

Low Temperature Synthesis of Tunnel Structure $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ using Citratoperoxotitanic Acid Tetranuclear Complex

Koichiro Ueda¹, Koji Tomita^{1,2}, Kazumi Fujita¹, Masato Kakihana², Shinya Sawai³

¹School of Science, Tokai University, 1117 Kitakaname Hiratsuka Kanagawa 259-1292, tomita@keyaki.cc.u-tokai.ac.jp,

²Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira Aoba-ku Sendai 980-8577,

³School of Applied Science, National Defense Academy, 1-10-20 Hashirimizu Yokosuka Kanagawa 239-8586

$\text{Ba}_2\text{Ti}_9\text{O}_{20}$ crystal lattice has a Hollandite-like structure, and this compound possesses high ionic conductivity because the TiO_6 octahedra form tunnel-like arrangement around Ba ions. It is used as an electronic material in high frequency devices due to its ferroelectricity and small temperature coefficient. The synthesis of pure material is very difficult because even small deviations from the required stoichiometry result in the formation of impurity phases with close to $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ chemical composition. Typical synthesis method of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ needs annealing at higher than 1523 K temperature to complete solid-state reaction and to produce this peculiar material with the uniform overall chemical composition. In this study we prepared the precursor for $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ by complex gelation method in which citratoperoxotitanic acid tetranuclear complex $[\text{Ti}_4(\text{C}_6\text{H}_4\text{O}_7)_4(\text{O}_2)_4]^{8-}$ was used as a Ti source. The homogeneous precursor was obtained by mixing the Ti complex, $\text{Ba}(\text{CH}_3\text{COO})_2$, and H_3BO_3 (as a flux) in an aqueous solution. The precursor was heat-treated at 1273 K, which is 230 K lower than the temperature of conventional solid-state reaction method, and single phase $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ was obtained. Crystallite size of the prepared particles was less than 100 nm that is desirable for ferroelectric materials.

Key words: $\text{Ba}_2\text{Ti}_9\text{O}_{20}$, ferroelectricity, solution method, flux, crystallite size

1. INTRODUCTION

1.1 $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics

Several compounds have been reported to form in the BaO-TiO_2 system. One of them, $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ phase, was first described by Jonker and Kwestroo in $\text{BaO-TiO}_2\text{-SnO}_2$ ternary system [1]. This solid has the tunnel structure [2] with barium ions staying in the tunnels made up by TiO_6 octahedra (Fig. 1). Because of its peculiar crystal structure, this compound possesses high ionic conductivity. In addition, this compound is used as an electric material [3] in high frequency devices due to its ferroelectricity [4-5], low density loss, high quality factor, high dielectric loss and small temperature coefficient [6]. Formation of pure $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ samples is very sensitive to the processing temperature and requires a strict control of composition and homogeneity. To avoid formation of BaTi_4O_9 and $\text{BaTi}_5\text{O}_{11}$ that have very close composition ratio of Ba and Ti to $\text{Ba}_2\text{Ti}_9\text{O}_{20}$, the ratio have to be strictly controlled. Solid state reaction between BaCO_3 and TiO_2 needs temperatures above 1523 K to obtain the $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ phase. Below 1523K, $\text{BaTi}_5\text{O}_{11}$, BaTi_4O_9 , and TiO_2 phases are obtained, instead of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ [7-8]. Although solid state reaction is the most common method for synthesis of ceramics due to its simplicity, it is not suitable for preparation of fine, dispersed and homogeneous multicomponent

powders. A particular limitation is connected with the need to use high temperatures to accelerate interdiffusion of the components.

At the same time, high processing temperature accelerates the growth of the particles, which may be a disadvantage for the ceramic materials. These problems inherent to conventional solid state reaction can be overcome by use of solution methods. In the later approach the atomic scale homogeneity is achieved already in the solution and therefore more homogeneous

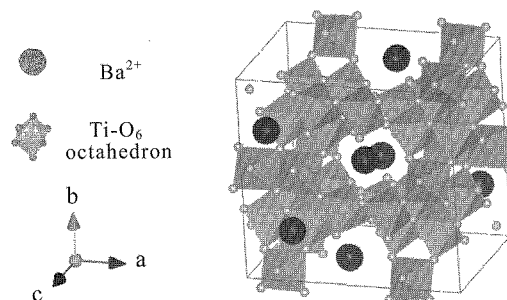


Fig. 1 Crystal structure of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ($a = 14.358(4)$, $b = 14.095(4)$, $c = 7.477(1)$, $\alpha = 95.53(3)^\circ$, $\beta = 100.55(3)^\circ$, $\gamma = 89.95(2)^\circ$, $Z = 2$, Space group = $P1\bar{1}$, ICSD No. 35582).

materials can be obtained than in the case of the solid state reaction while the heat treatment requires lower temperatures. Due to these merits metal-alkoxide method [9], coprecipitation method, Pechini-type polymerizable method [10] became the most popular solution techniques, which are used to obtain the multicomponent ceramics. $Ba_2Ti_9O_{20}$ is also made by these solution methods, but all of these approaches need at least 1423 K to obtain the single phase $Ba_2Ti_9O_{20}$ ceramics [11-13].

1.2 Citratoperoxotitanic acid tetranuclear complex

Ti^{4+} ion hydrolyzes very easily and precipitates as the hydrated oxide ($TiO_2 \cdot nH_2O$). For this reason, titanium organometallic compounds, $TiCl_4$ and $Ti(SO_4)_2$ are to be used in the solution methods. $TiCl_4$ and $Ti(SO_4)_2$ are stable only in the strong acidic solution. So titanium organometallic compounds are widely used in the metal-alkoxide method, but in this case organic solvents are indispensable, while the precursors are expensive and water-sensitive. From the environmental point of view, due to their cost and difficulties in handling, these reagents are not convenient precursors for the solution methods. On the other hand, citratoperoxotitanic acid tetranuclear complex $[Ti_4(C_6H_4O_7)_4(O_2)_4]^{8-}$ [14-15] is composed only of hydrogen peroxide, ammonium, and citric acid, and it is stable in the aqueous solution for several years. In addition, it is stable in the wide range of pH. Due to these properties, Ti^{4+} could be conveniently combined with another metal cation or an inorganic compound, which makes this water soluble titanium compound a remarkable starting reagent, to obtain the homogeneous precursors and fabricate materials without aggregation of particles after the heat processing [16]. In this study, environmentally benign citratoperoxotitanic acid tetranuclear complex was used as the source of titanium in the synthesis of the single-phase $Ba_2Ti_9O_{20}$ ceramics at lower temperature than it was reported for any other method.

2. EXPERIMENTAL

9 mmol of Ti powder (Toho Titanium Limited, Tokyo, Japan) was added to an ice-cold solution of 36 ml of 30 % H_2O_2 (Kanto Chemical, Tokyo, Japan) and 9 ml of 28 % NH_3 (Kanto Chemical, Tokyo, Japan). Two hours later, a clear solution of Ti-peroxo acid was obtained. 9 mmol of citric acid (Wako Pure Chemical Industries, Osaka, Japan) was added into this solution to obtain citratoperoxotitanic acid tetranuclear complex stable in aqueous solution, followed by addition of 2 mmol of $Ba(CH_3COO)_2$ (Kanto Chemical, Tokyo, Japan) and 3 wt% flux (H_3BO_3 (Kanto Chemical, Tokyo, Japan), $NaCl$ (Wako Pure Chemical Industries, Osaka, Japan), $LiCl$ (Wako Pure Chemical Industries, Osaka, Japan), H_3PO_4 (Kanto Chemicals, Tokyo, Japan)).

In the synthesis of $Ba_2Ti_9O_{20}$ powder, the precursor solution was heated at 393 K on a hot plate with continuous stirring until a 'gel' was obtained (precursor gel), then it was heated for 2 h at 623 K in a mantle heater resulting in a dark brown fluffy mass. It was lightly ground into a powder using an agate mortar. This powder was heat-treated at 873 K for 2 h and yielded a fine white product. It was ground into a powder again in the agate mortar (powder precursor). Finally the powder

or the pelletized precursor was put into an alumina boat and heat-treated at 1073-1473 K for 10 h in air followed by natural cooling to room temperature.

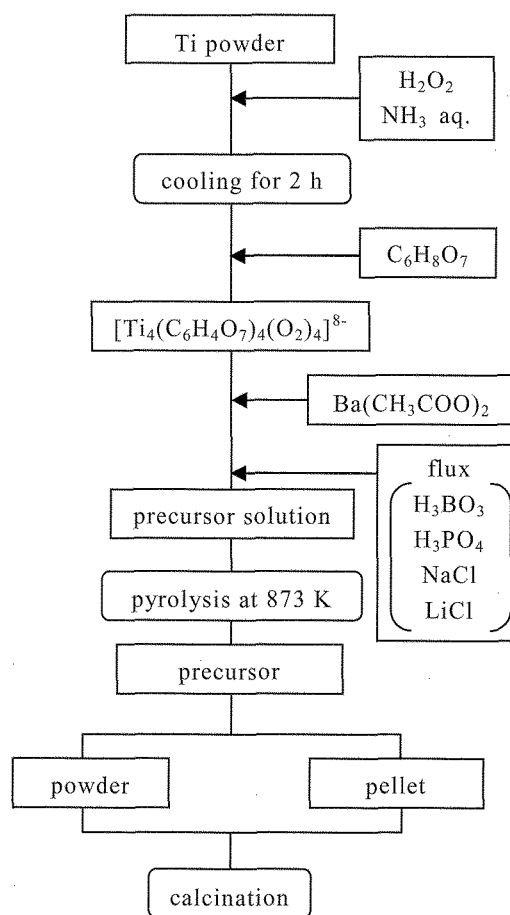


Fig. 2 Synthesis procedure of $Ba_2Ti_9O_{20}$

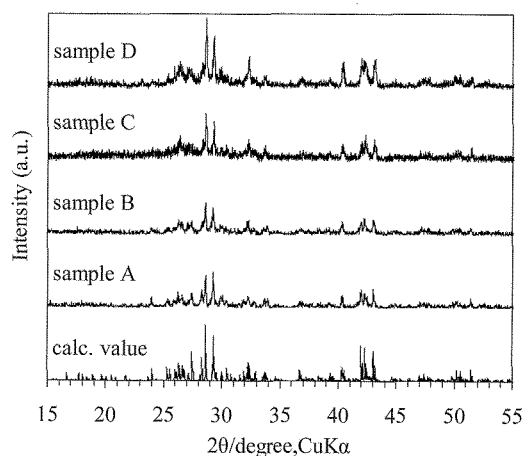


Fig. 3 XRD patterns of $Ba_2Ti_9O_{20}$ (Calcination conditions; Sample A: powder, 1573 K, no-flux. Sample B: pellet, 1473 K, no-flux. Sample C: powder, 1273 K, 3 wt% H_3BO_3 . Sample D: pellet, 1273 K, 3 wt% H_3BO_3 . Calculated value; ICSD No. 35582)

3. RESULTS AND DISCUSSION

3.1 Process temperature and precursors

Figure 3 shows the XRD patterns of the samples after processing under different synthesis conditions. Without a flux, precursor powder needed 1573 K to produce the single phase $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ (Fig. 3 sample A). On the other hand, a pelletized sample transformed to a single phase product at 1473 K (Fig. 3 sample B). So, the pelletized precursor powder could reduce the processing temperature by 100 K. The temperature is only slightly low compared with solid state reaction. However we can avoid mixing processes that causes contamination from the mortar. Table I summarizes the effects of different fluxes on the final phase composition of the prepared samples. One may notice that H_3BO_3 and NaCl are effective to obtain the $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ phase. After further optimization of the processing conditions, $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ single phase could be obtained at 1273 K - 10 h, with H_3BO_3 as a flux. We should also notice that the pelletized precursor resulted in the formation of small amount of $\text{BaTi}(\text{BO}_3)_2$ (Fig. 4 (a) - X) together with another by-product which we could not identify (Fig. 4 (b) - Y) after processing (sample D). However powder precursor yielded only pure $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ (sample C) under the same conditions; besides using powder precursor we could obtain $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ phase at as low as 1173 K. On the other hand, at lower temperature such as 1163K no precursors lead to formation of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ phase.

Table I Effects of fluxes on phase composition of final samples.

		appeared phase		
		TiO_2	$\text{BaTi}_5\text{O}_{11}$	$\text{Ba}_2\text{Ti}_9\text{O}_{20}$
flux	H_3BO_3	No	No	Yes
	H_3PO_4	Yes	No	No
	NaCl	No	No	Yes
	LiCl	Yes	No	No

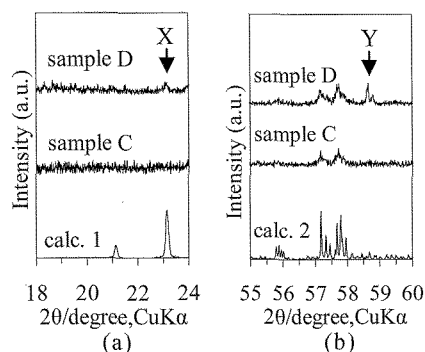


Fig. 4 Comparison of the observed XRD patterns of sample C: (powder, 1273 K, 3 wt% H_3BO_3) and sample D: (pellet, 1273 K, 3 wt% H_3BO_3) with calculated patterns of $\text{BaTi}(\text{BO}_3)_2$: (calc. 1; ICSD No. 97972), and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$: (calc. 2; ICSD No. 35582)

Figure 5 presents the XRD patterns of sample C and calculated patterns of the by-products which may appear below 1273 K in addition to $\text{Ba}_2\text{Ti}_9\text{O}_{20}$. For this purpose we focus on the range of $2\theta = 22 - 31^\circ$, which contains the strongest peaks of all the possible compounds such as $\text{BaTi}_5\text{O}_{11}$, BaTi_4O_9 , $\text{BaTi}(\text{BO}_3)_2$ that may accompany $\text{Ba}_2\text{Ti}_9\text{O}_{20}$. Thus by considering this XRD pattern, sample C was identified as $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ phase, because the main peaks of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ were clearly identified and there were no peaks of secondary phases.

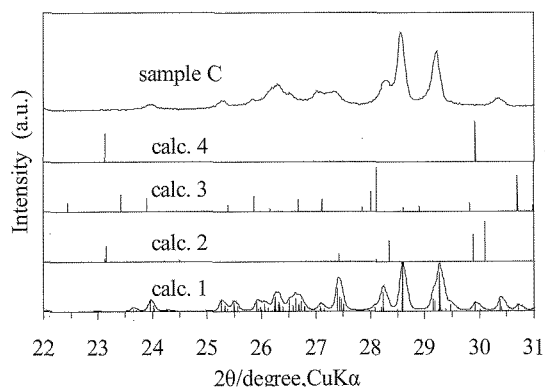


Fig. 5 Comparison of the observed XRD pattern of sample C: (Annealing conditions: powder, 1273 K, 3 wt % H_3BO_3), with calculated patterns of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$: (calc. 1; ICSD No. 35582), BaTi_4O_9 : (calc. 2; ICSD No. 31783), $\text{BaTi}_5\text{O}_{11}$: (calc. 3; ICSD No. 26147), and $\text{BaTi}(\text{BO}_3)_2$: (calc. 4; ICSD No. 97972).

3.2 Mechanism of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ phase synthesis

The differences of the minimum temperature needed to obtain the $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ are depending on the differences in the $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ formation mechanisms for each precursor. Preparation of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ without a flux resulted in the formation of $\text{BaTi}_5\text{O}_{11}$ and BaTi_4O_9 when the processing temperature was relatively low. Therefore it appears that initially titanium rich phase $\text{BaTi}_5\text{O}_{11}$ and barium rich phase BaTi_4O_9 is synthesized. Then they are consumed in the second step to form the $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics at the contact points when the temperature is more favorable for the formation of desired compound.

This mechanism can be described as solid state reaction between BaTi_4O_9 and $\text{BaTi}_5\text{O}_{11}$. And therefore short diffusion distances are essential for preparation of single phase product. When 3 wt% - H_3BO_3 is used as a flux, formation of $\text{BaTi}_5\text{O}_{11}$ and BaTi_4O_9 is accompanied by a new phase $\text{BaTi}(\text{BO}_3)_2$. However this intermediate phase disappears when BaTi_4O_9 and $\text{BaTi}_5\text{O}_{11}$ react to produce $\text{Ba}_2\text{Ti}_9\text{O}_{20}$. Considering the improved kinetics of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ formation, especially at lower temperatures, we may conclude that it is $\text{BaTi}(\text{BO}_3)_2$ which play the role of flux in this system. In addition, any precursor could not produce the $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ phase at 1163 K. Therefore, it may indicate that due to the thermodynamic restrictions $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ can not form at lower temperatures.

3.3 Estimation of the crystallite size of the ferroelectric materials

Table II summarizes the relationship between crystalline size and synthesis conditions of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$.

The crystalline sizes were calculated by Scherrer's equation [17]. The obtained data indicate that, sample A, which was prepared at 1573 K has a proper size of crystallite as the ferroelectric material. Generally, it is considered that the ferroelectric materials should be polycrystalline with less than 100 nm crystallite size. The sample B which was pelletized also has the suitable crystallite size, even though the determined value is slightly larger than for sample A. The difference of crystallite size between sample A and sample B depends on their styles (powder or pellet) in calcination. It is interesting to note that sample C and sample D, which include H_3BO_3 as a flux in the precursor have the crystallite size equal to sample A, and therefore they also possess a proper crystallite size. In addition, $Ba_2Ti_9O_{20}$ ceramics could not be obtained from the powder precursors in any reported works when other methods were used. Nevertheless, it was obtained successfully in this work from a powder precursor (sample C). The optimal crystallite size for $Ba_2Ti_9O_{20}$ ceramics was obtained by this approach after annealing at 1273 K. Figure 6 shows the SEM image of sample C. There is no pronounced sign of sintering. It means that, 1273 K is sufficient temperature to obtain the $Ba_2Ti_9O_{20}$ ceramics and low enough for noticeable sintering of grains. In other words, 1273 K is the suitable not only for obtaining $Ba_2Ti_9O_{20}$ phase but also for achieving optimal crystallite size and particle size. They are able to be sintered any requested size by HIP (Hot Isostatic Press), because this polycrystals have large surface energy.

Table II The Relationship between crystallite size and synthesis conditions of $Ba_2Ti_9O_{20}$

Sample	Temp. (K)	H_3BO_3	Style	Crystallite size (nm)
A	1573	-	powder	59
B	1473	-	pellet	69
C	1273	3 wt%	powder	58
D	1273	3 wt%	pellet	59

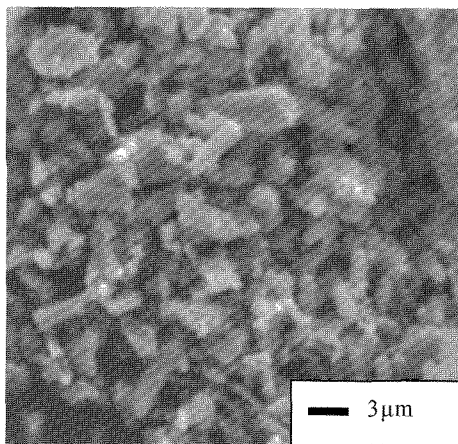


Fig.6 SEM image of sample C

4. Conclusion

In this work an aqueous solution method was developed for synthesis of $Ba_2Ti_9O_{20}$ material for the first time. The tetranuclear complex of titanium (citratoperoxotitanic acid) was utilized as an original water-soluble Ti source. Use of citratoperoxotitanic acid is advantageous from the viewpoint of environmental, economic and safety considerations when compared to Ti alkoxides, $TiCl_4$ or $Ti(SO_4)_2$ starting compounds. In combination with H_3BO_3 flux it was possible to obtain $Ba_2Ti_9O_{20}$ phase at 230 degrees lower temperature than in the case of synthesis by a solid state reaction. It was also established that below 1163 K $Ba_2Ti_9O_{20}$ compound did not form probably due to the thermodynamic reasons. The crystalline powder prepared at low temperature consisted of particles of 100 nm size, which makes the proposed solution method an excellent technique for preparation of single phase fine $Ba_2Ti_9O_{20}$ ceramics.

5. References

- [1] G. H. Jonker and W. Kwestroo, *J. Am. Ceram. Soc.*, **41**, 390-394 (1958).
- [2] G. D. Fallon and B. M. Gatehouse, *Solid State Chem.*, **49**, 59-64 (1983).
- [3] I. Teoreanu and E. Andronescu, *Ceram. Int.*, **22**, 305-307 (1996).
- [4] H. M. O'bryan, Jr., and J. Thomson, Jr., *J. Am. Ceram. Soc.*, **57**, 450-453 (1974).
- [5] K. Plourde, D. F. Linn, H. M. O'bryan Jr. and J. Thomson Jr, *J. Am. Ceram. Soc.*, **58**, 418-420 (1975).
- [6] S. Wu and G. Wang, *J. Euro. Ceram. Soc.*, **23**, 2565-2568 (2003).
- [7] J. Wu and H. Wang, Factors, *J. Am. Ceram. Soc.*, **71**, 869-875 (1988).
- [8] H. Wang, *J. Am. Ceram. Soc.*, **78**, 1134-1135 (1995).
- [9] S. Sakka and T. Yoko, *Structure and Bonding*, **77**, 89-118 (1992).
- [10] M. Kakihana and M. Yoshimura, *Bull Chem Soc of Jpn.*, **72**, 1427-1443 (1999).
- [11] J. J. Ritter, R. S. Roth, and J. E. Blendell, *J. Am. Ceram. Soc.*, **69**, 155-162 (1986).
- [12] L. Chu, and G. Hsiue, *J. Euro. Ceram. Soc.*, **24**, 1781-1785 (2004).
- [13] H. Wang and M. Chung, *Mater. Chem. and Phys.*, **77**, 853-859 (2002).
- [14] M. Kakihana, M. Tada, M. Shiro, V. Petrykin, M. Osada and Y. Nakamura, *Inorg. Chem.*, **40**, 891-894 (2001).
- [15] M. Tada, Y. Yamashita, V. Petrykin, M. Osada, K. Yoshida, and M. Kakihana, *Chem. Mater.*, **14**, 2845-2846 (2001).
- [16] K. Tomita and Masato Kakihana, *Trans. Mater. Res. Soc. Jpn.*, **28**, 377-380 (2003).
- [17] B. D. Cullity, "Elements of X-ray Diffraction", 2nd edition, Addison-Wesley pub., (1978) pp.102

(Received December 7, 2007 ; Accepted July 15, 2008)