Synthesis of a New Compound NaGaTi₅O₁₂

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新物質 NaGaTi₅O₁₂ の合成

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Single crystals of a new compound NaGaTi₅O₁₂ were synthesized by the flux method. This crystal always occurred in coexistence with Na_{1-x}Ti_xGa_{5-x}O₈ crystals. The best crystal was obtained by slow-cooling after keeping at 1350°C for 10 h using a mixture of 35 mol% crystal composition of (Mo₂O)₁(Ga₂O₃)₁(TiO₂)₁ and 65 mol% flux composition of (Na₂O)₁(MoO₃)_{1.5} as a compositional condition in the flux melt. This crystal structure consists of peculiar framework with one-dimensional tunnel structure of a new type which is a monoclinic system with $a=15.202$ (Å), $b=3.732$ (Å), $c=9.317$ (Å) and $\beta=122.04^\circ$. This compound was identified as a high temperature phase of Na-Ga-freudenbergite (Na_{0.7}Ga_{0.7}Ti_{3.3}O₈) which transformed at 1238°C, and melted at 1336°C.

Key-words: New tunnel structure, Sodium gallotitanate, NaGaTi₅O₁₂, Flux growth

1. Introduction

A new compound NaGaTi₅O₁₂ (hereafter NGTO) was synthesized by the flux method. This crystal structure was coincident with that predicted as a possible structure in alkali-metal titanates by Andersson and Wadsley¹⁾ and the hypothetical substance has been given to have a composition A₂Ti₆O₁₂ (A=alkali-metals).

We succeeded in synthesizing the NGTO crystals by replacing Ti sites in the Na₂Ti₆O₁₂ with Ga. In this paper, the growth conditions, chemical composition,

structure and thermal stability of single crystals are described.

2. Experimental

Starting materials were TiO₂, Ga₂O₃ and MoO₃ powders of 99.99% purity and Na₂CO₃ powder of 99.9%. The flux employed was a mixture of Na₂CO₃ and MoO₃ powders. A 100 ml Pt-crucible which was tightly covered with fitted lid was used in this work. The growth crystals were taken out from the crucible by dissolving the flux in hot water. The chemical compositions of single crystals were determined by the EPMA method.

3. Results and discussion

3.1 Single crystal synthesis

Table 1 exhibits the compositional conditions in the flux melts and the obtained results for the single crystal growth of NGTO. In the compositional conditions of the flux melts shown in Table 1, the crystal composition is the composition of the mixture of crystal components and the flux composition is that of the mixture of flux components using as the solvent. The NGTO single crystals were synthesized by slow-cooling after keeping at 1350°C for 10 h using a mixture of a crystal composition of (Na₂O)₁(Ga₂O₃)₁(TiO₂)₁ in 30-35 mol% and a flux composition of (Na₂O)₁(MoO₃)_{1.5} in 65-70 mol%. The slow cooling operation was carried out to 1000°C with a rate of 4°C/h. The weight loss of the bulk composition dur-

Table 1. The compositional conditions in flux melts and the obtained results for the growth of NaGaTi₅O₁₂ single crystals by the flux method.

Temperature High→Low (°C)	Crystal composition (C) (Na ₂ O)-(Ga ₂ O ₃)-(TiO ₂) (Molar ratio)			Flux comp. (F) (Na ₂ O)-(MoO ₃) (Molar ratio)		Melt cmpo. C/F (Mol%)	Crystals*
1350→1000	0.5	0.5	5.0	1.0	1.5	30/70	TiO ₂ , NTGO
1350→1000	0.5	0.5	3.5	1.0	1.5	20/80	TiO ₂ , NTGO
1350→1000	0.75	0.5	1.5	1.0	1.5	20/80	TiO ₂ , NTGO
1300→1000	1.0	1.0	1.0	1.0	1.5	30/70	NTGO, NGTO, (TiO ₂)
1350→1000	1.0	1.0	1.0	1.0	1.5	35/65	NTGO, NGTO
1350→1000	2.0	1.0	1.0	1.0	1.5	30/70	NTGO, Na ₂ Ti ₃ O ₇
1350→1000	1.0	1.0	1.0	1.0	1.25	30/70	NTGO, Na ₂ Ti ₃ O ₇

* NGTO=NaGaTi₅O₁₂, NTGO=Na_{1-x}Ti_xGa_{5-x}O₈, TiO₂=rutile, ()=small amount

ing a growth process was below 1 wt%. However, the NGTO crystals always occurred in coexistence with $\text{Na}_{1-x}\text{Ti}_x\text{Ga}_{5-x}\text{O}_8$ crystals.²⁾ The NGTO crystals could not be synthesized when the crystal composition in a flux melt was stoichiometrical with that of NGTO, and rutile and $\text{Na}_{1-x}\text{Ti}_x\text{Ga}_{5-x}\text{O}_8$ crystals were always prepared. Especially, rutile was very predominant with a acicular form. The NGTO crystals were synthesized under some conditions which $\text{Na}_{1-x}\text{Ti}_x\text{Ga}_{5-x}\text{O}_8$ crystals occurred predominantly instead of rutile. Consequently, the monophase of NGTO crystals is not yet obtained. Figure 1 shows the NGTO single crystals grown by the flux method. Those crystals are obtained in an acicular form elongating along the *c*-axis (or the tunnel axis) with transparency or translucence. Figure 2 shows crystal structure projected on the (010) plane of NGTO, and the crystallographical properties are exhibited in Table 2. The crystal structure is characterized by a new type of tunnel framework consisting of treble

(Ga, Ti) O_6 octahedral ribbon. This tunnel framework and the crystallographical properties resemble that of sodium hexatitanate $\text{Na}_2\text{Ti}_6\text{O}_{13}$ which has been reported by Andersson and Wadsley¹⁾ except for the β angle is different. An only Na ion is able to occupy in a unit tunnel. The detail of structure analysis is to be published by Michiue et al.³⁾ Table 3 shows the chemical compositions of NGTO crystals analyzed by the EPMA method. The formula was calculated on the basis of atomic ratio as O_{12} in a chemical composition. As the results, the general formula indicated to be $\text{NaGaTi}_5\text{O}_{12}$ as a stoichiometrical composition.

3.2 Polycrystal synthesis

The NGTO polycrystal was also prepared by the solid reactions. It was found that the polycrystal was synthesized at temperatures of 1250°C or above. At temperatures of 1200°C or below, only Na-Ga-freudenbergite, $\text{Na}_{0.7}\text{Ga}_{0.7}\text{Ti}_{3.3}\text{O}_8$, was always synthesized using the same starting composition. The ob-

Fig. 1. $\text{NaGaTi}_5\text{O}_{12}$ single crystals grown by the flux method; (A) Stereoscopic photomicrograph, (B) SEM image.

Fig. 2. The crystal structure projected on the (010) plane of $\text{NaGaTi}_5\text{O}_{12}$ crystal.

Table 2. The crystallographical properties of $\text{NaGaTi}_5\text{O}_{12}$ comparing with that of $\text{K}_2\text{Ti}_6\text{O}_{13}$.

$\text{NaGaTi}_5\text{O}_{12}$ (NGTO)	$\text{K}_2\text{Ti}_6\text{O}_{13}$ (KTO)
Monoclinic, (C2/m)	Monoclinic, (C2/m)
$a(\text{\AA}) = 15.202$	15.131
$b(\text{\AA}) = 3.732$	3.745
$c(\text{\AA}) = 9.317$	9.159
$\beta^\circ = 122.04$	99.3
$V(\text{\AA}^3) = 448.1$	512.1
$D(\text{g}\cdot\text{cm}^{-3}) = 3.88$	3.51
$z = 2$	2

Table 3. The chemical compositions of $\text{NaGaTi}_5\text{O}_{12}$ single crystals analyzed by the EPMA method

No.	(Na_2O)	(Ga_2O_3) (wt%)	(TiO_2)	Total	Chemical compositions
1	6.245 (6.152)	17.522 (17.260)	77.751 (76.588)	105.518 (100.000)	$\text{Na}_{1.04}\text{Ga}_{0.96}\text{Ti}_{5.01}\text{O}_{12.00}$
2	6.396 (6.339)	17.182 (17.029)	77.328 (76.640)	100.898 (100.000)	$\text{Na}_{1.07}\text{Ga}_{0.95}\text{Ti}_{5.02}\text{O}_{12.00}$
3	6.328 (6.211)	19.147 (18.795)	76.403 (75.00)	101.870 (100.000)	$\text{Na}_{1.05}\text{Ga}_{1.05}\text{Ti}_{4.94}\text{O}_{12.00}$

tained Na-Ga-freudenbergite transformed into a NGTO phase by reheating at 1250°C. Figure 3 shows a DTA curve of Na-Ga-freudenbergite which was prepared at 1200°C for 25 h with a stoichiometrical NaGaTi₅O₁₂ composition. It indicates that the freudenbergite transforms irreversibly to an NGTO

Fig. 3. A DTA curve of Na-Ga-freudenbergite polycrystal prepared at 1200°C for 25 h with a NaGaTi₅O₁₂ composition.

phase at 1238°C and melt at 1336°C. This phase transformation is represented by no change of composition as follows;

We also tried to synthesize KGaTi₅O₁₂ and LiGaTi₅O₁₂ compounds which replaced Na ion in the NGTO with K or Li ions at 1250°C for 25 h. As the results, it was unsuccessful, and rutile and priderite, K₂Ga₂Ti₆O₁₆, were obtained in the former, and in the latter, rutile and LiGaTiO₄.⁴⁾ Furthermore, we tried to prepare a NaAlTi₅O₁₂ compound as the analogue of NGTO at 1200° and 1250°C for 20 h. However, only Na-Al-freudenbergite, Na_{0.7}Al_{0.7}Ti_{3.3}O₈, was obtained. This freudenbergite decomposed into freudenbergite (perhaps Na_{0.7-x}Al_{0.7-x}Ti_{3.3+x}O₈) and Na-β"-Al₂O₃ phases at 1350°C for 20 h.

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