratios at the two sites were refined imposing the constraint conditions so as to keep the Cr/Ti ratio in the whole structure at $1/3$. Different Cr/Ti ratios were obtained for the two sites as listed in Table 3. However, special care must be paid for the

Table 4
Interatomic distances (\AA) in $\text{Na}_2\text{Cr}_2\text{Ti}_6\text{O}_{16}$

$M1-O1$	2.021(3)	$M2-O2$	2.010(3)		
$M1-O1 \times 2$	1.9695(18)	$M2-O2 \times 2$	1.9728(18)		
$M1-O3$	1.928(3)	$M2-O3 \times 2$	1.9558(18)		
$M1-O4 \times 2$	1.9562(17)	$M2-O4$	1.926(3)		
Average	1.967(1)	Average	1.962(1)		
$\text{Na1-O1} \times 2$	2.491(7)	Na2-O1	2.55(10)	$\text{Na3-O1} \times 2$	2.551(3)
$\text{Na1-O2} \times 2$	2.489(7)	Na2-O1	2.84(11)	$\text{Na3-O2} \times 2$	2.580(3)
Na1-O4	2.654(10)	Na2-O2	2.96(11)		
		Na2-O2	2.47(11)		

Table 3
Occupancies, atomic coordinates, and thermal parameters of $\text{Na}_2\text{Cr}_2\text{Ti}_6\text{O}_{16}$

Atom	Occupancy	x	y	z	$U_{\text{eq}}/U_{\text{iso}}(\text{\AA}^2)$
Na1	0.304(15)	0.0866(9)	0.5	-0.0100(9)	0.026(3)
Na2	0.058(14)	0.028(10)	0.28(4)	0.003(10)	0.10(3)
Na3	0.16(6)	0	0	0	0.06(2)
$M1$ (Cr/Ti)	0.279/0.721(18)	0.35357(7)	0	0.82884(7)	0.00782(16)
$M2$ (Cr/Ti)	0.221/0.779(18)	0.83459(7)	0	0.65171(7)	0.00819(16)
O1	1	0.1576(3)	0	0.8021(3)	0.0064(6)
O2	1	0.7930(3)	0	0.8495(3)	0.0059(5)
O3	1	0.5419(3)	0	0.8267(3)	0.0077(6)
O4	1	0.8437(3)	0	0.4577(3)	0.0077(6)
Atom	U^{11}	U^{22}	U^{33}	U^{13}	
Na1	0.022(4)	0.026(5)	0.030(4)	-0.003(3)	
$M1$	0.0088(3)	0.0052(3)	0.0094(3)	-0.0019(2)	
$M2$	0.0111(3)	0.0050(3)	0.0085(3)	0.0026(2)	
O1	0.0080(10)	0.0060(10)	0.0053(9)	0.0004(8)	
O2	0.0050(9)	0.0055(10)	0.0071(9)	0.0001(8)	
O3	0.0057(9)	0.0058(10)	0.0114(11)	-0.0005(8)	
O4	0.0118(11)	0.0072(11)	0.0041(9)	0.0017(8)	

$$U^{12} = U^{23} = 0.$$

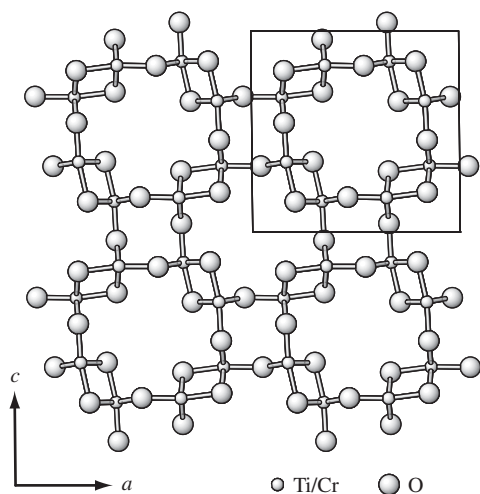


Fig. 2. Framework structure of $\text{Na}_2\text{Cr}_2\text{Ti}_6\text{O}_{16}$ projected along the b -axis.

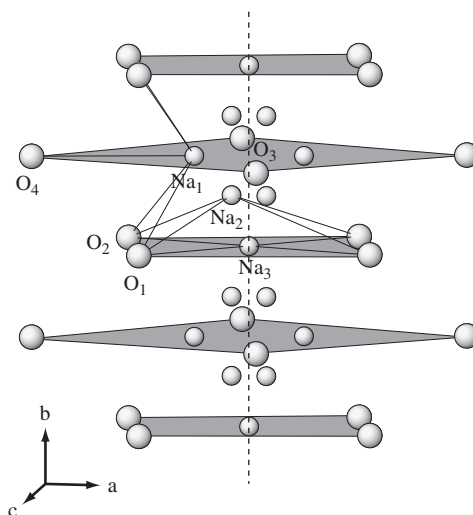


Fig. 4. Coordination environments of Na ions.

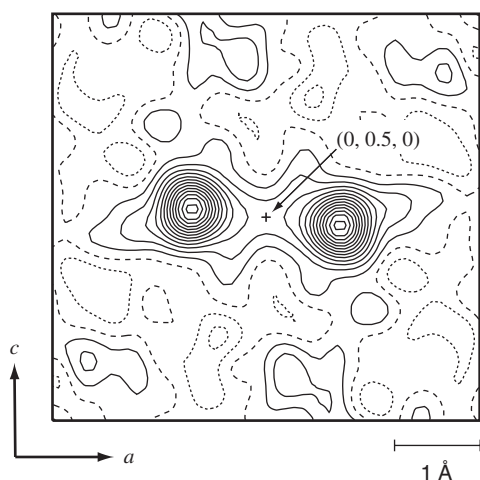


Fig. 3. Difference Fourier map at the $y = 0.5$ section for a structure model containing no Na ions. Contour intervals are $0.5e/\text{Å}^3$. The solid and dotted lines represent positive and negative densities, respectively. The broken lines are zero levels. The center of the map is $(0, 0.5, 0)$.

Ti/Cr occupation ratios at the two sites, because these are related to the question mentioned in the previous part; whether the symmetry of this hollandite at 1350°C is tetragonal or monoclinic. If the tetragonal hollandite is formed at 1350°C , the Cr/Ti ratios at $M1$ and $M2$ sites should be the same to each other, because these sites are equivalent in the tetragonal symmetry. It seems that the exchange of metal ions between the two sites during the cooling process of the sample is impossible. Therefore, the Cr/Ti ratios at $M1$ and $M2$ sites must be the same to each other even after transformation to the monoclinic form. On the other hand, if the structure is monoclinic at 1350°C , the Cr/Ti ratios at the two metal sites can be different from each other. The significance of the different Cr/Ti ratios from the present results in Table 3 is ambiguous, because the difference of the occupation factors for Ti between the

two sites, $0.058 (= 0.779 - 0.721)$, is close to three times their estimated error, $0.054 (= 3 \times 0.018)$.

In order to consider this problem more carefully, the two models were compared. The first one (model I) is that mentioned above. In the second model (model II), the Cr/Ti ratio was fixed to $1/3$ at both of the $M1$ and $M2$ sites. A reliability factor $wR_{\text{all}}(F^2) = 0.0896$ in model II was slightly larger than the value $wR_{\text{all}}(F^2) = 0.0895$ in model I. It should be noted that one additional parameter was needed in the latter. In order to judge the validity of the models, the Hamilton method [16] was used. The following hypothesis was tested: “The structure is described enough by model II.” As the numbers of parameters are 51 for model II and 52 for model I, the dimension of the hypothesis is $1 (= 52 - 51)$. The numbers of degrees of freedom for the refinement are $881 (= 933 - 52)$. Then, the critical value for the 5% significance level is $R_{1,881,0.005} = 1.0022$. The ratio of reliability factors of the two models, $wR_{\text{all}}(\text{model II})/wR_{\text{all}}(\text{model I}) = 0.0896/0.0895 = 1.001$, is smaller than the critical value. Namely, the above hypothesis cannot be rejected at the 5% significance level. Thus, we cannot confirm the significance of the different Cr/Ti ratios at the $M1$ and $M2$ sites unfortunately. Neutron diffraction experiments will be useful to solve the problem.

4. Discussion

The distortion of the framework structure is common in hollandite structures. Tetragonal hollandite $\text{Ba}_{1.23}(\text{Al},\text{Ti})_8\text{O}_{16}$ was formed, while $\text{Ba}_{1.28}(\text{Fe},\text{Ti})_8\text{O}_{16}$ had the monoclinic form. Tetragonal–monoclinic transformation controlled by the molar composition has been observed in the solid-solution system $\text{Ba}_{1.23}(\text{Al},\text{Ti})_8\text{O}_{16}$ – $\text{Ba}_{1.28}(\text{Fe},\text{Ti})_8\text{O}_{16}$ [17]. Recently, it was reported that structures of $\text{Ba}_x\text{Fe}_{2x}\text{Ti}_{8-2x}\text{O}_{16}$ and $\text{Ba}_x\text{Fe}_x\text{Ti}_{8-2x}\text{O}_{16}$ were tetragonal at $x = 1.0$, but monoclinic at ca. $x = 1.2$ and above [18].

Tetragonal–monoclinic transformation of the former was observed between $x = 1.1$ and 1.2 [19]. It is known that the symmetry of a hollandite structure becomes monoclinic when the ratio of the cation radii $R_A/R_{M,Ti}$ (R_A : crystal radius of the tunnel cation A , $R_{M,Ti}$: composition-weighted mean of crystal radii for framework cations M and Ti) is small. The tetragonal/monoclinic boundary was approximately $R_A/R_{M,Ti} = 2.08$ [20], although this is not the case for some hollandite structures. The ratio $R_{Na}/R_{Cr,Ti}$ of $Na_xCr_xTi_{8-x}O_{16}$ is 1.767 for $x = 1.7$ and 1.766 for $x = 2.0$, which is little changed by the Cr substitution for the Ti, as the crystal radius is 0.745 Å for Ti^{4+} and 0.755 Å for Cr^{3+} in the 6-coordination [21]. Thus, expected structures are not tetragonal but monoclinic in all of the composition range $1.7 \leq x \leq 2.0$.

The deformation of the Na ion distribution in the tunnel associated with the tetragonal–monoclinic transformation was reported in $Na_xCr_xTi_{8-x}O_{16}$ ($x \approx 1.7$) [9]. In the tetragonal form at room temperature, equivalent four peaks were observed in an electron density map at $y = 0.5$, which deformed to that containing the two higher peaks and the two weaker ones in the low-temperature phase of the monoclinic symmetry. As only two peaks are observed in Fig. 3, the deviation from the four-fold symmetry of the Na ion distribution is more prominent in $Na_2Cr_2Ti_6O_{16}$ than in the monoclinic form of $Na_xCr_xTi_{8-x}O_{16}$ ($x \approx 1.7$). This may be related to the fact that the unit cell of the former ($a/c = 1.033$) is more distorted than that of the latter ($a/c = 1.013$). However, such an effect has never been reported for other monoclinic hollandite structures, probably because the tunnel ions deviate little from the center axis of the tunnel. Precise analyses for the anisotropy of thermal parameters (i.e., probability density functions) will make it possible to clarify the deformation of the tunnel ion distribution in those hollandites, too.

As mentioned in the previous section, the significance of different Cr/Ti ratios at the framework metal sites, $M1$ and $M2$, was unclear from the statistical judgment. Therefore, the question for the symmetry at 1350 °C still remains unsolved. One of the best ways to clarify the symmetry of hollandite $Na_xCr_xTi_{8-x}O_{16}$ ($1.8 \leq x \leq 2.0$) is to carry out the X-ray diffraction measurement at high temperatures. However, the experiment by keeping the sample at temperatures so high as 1350 °C is not a trivial one. In addition, a serious problem would be the evaporation of Na ions leading to the decrease of the Na content during the heating process. Actually, when a Pt tube was imperfectly sealed in the synthetic study for phase relations, the product was the mixture of tetragonal and monoclinic forms. The isomorphous tetragonal–monoclinic phase transformation of $Na_xCr_xTi_{8-x}O_{16}$ ($x \approx 1.7$), which was in between room temperature and -50 °C as confirmed by X-ray diffraction measurements, was not detected by the DSC measurement. Thus, it is difficult to clarify the symmetry of the hollandite structures at 1350 °C by experiments directly. Instead, speculative discussion

based on structural data from the present analysis can be given. The Cr/Ti ratio at the $M1$ site is larger than that at the $M2$ site as shown in Table 3. The mean metal–oxygen distance for the $M1$ site is larger than that for the $M2$ (Table 4). These results are reasonable from a viewpoint of crystal chemistry considering the ionic radius 0.605 Å for Ti^{4+} and 0.615 Å for Cr^{3+} [21]. This suggests that the difference of the Cr/Ti ratios at the two metal sites is significant, implying the monoclinic structure at 1350 °C. The pronounced deformation of the Na ion distribution as discussed in the previous paragraph also contributes to keep the monoclinic structure at high temperatures. Therefore, the Na-hollandite would behave differently to the Ba-hollandites which show tetragonal–monoclinic transformation below 500 K [22,23].

In summary, there are three characteristics related to the symmetry of the present hollandite structure: (i) distortion of the framework structure, (ii) deformation of the Na ion distribution in the tunnel, and (iii) different Cr/Ti ratios between the two metal sites in the framework structure. The first one is common in hollandite structures which show the tetragonal–monoclinic transformation. The second one was observed in the low-temperature phase of $Na_xCr_xTi_{8-x}O_{16}$ ($x \approx 1.7$) [9] and more prominent in $Na_2Cr_2Ti_6O_{16}$. The third one was first pointed out in this hollandite, although further experiments are necessary to confirm its significance.

Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2006.05.007.

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