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Growth and properties of $Na_8Ti_5O_{14}$ crystals

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Transparent single crystals of $Na_8Ti_5O_{14}$ have successfully been grown by the pulling method from a melt of sodium and titanium oxides with the molar ratio of Na_2O to TiO_2 of 1 to 1.25. X-ray fluorescence and neutron activation analyses were used to determine the composition of the crystals, which corresponded to the formula $Na_{7.95}Ti_5O_{13.98}$. The crystal structure was found to be triclinic with space group of P_1, by using X-ray diffraction and piezoelectric examinations. A phase transition was found to exist at 365 ±5° C from measurements of DTA, thermal dilatometry and dielectric properties.

1. Introduction

Several sodium titanate compounds have been reported in the binary system of Na_2O and TiO_2 [1–3]. It is already known that the compound $Na_8Ti_5O_{14}$, which is a member of sodium titanate family, can be obtained by calcinating or melting a mixture of Na_2O and TiO_2 with the stoichiometric composition [4–6]. The phase diagram of the Na_2O–TiO_2 system has been presented by many authors [7, 8, 9]. Washburn and Bunting [7], and Belyaev and Belyaeva [9] showed that $Na_8Ti_5O_{14}$ melts congruently at 1030° C. Batygin [10] stated in his report on the study of formation of sodium titanates, that $Na_8Ti_5O_{14}$ could be the same compound of sodium metatitanate as found in the ASTM index [11]. He also described that sodium metatitanate was metastable and decomposed on heating above 680° C to $Na_8Ti_5O_{14}$ and Na_2O. Anderson and Wadsley [12, 13] examined the relations between crystal structure and chemical composition in the sodium titanates, and found that these compounds may be expressed by the general formula $Na_2O \cdot nTiO_2$, where n is 1, 2, . . . , 6. However, the compound $Na_8Ti_5O_{14}$ remains unclarified.

The purpose of the present study was to obtain good single crystals of $Na_8Ti_5O_{14}$, and to elucidate its physical and chemical properties.

2. Experimental

2.1. Materials

Reagent grade Na_2CO_3 and TiO_2 of 99.9% purity, supplied from Wakô Chemical Co, were used. The reactants were weighed and mixed in a polyethylene ball-miller for several hours.

2.2. Differential thermal analysis (DTA)

To confirm the phase diagram of the Na_2O–TiO_2 binary system [7–9] a standard high temperature DTA apparatus, type "M8006", supplied by Rigaku Electric Co, was used. 1g samples of Na_2CO_3 and TiO_2 powders were used to determine their melting points with a temperature increasing at $20° C\,min^{-1}$. A search for phase transition in the $Na_8Ti_5O_{14}$ crystal was also carried out using this apparatus.

2.3. Crystal growth

Growth of the $Na_8Ti_5O_{14}$ crystals was obtained using the pulling method. Approximately 60g melt of Na_2O and TiO_2 was placed in a 50 ml platinum crucible. The growth furnace used in the present experiment is shown in Fig. 1. The crucible was heated at a known rate by silicon carbide heaters and the crystal was pulled using a seed crystal which was prepared by cooling a melt of Na_2O and TiO_2 of molar ratio of 1 : 1. The seed was fastened to a platinum holder and inserted from the top of the furnace. To observe crystal growth, two holes were bored in the furnace: one for viewing and the other for illumination, as shown in Fig. 1. The temperature gradient in the furnace was such that the top of the crucible was about 5° C cooler than the surface of the melt. No control on the atmosphere was carried during the growth experiment.

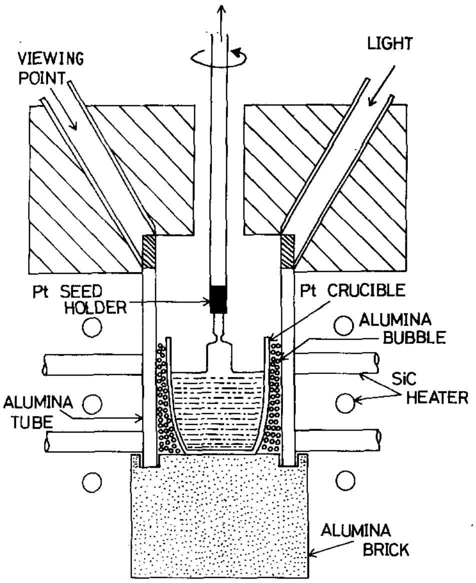

Figure 1 Apparatus used for growth of $Na_8Ti_5O_{14}$ crystals.

The most appropriate growth conditions were as follows: the average pulling rate was $1\,mm\,h^{-1}$, rotation rate was 40 rpm and the average weight of the crystal was about 5g. After growth was completed, the crystal was cooled to room temperature at a rate less than $70°\,C\,h^{-1}$ in order to eliminate, as much as possible, crack formation during cooling.

2.4. Analysis of the crystals

The titanium content of crystals was determined by X-ray fluorescent analysis, and the sodium content by a neutron activation technique. The powdered specimen was irradiated in a JRR-3 nuclear reactor and subjected to non-destructive gamma ray spectrometry by using a Ge(Li) detector.

Plots of temperature dependence on dielectric constant were obtained by means of a wide band capacitance bridge "TR-1C" (Andô Electric Co). Dilatometric measurements were carried out using a differential transformer "ICS-025" supplied by Shinkô Electronics Co.

3. Results and discussion

The single crystals of $Na_8Ti_5O_{14}$ were successfully obtained from the melt of stoichiometric composition and of molar ratio Na_2O;TiO_2 of 1 : 1. Typical crystals, as shown in Fig. 2, were transparent and white or very slightly yellow in colour with a well developed (0 1 0) face. Preliminary optical absorption experiments showed that the crystals had no marked absorption between 340 and 2500 nm.

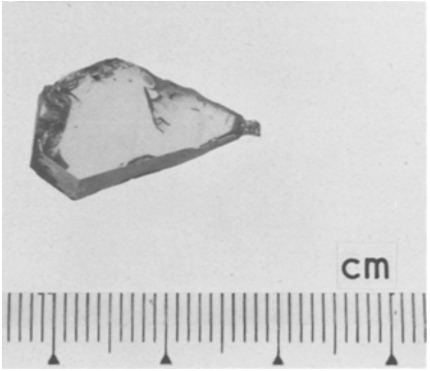

Figure 2 Typical as-grown crystal of $Na_8Ti_5O_{14}$.

The as-grown and polished crystals were examined under a polarized or a dark-field microscope. They were biaxially negative and the refractive index along the [0 1 0] axis was about 1.76. Almost all crystals were found to be free from optically visible inclusions. The imperfections commonly observed were cracks, which were probably introduced by thermal strain during cooling.

Fig. 3 shows thermal expansions between room temperature and 600° C. It is apparent that a remarkable anomaly exists above 300° C. The axis perpendicular to the (0 1 0) face showed a sharp contraction as the temperature increased, and at same time an enhanced elongation was observed along an axis parallel to (0 1 0). This behaviour is due to a phase transition which will be described later.

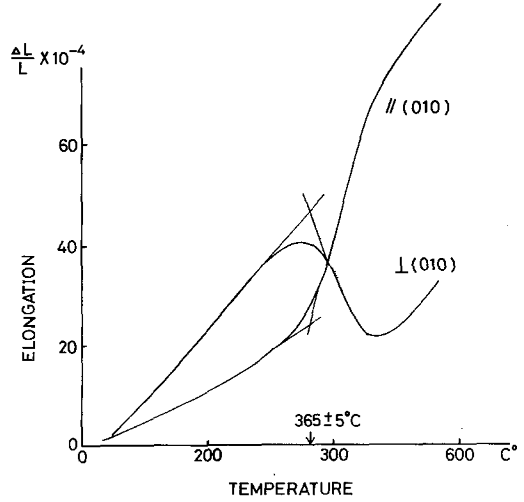

Figure 3 Thermal expansion of $Na_8Ti_5O_{14}$ crystal.

TABLE I Chemical composition of $Na_8Ti_5O_{14}$ crystals

	Na (wt %)	Ti (wt %)	Atomic ratio Ti : Na
Analytical (mean)	27.8	36.4	0.629
Theoretical	28.4	37.0	0.625

Analytical formula: $Na_{7.95}Ti_5O_{13.98}$.

Analytical data of two typical crystals, grown from the melt of molar ratio Na_2O:TiO_2 of 1 : 1, are listed in Table I. The results indicate an average chemical formula of $Na_{7.95}Ti_5O_{13.98}$, which indicates about a 1% deficiency in sodium content from the stoichiometric composition.

The X-ray powder pattern of a selected, transparent crystal, obtained together with an internal standard of Si powder using an ordinary diffractometer, apparently showed that the lines had a close resemblance to those reported by Batygin [10] and were nearly the same as the patterns published in the ASTM index for "sodium metatitanate" [11] (see Table II). From the facts that the composition of our crystals was very close to the formula $Na_8Ti_5O_{14}$, and that the X-ray patterns were very similar to those of the ASTM card, we support Batygin's conclusion that "the sodium metatitanate in the ASTM card would be $Na_8Ti_5O_{14}$".

DTA and X-ray measurements on the mixed and calcinated powders of Na_2CO_3 and TiO_2 showed that the compound $Na_8Ti_5O_{14}$ was stably formed above 1000° C in any composition between Na_2O:TiO_2 of 1.00 and 1.25, and that no other titanate compound was detected in this composition range. These results are in reasonable agreement with Batygin's observation that Na_2TiO_3* was only stable below 680° C, and decomposed to $Na_8Ti_5O_{14}$ and Na_2O above this temperature [10]. The phase diagrams of Na_2O–TiO_2 reported by Washburn and Bunting [7], and by Belyaev and Belyaeva [9] seem to contain some inaccurate information on the stability and melting behaviour of Na_2TiO_3. However, Budnikov and Tresvyatski's diagram is

TABLE II X-ray powder patterns of sodium titanates

$Na_8Ti_5O_{14}$ (Present work)		$Na_8Ti_5O_{14}$ (Batygin [10])		Na_2TiO_3 (ASTM [11])	
d	I/I_0	*d*	I/I_0	*d*	I/I_0
9.59	39	9.9	20	10.0	20
7.31	55	7.3	70	7.2	70
7.04	38	7.1	65	–	–
4.93	5	4.83	5	–	–
4.80	5	–	–	–	–
4.16	3	4.15	10	–	–
4.051	9	4.02	20	4.01	30
3.965	9	3.95	15	–	–
3.641	9	–	–	–	–
3.440	7	3.42	8	–	–
3.298	5	–	–	–	–
3.052	20	3.05	10	–	–
2.910	15	–	–	–	–
2.866	13	2.86	15	–	–
2.643	11	2.64	30	2.63	30
2.621	9	2.62	35	–	–
2.604	11	–	–	–	–
2.520	12	2.52	10	–	–
2.314	85	2.30	60	2.30	60
2.225	100	2.22	100	2.22	100
2.212	65	–	–	–	–
1.973	4	–	–	–	–
1.931	9	1.93	8	1.944	8
1.850	5	–	–	–	–
1.638	20	1.63	15	1.663	15
1.625	18	1.62	15	–	–
1.582	20	1.58	20	1.598	15
1.571	11	1.56	20	1.578	15
1.554	4	1.55	15	1.561	15

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*The structure of Na_2TiO_3 is supposed to be f c c with a cell dimension of $a_0 = 4.50$ Å.

partly correct because the compound Na_2TiO_3 is not described in their illustration [8].

X-ray measurements indicated that the crystal was triclinic with cell dimensions of $a_0 = 10.31$ Å, $b_0 = 4.05$ Å, $c_0 = 7.78$ Å, $\alpha = 82.4°$, $\beta = 110.5°$ and $\gamma = 102.8°$ (see Fig. 4). The pycnometric and X-ray densities at room temperature were 3.38 and 3.32 g cm^{-3} for $Z = 1$, respectively. The fact that a piezoelectric effect was observed on a cleaved surface of (0 1 0), indicates that the crystal belongs to the space group P_1. However, more detailed crystal structure is yet to be determined. The magnitude of the electro-mechanical coupling constant was of the same order as that of d_{11} in quartz.

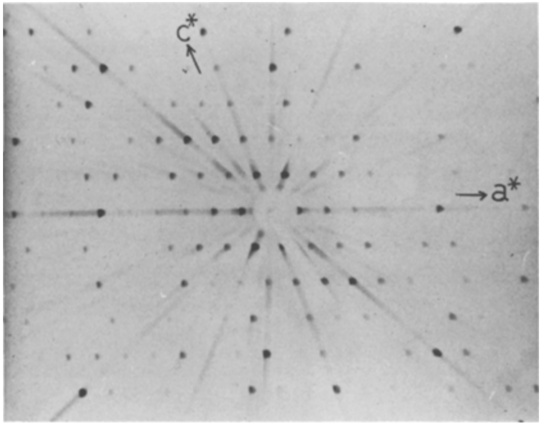

Figure 4 Precession photograph of cleaved (0 1 0) plane (Mo/Zr).

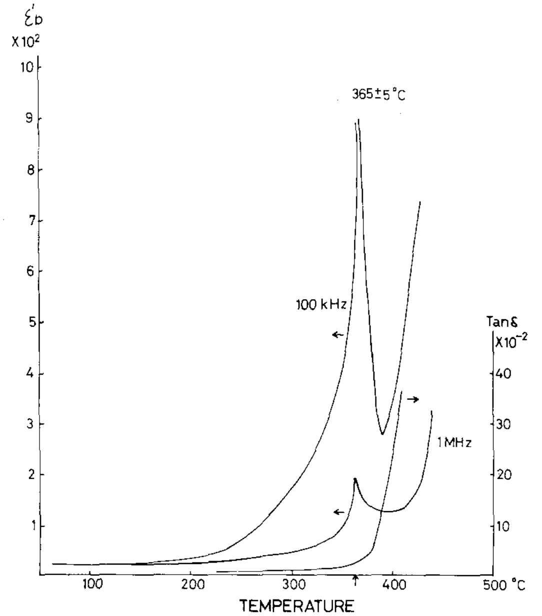

Figure 5 Curve of dielectric constant versus temperature, from which the transition temperature was determined. The peak value of dielectric constant is ~ 1.5×10^3 at 365 ± 5° C.

The dielectric constant was measured as a function of temperature along the [0 1 0] axis, as illustrated in Fig. 5. A sharp peak, the value of which reached about 1.5×10^3, appeared at 365 ± 5° C. This anomaly is thought to be due to a phase transition from the ferroelectric or antiferroelectric state to a paraelectric one, with an increase in temperature. Another increase in the dielectric constant appeared above 400° C. This is believed to be caused by a loss current in the crystal, because a considerable decrease in electrical resistivity was observed in this temperature range.

Further attempts to ascertain the phase transition at 365° C were performed using DTA. As shown in Fig. 6, a small endothermic effect was clearly detected on a powdered sample of the single crystal. The temperature where the effect began to appear was about 365° C, which coincides well with the temperatures obtained from dilatometric and dielectric measurements.

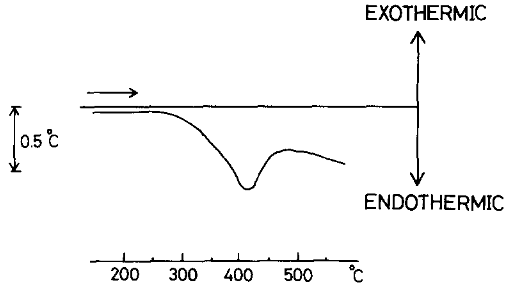

Figure 6 DTA curve of powdered $Na_8Ti_5O_{14}$.

In order to obtain a complete confirmation of the ferro- or antiferroelectricity in the $Na_8Ti_5O_{14}$ crystal, several attempts to obtain a hysteresis relation between electric field and polarizability were carried out along the [0 1 0] axis using a modified Saweyer–Tower circuit. However, no hysteresis loop was observed at a temperature between 20 and 360° C under an applied field of 6 kV cm^{-1}. The failure of this experiment could be attributed to a high coersive field and a low electrical resistivity of the specimen.

4. Conclusion

The experiments showed that good single crystals of $Na_8Ti_5O_{14}$ can be grown by pulling from a melt of Na_2O and TiO_2. The fact that the $Na_8Ti_5O_{14}$ crystals were successfully pulled from a melt of molar ratio Na_2O:TiO_2 of 1.00 to 1.25, indicates that $Na_8Ti_5O_{14}$ is a stable compound near the melting point. The results are in reasonable agreement with the experimental results of Batygin, where the compound Na_2TiO_3 was only stable below 680° C and decomposed to $Na_8Ti_5O_{14}$ and Na_2O above this temperature.

TABLE III Properties of $Na_8Ti_5O_{14}$ crystals

Analytical formula: $Na_{7.95}Ti_5O_{13.98}$
Melting point: ~ 1030° C (congruent)
Crystal structure: probably tricrinic (P_1)
$a_0 = 10.31$ Å; $b_0 = 4.05$ Å; $c_0 = 7.87$ Å; $\alpha = 82.4°$;
$\beta = 110.5°$; $\gamma = 102.8°$; $V_X = 325.4$ Å^3
Density: 3.32 g cm^{-3} (X-ray), 3.38 g cm^{-3} (pycnometric)
Optical property: biaxially negative
Refractive index: 1.76 (along b^*-axis, W-lamp)
Transition temperature: 365 ± 5° C
Hardness: about 5 Mohs
Cleavage: mainly (0 1 0).

From the measurements on DTA, dilatometry and the dielectric constant, it is concluded that a phase transition exists in this crystal at 365 ± 5° C. Table III is a summary of the properties.

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