Controlled hydrothermal synthesis of different sizes of BaTiO$_3$ nanoparticles for microwave absorption

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Abstract

Different sizes of barium titanate (BaTiO$_3$) nano-particles were synthesized from precursor H$_2$Ti$_3$O$_7$ nanotubes through facile hydrothermal synthesis by using EtOH/H$_2$O as mixing solvent. Field-emission scanning electron microscopy (FESEM) was mainly used to investigate the effects of solution alkalinity, polarity, and hydrothermal temperature on the size and morphology evolution of BaTiO$_3$ nanoparticles. The results indicate that the presence of strong alkalinity improved the size evenness of BaTiO$_3$ nanoparticles possibly because of the re-dissolution and re-precipitation of TiO$_3^{2-}$ ions. BaTiO$_3$ nanoparticles with the average diameters of approximately 21 and 53 nm were obtained in 9:1 and 1:1 EtOH/H$_2$O (v/v) hydrothermal medium, respectively. Compared with that, the size of BaTiO$_3$ particles prepared in pure distilled water reached up to $\sim$512 nm. As for the reason, the addition of EtOH could lower the polarity of hydrothermal medium and make the medium reach the supersaturation more easily, thus limiting the size growth of BaTiO$_3$ particles. In addition, the presence of EtOH led to easier formation of BaTiO$_3$ nanoparticles even at mild hydrothermal temperature, but the particle size was limited even though the temperature was much increased. This is possibly due to lowered interfacial activity in the presence of EtOH. By adjusting solution alkalinity, EtOH/H$_2$O volume ratios, and hydrothermal temperature, BaTiO$_3$ nanoparticles with the average sizes of approximately 21, 53, 104, 284, and 512 nm, were obtained, and more different and controlled nano-sizes can be expected by further hydrothermal adjustment. In the end, microwave absorption evaluation indicated that decreased size of the BaTiO$_3$ particles enhanced the reflection loss. One possible reason is that the decreased nano-size led to the increased specific surface area of the BaTiO$_3$ nanoparticles.

1. Introduction

Microwave absorption materials have been receiving much attention not only due to their prevention for human body from electromagnetic (EM) wave radiation, and surrounding electronic devices from EM interference (EMI), but also because of their promising applications in both aviation and military fields [1, 2]. For ideal microwave absorber, many properties are desired such as strong absorption ability, wide absorption band, light weight, thinner absorbent, high temperature resistance and chemical resistance. With rapid development of information technology, conventional microwave absorption materials, such as transition metals (e.g., Fe, Ni, and Co), and their oxides, alloys, and ferrites, have not been capable of meeting increasing performance requirements due to their narrow absorption bands, dissolution in acid, weak resistance to oxidation, and large densities.
In recent years, instead of conventional metallic materials, various new-type materials have been developed as microwave absorption materials, which mainly include electrically conductive polymers, micro/nano-carbon materials, and inorganic electro-ceramics. Conductive polymers such as polyaniline (PANI) and polypyrrole (PPY) are much used in the field of microwave absorption due to their flexible adjustability in electric conductivity for ideal microwave absorbers [3–5]. Carbon based micro/nano-materials, such as carbon nanotube (CNT), graphene, carbon black (CB), and carbon nanofiber (CNF), are also often used as microwave absorption fillers because of their good electrical conductivity and unique 1-, 2-, and 3-dimensional structures [6–10]. Electro-ceramics, such as lead zirconate titanate (PZT), barium titanate (BTO), and silicon carbide (SiC) are mostly applied to communications, energy conversion and storage, electronics and automation by utilizing their unique electrical, optical and magnetic properties. As far as we know, compared with above-mentioned conductive polymers and carbon materials, the investigation of electro-ceramic materials in microwave absorption fields is still not enough. Among those electro-ceramics, BTO has excellent dielectric, ferroelectric, and piezoelectric properties, and is considered to be promising for use as microwave absorbing material [11–13]. In our group, lots of BTO based researches concerning microwave absorption have been studied such as the developments of BTO/CNT and BTO/PANI nanocomposites [14–17].

BTO (i.e., BaTiO3) is a perovskite-type electro-ceramic which consists of BaO2 cuboctahedra and TiO6 octahedra [18]. This ceramic has been found promising for uses as photonic crystals, thermistors, transducers, piezoelectric and electromagnetic devices due to its excellent ferroelectric, pyroelectric, dielectric and piezoelectric properties [19–22]. In addition, it is well known that the structural and physical properties of perovskite nanocrystals, such as BaTiO3, are highly related to their size, shape, and crystallinity [23–25]. For example, BaTiO3 has a transition from paraelectric (PE) cubic phase to ferroelectric (FE) tetragonal phase as the temperature goes down from above ∼130 °C. And also, when the size of BaTiO3 particles decreased, the tetragonality degree decreases as well.

Some approaches such as sol-gel processing [26], molten salt reaction [27], chemical co-precipitation [28], solvothermal synthesis [29], solid-state calcination [30], and hydrothermal method [31], have been developed for preparing BaTiO3 with different nanostructures (rod, wire, cube, tube, sphere, etc), which range in size from several nanometers to hundreds of nanometers. Among these approaches, hydrothermal treatment attracted much attention because of its low cost, environmental benignity, easy adjustment, and high product purity.

Based on this approach, Che and co-workers hydrothermally produced 1D ferroelectric BaTiO3 nanowires by Ostwald ripening and cation exchange mechanism using aqueous and ethonal mixing medium. Those nanowires have uniform diameter of ~6 nm and a length up to tens of micrometers [32]. Zhu et al provided a hydrothermal synthesis strategy for morphology controlled BaTiO3. In the research, BaTiO3 was prepared by the ion exchange of K2Ti4O9 precursor, and the nanostructure could change from whiskers to particles by manipulating the alkalinity and reaction temperature [33]. However, there are limited approaches for the controllable preparation of BaTiO3 with different sizes. Because it is not very clear how some vital factors in reaction medium such as temperature, solution polarity, and alkalinity influence the evolution of BaTiO3 nanoparticles.

In this research, we used easily available BaCl2 and TiO2 as raw materials and successfully synthesized sphere-like BaTiO3 nanoparticles with different sizes ranging from ~20 nm to ~500 nm by facile hydrothermal treatment using ethanol and deionized water (EtOH/H2O) as mixing medium under alkaline condition. The effects of temperature, solution polarity, and alkalinity in this hydrothermal system on the size and morphology evolution of the BaTiO3 were discussed in detail. In the end, microwave absorption evaluation showed that the reflection loss was increased with the decrease of BaTiO3 nano-size possibly because of the increased specific surface area of BaTiO3 nano-particles.

2.Experimental

2.1.Materials

TiO2 was bought from Kojundo Chemical Laboratory Co, Ltd, Japan. In addition to that, sodium hydroxide (NaOH), barium chloride (BaCl2), hydrochloric acid (HCl, 35.0–37.0 wt%), ethyl alcohol (EtOH, 99.5 wt%), paraffin (m.p. 60 °C–62 °C), and deionized water were all purchased from Wako Pure Chemical Industries, Ltd, Japan. All those chemicals were used without further purification.

2.2.Preparation of H2Ti3O7 precursor

As shown in figure 1 (a), 20 g TiO2 powder was poured in 60 ml 8 M NaOH aqueous solution, followed by magnetic stirring for 6 h. After that, the suspension was transferred in a stainless-steel auto-clave for hydrothermal synthesis. The autoclave was then heated up to 150 °C in a constant-temperature drying oven and maintained for 24 h. After that, the solid product was centrifuged out of the hydrothermal solution, and then
immersed overnight by using 0.1 M HCl solution. Finally, the whitish H$_2$Ti$_3$O$_7$ was obtained by repeated centrifugation, washing and drying.

### 2.3. Preparation of BaTiO$_3$

As shown in figure 1 (b), BaCl$_2$ was firstly dissolved in deionized water, followed with the addition of the as-prepared H$_2$Ti$_3$O$_7$ precursor and sonication for 0.5 h at room temperature. Then, the suspension was applied to magnetic stirring, and a certain volume of EtOH was subsequently poured in. After that, excessive NaOH solution, which was more than the required alkali amount for complete conversion of H$_2$Ti$_3$O$_7$, was dropwise injected into the stirring suspension to maintain a certain concentration of solution alkalinity. Following with that, hydrothermal treatment was applied for 24 h. At last, the white BaTiO$_3$ powder was obtained by repeated centrifugation, washing and drying.

As above-mentioned, in this hydrothermal system, part of the OH$^-$ ions was used to complete conversion of H$_2$Ti$_3$O$_7$ into BaTiO$_3$. The other part of the OH$^-$ ions was used to maintain an alkaline hydrothermal environment, and the OH$^-$ concentration for this part was set as 0 M, 0.5 M, and 1 M, respectively, for investigating the effect of the alkali concentration on the morphology evolution of BaTiO$_3$. In addition, to study the effect of the temperature on BaTiO$_3$ size, different hydrothermal temperatures were set including 50 °C, 140 °C, 160 °C and 180 °C. In order to understand the effect of solution polarity on BaTiO$_3$ size, different volume ratios (v/v) of EtOH and H$_2$O were set in this hydrothermal treatment including 0:1, 0.5:1, 1:1, and 9:1, respectively.

### 2.4. Evaluation method

The morphologies of the as-prepared BaTiO$_3$ nanoparticles were observed by using field emission scanning electron microscopy (FE-SEM, Hitachi S-5000, 20 kV) and transmission electron microscopy (TEM, JEM-2100, JOEL, Japan) with an accelerating voltage of 200 kV. X Ray Diffraction (XRD, MiniFlex300, Japan) was used to characterize the crystal structure of the BaTiO$_3$ samples. In addition, x-ray photoelectron spectrometry (XPS, Kratos Axis Ultra DLD) was also utilized to evaluate the chemical composition and states of the samples by using a standard Mg Ka (1256.6 eV) x-ray source operating at 10 mA and 15 kV.

Microwave absorption effect was evaluated in the frequency range of 0.1–15 GHz by calculating the real and imaginary parts of permittivity and permeability, which were obtained by measuring scattering parameters using a vector network analyzer (37247D, Anritsu Co. Ltd). The test samples for microwave absorption evaluation were prepared by mixing with paraffin by the weight percentage of 50%, and they had O–shape rings with inner diameter = 3 mm, outer diameter = 7 mm, and thickness = 2 mm.

### 3. Results and discussion

#### 3.1. Structure property of BaTiO$_3$

Na$_2$Ti$_3$O$_7$ could be synthesized from TiO$_2$ source through hydrothermal reaction under strong alkaline environment [34]. Then, H$_2$Ti$_3$O$_7$ was obtained based on Na$^+$ / H$^+$ exchange of the Na$_2$Ti$_3$O$_7$ through HCl solution treatment [35]. Figure 2(a) shows the tube-shape morphology of the as-prepared H$_2$Ti$_3$O$_7$ precursor with the diameter of 12 nm and the length of 156 nm on average. After its hydrothermal reaction with BaCl$_2$, the tube-shape morphology changed to the BaTiO$_3$ precursor.
under alkaline condition, sphere-like BaTiO3 nano-particles were formed with the average diameter of approximately 284 nm, as shown in figure 2(b). Combining with their transmission observation (figure 2(c)), it can be known that these nano-spheres are the aggregate of many small active nanoparticles with different degrees of mutual fusion. Besides, XPS was applied to verify the chemical composition and elements state of the H2Ti3O7 and BaTiO3. As shown in figure 2(d), the spectrum confirmed the presence of the titanium (Ti 2s, 2p, 3p) and oxygen (O 1s) in H2Ti3O7, and the barium (Ba 3d, 4p, 4d), titanium (Ti 2s, 2p, 3p) and oxygen (O 1s) in BaTiO3, respectively. For H2Ti3O7, the Ti/O ratio of the Ti 2p3/2 and Ti 2p1/2 at position 457.4 eV and 462.1 eV, and the O 1s at position 528.2 eV is approximately 0.41. This indicates the consistency with the H2Ti3O7 structure composition (Ti/O ratio, ∼0.43). Besides, in the BaTiO3 spectrum, two new peaks, located at 792.1 eV and 776.9 eV, respectively, can be ascribed to the Ba 3d3/2 and 3d5/2.

3.2. Effect of alkali concentration on BaTiO3 size

With regard to the mechanism for hydrothermal synthesis of BaTiO3, there are presently two proposals. More convincible one of the two transformation mechanisms is that the dissolved Ba2+ ions react topo-chemically with the titanium precursor, such as the H2Ti3O7, and then the BaTiO3 forms through heterogeneous nucleation [25, 36]. The participation of alkali is a prerequisite for conversion of H2Ti3O7 precursor into BaTiO3, as can be seen from equations (1)–(2):

\[
\text{H}_2\text{Ti}_3\text{O}_7 + 2\text{OH}^- + 2\text{Na}^+ \rightarrow \text{Na}_2\text{Ti}_3\text{O}_7 + 2\text{H}_2\text{O} \quad (1)
\]

\[
\text{Na}_2\text{Ti}_3\text{O}_7 + 3\text{Ba}^{2+} + 4\text{OH}^- \rightarrow 3\text{BaTiO}_3 + 2\text{Na}^+ + 2\text{H}_2\text{O} \quad (2)
\]

To investigate the effect of alkali environment in the hydrothermal system on the size of BaTiO3 nanoparticles, except for the basically required alkaline amount for complete transformation of H2Ti3O7 into BaTiO3, extra NaOH was added to maintain an alkalinity environment of 1 M OH–. Figures 3(a)–(d) show the morphologies and corresponding size distribution of the two BaTiO3 samples, which were hydrothermally prepared without the presence of extra NaOH or at 1.0 M OH– concentration environment. The result indicated that the sphere-shape BaTiO3 nanoparticles with the average diameter of ∼112 nm, which were prepared under 1 M NaOH solution, exhibited relatively uniform size compared to those BaTiO3 obtained without extra addition of alkali. This is possibly because of the re-dissolution of the BaTiO3 from the surface of large particles and the re-precipitation of the dissolved TiO32– onto small particles, as seen from equation (3) [31, 33]. In detail, there are amounts of TiO32– on the surface of the irregular BaTiO3 particles which were initially formed under strong alkaline hydrothermal environment. Due to the specific surface area difference of the large and small particles, more TiO32– could transfer and precipitate on the small particles until a balanced particle size distribution was reached. At present, there are not enough researches concerning how the alkalinity
concentration influences the BaTiO$_3$ size. The proposed explanation in this research is plausible, but convincing mechanism needs further demonstration based on experimental investigation.

$$\text{BaTiO}_3 \downarrow + \text{OH}^- \rightarrow \text{TiO}_2^{2-} + \text{BaOH}^+ \rightarrow \text{BaTiO}_3 \downarrow + \text{OH}^-$$  \hspace{1cm} (3)

### 3.3. Effect of solution polarity on BaTiO$_3$ size

H$_2$O and EtOH have different solvent polarity, so they were mixed together by different degrees of volume ratios to investigate the effect of solution polarity on BaTiO$_3$ size. Since the dielectric constant for a solvent represents a measure of its polarity. The higher dielectric constant of the solvent indicates its larger polarity. Therefore, high polar H$_2$O molecules with a dielectric constant of 80 at approximately 20°C were mixed with low polar EtOH molecules with a dielectric constant of 25. By this way, the solutions with different polarities could be prepared, and increasing addition of EtOH is supposed to lower the polarity of the solution. In this research, in order to investigate the effect of solution polarity on BaTiO$_3$ size, EtOH/H$_2$O mixed solvents with the volume ratios of 0:1, 0.5:1, 1:1, and 9:1, were used to prepare the hydrothermal solution with different polarities. Figures 4(a) – (d) show the morphologies of the BaTiO$_3$ nanoparticles, which were prepared under different solution polarities. It can be seen from the figures that, the average size of the BaTiO$_3$ particles gradually decreased from $\sim$512 nm (figure 4(a)) to $\sim$21 nm (figure 4(d)) with the increase of EtOH volume ratio, namely, the decrease of solvent polarity. As for the reason, H$_2$O is a high polar solvent with a dielectric constant of 80, while EtOH has a low dielectric constant of 25, weak polarity, and low surface tension. In addition, the surface tension of distilled water can go up to $7.3 \times 10^{-2}$ N·m$^{-1}$ while EtOH is only $2.3 \times 10^{-2}$ N·m$^{-1}$ at 25°C. Therefore, after the addition of EtOH, lowered polarity and dielectric constant of the solution made the hydrothermal medium reach supersaturation more easily, thus limiting the crystal activity of the BaTiO$_3$ nanoparticles and their further outward growth. As a result, it is reasonable that the size of BaTiO$_3$ nanoparticles decreased with the decrease of the solution polarity.

The dielectric constant for the mixed solution was calculated based on the volume percentages of the two solvents under room temperature, as can be seen in the following equation:

$$\varepsilon = \varphi_1 \varepsilon_{25} + \varphi_2 \varepsilon_{80}$$  \hspace{1cm} (4)

where $\varepsilon$ refers to the dielectric constant after mixing, $\varphi_1$ and $\varphi_2$ represent the volume percentages of H$_2$O and EtOH solvents, respectively. This equation was used as a reference to investigate the dielectric constant change under different mixing ratios of H$_2$O and EtOH. With the addition of EtOH volume up to 9:1, the dielectric constant of EtOH/H$_2$O mixed solvent decreased from the 80 of pure water medium to the 30.5 of the mixed solvent. Figure 4(e) presents the size variation relation of BaTiO$_3$ nanoparticles with decreasing dielectric constant of the mixed solvent. According to the size variation trend, there is a possible exponential relationship
between the particles size \((D)\) of BaTiO\(_3\) and the dielectric constant \((\varepsilon)\) of the mixed solvent. Therefore, based on curve fitting, an equation shown below:

\[
D = 0.298 \cdot e^{0.093 \cdot \varepsilon} + 15.688
\]  

(5)

was proposed to better understand the relation between the particle size and the dielectric constant, as also seen in figure 4(e). It can be known from this equation that the minimum BaTiO\(_3\) size, which can be obtained from this mixed EtOH/H\(_2\)O solvent, is \(\sim\)18.7 nm. This equation could be possibly referred to prepare desired BaTiO\(_3\) size, which can approximately range in 20–500 nm by adjusting the dielectric constant of the hydrothermal solution. For further research, more experimental will be carried out to demonstrate its validity so as to obtain more precise relation between the BaTiO\(_3\) particle size and the dielectric constant.

Figure 4(f) shows the XRD patterns of the two BaTiO\(_3\) samples separately with the average sizes of 53 and 512 nm (named as BaTiO\(_3\)-53 and BaTiO\(_3\)-512, respectively). All diffraction peaks can be labelled and attributed to the tetragonal structure of BaTiO\(_3\) with \(P4mm\) space group (JCPDS data No. 05–0626). The corresponding lattice constants of the BaTiO\(_3\)-53 and BaTiO\(_3\)-512 are \(a = 4.003\ \text{Å}, b = 4.003\ \text{Å}, c = 4.007\ \text{Å}\), and \(a = 4.004\ \text{Å}, b = 4.004\ \text{Å}, c = 4.03\ \text{Å}\), respectively. Calculation indicated that, the tetragonality \((c/a)\) of BaTiO\(_3\) increases from low value of 1.001 up to 1.007 with the increase of its particle size. In addition, it is obvious that the \(\{111\}\) facet of BaTiO\(_3\)-512 is intensified than that of BaTiO\(_3\)-53. By taking \(I_{\{111\}}/I_{\{200\}}\) as reference, there is a dramatic increase from the 0.823 of BaTiO\(_3\)-53 to the 1.401 of BaTiO\(_3\)-512. This is possibly because of the splitting of \(\{200\}\) peak, thus making the peak intensity of the \(\{200\}\) weakened. As shown in the inset of figure 4(f), a splitting peak in BaTiO\(_3\)-512 curve comes out at approximately 45.1° position. This further demonstrates the strengthening of the tetragonality of the BaTiO\(_3\)-512 [31].

### 3.4. Effect of temperature on BaTiO\(_3\) size

Figures 5(a) and (b) show the effect of the hydrothermal temperature of 50°C and 140°C on the size of the BaTiO\(_3\) nanoparticles prepared in pure distilled water medium. It can be seen from figure 5(a) that, there are still lots of tube-shape substance except for the formation of a few BaTiO\(_3\) domains, as marked in red dot line. These substances are considered to be Na\(_2\)Ti\(_3\)O\(_7\) nanotubes, which were formed from transformation of H\(_2\)Ti\(_3\)O\(_7\) precursor. Furthermore, some of those Na\(_2\)Ti\(_3\)O\(_7\) nanotubes aggregated together due to nano-size effect. Failed transformation of the Na\(_2\)Ti\(_3\)O\(_7\) precursor into BaTiO\(_3\) is possibly because the mild hydrothermal temperature led to relatively low activation energy (i.e., interfacial energy) of the Na\(_2\)Ti\(_3\)O\(_7\) precursor, and this low interfacial energy resulted in difficult ion exchange between Na\(^+\) and Ba\(^{2+}\). After rising hydrothermal temperature up to 140°C, it can be seen there is a shape transition from the tube to sphere-like particles with the average diameter of more than 500 nm, as shown in figure 5(b). This is because the interfacial energy of those Na\(_2\)Ti\(_3\)O\(_7\) intermediates obviously increased with rising temperature. And this led to the ion exchange between Na\(^+\) and...
Ba$^{2+}$ in the presence of OH$^-$ ions, followed by direct in site fusion of the BaTiO$_3$, which was formed from those aggregates of Na$_2$Ti$_3$O$_7$ nanotubes, as shown in the inset of figure 5(b).

While 1:1 (v/v) EtOH/H$_2$O mixed solvent was applied as hydrothermal medium under mild temperature of 50 °C, the sphere-shape BaTiO$_3$ particles with the average diameter of approximately 50 nm were obtained, as shown in figure 5(c). Compared with pure water medium, decreased dielectric constant ($\varepsilon$ < 52.5) of the mixed solvent made the hydrothermal solution reach saturation even under the mild temperature (i.e., 50 °C). Therefore, this lowered the reaction barrier of the ion exchange between the Na$^+$ and Ba$^{2+}$, thus leading to the formation of BaTiO$_3$. In addition, the presence of EtOH limited the interfacial energy of the BaTiO$_3$ crystal particles which were formed on the surface of Na$_2$Ti$_3$O$_7$ intermediate. Therefore, unlike direct in site fusion of the BaTiO$_3$ species on the Na$_2$Ti$_3$O$_7$ surface under pure water medium (as seen in the inlet of figures 5(a) and (b)), lots of small BaTiO$_3$ crystal particles took off from the surface of the Na$_2$Ti$_3$O$_7$ nanotubes. In addition, compared to H$_2$O, EtOH has lower surface tension. Therefore, the addition of EtOH into the hydrothermal medium decreased the interfacial tension and energy of the BaTiO$_3$ particle surface. The lowered interfacial activity suppressed the aggregation of the BaTiO$_3$ nanoparticles, and resulted in the stable existence of the smaller nanoparticles due to the increased energy barrier that formed due to the solvation of the particle surface. In other words, because of the low interfacial activity, those small BaTiO$_3$ particles were limited to some extent for further growth or fusion with each other. This is the possible reason why those BaTiO$_3$ nano-particles are not as large as the BaTiO$_3$ particles prepared in pure water medium.

After rising the temperature up to 140 °C, there is no obvious change in size, as can be seen in figure 5(d). This is possibly because the increased temperature didn’t obviously improve the interfacial activity of the BaTiO$_3$ crystal particles due to the presence of much EtOH. As a result, it comes to a conclusion that the decrease of dielectric constant in hydrothermal medium could possibly improve the ion exchange between Na$^+$ and Ba$^{2+}$ even under mild hydrothermal temperature. At the same time, the presence of EtOH would also decrease the interfacial activity of the BaTiO$_3$ crystal particles, and thus limit the growth of BaTiO$_3$ nanoparticles.

### 3.5. Possible formation mechanism

With regard to the evolution mechanism of the BaTiO$_3$ in hydrothermal medium, the structure of H$_2$Ti$_3$O$_7$ precursor is firstly discussed. H$_2$Ti$_3$O$_7$ crystal consists of many aligned TiO$_6$ octahedras. These TiO$_6$ octahedras constructs open layered structures of H$_2$Ti$_3$O$_7$ with zigzag staggered sheets by edge- and corner-sharing, as illustrated in figure 6(a). The H$^+$ in H$_2$Ti$_3$O$_7$ is first displaced by Na$^+$ without obvious structure change in NaOH alkaline environment. Subsequently, the ion exchange between the Na$^+$ and Ba$^{2+}$ is induced by the open layer structure of the intermediate Na$_2$Ti$_3$O$_7$. As seen in figure 6(b), the Na$^+$ sites in the crystal structure of the Na$_2$Ti$_3$O$_7$ intermediate are occupied by Ba$^{2+}$ ions, and then converted to perovskite structure [33]. At the same
time, the BaTiO$_3$ species, which were formed from the Na$_2$Ti$_3$O$_7$ nanotubes in the presence of alkali, take off from the surface of the Na$_2$Ti$_3$O$_7$ or fuse with each other possibly due to unstable structure of the tube status.

Figure 7(a) described the possible transformation process from H$_2$Ti$_3$O$_7$ nanotubes to BaTiO$_3$ nanoparticles. Based on ion exchange, the H$_2$Ti$_3$O$_7$ nanotubes firstly transformed to Na$_2$Ti$_3$O$_7$ intermediate without obvious structure change in the presence of alkali. After that, according to different dielectric constant of hydrothermal solutions, there are two possible transformation routes for the Na$_2$Ti$_3$O$_7$ intermediate doped with Ba$^{2+}$. In low dielectric constant, the BaTiO$_3$ crystal particles, which formed from the surface of the Na$_2$Ti$_3$O$_7$ nanotubes due to ion exchange with the assistance of OH$^-$, took off from the tube surface because of relatively lower interfacial activity. By contrast, in high dielectric constant, Ba$^{2+}$ doped Na$_2$Ti$_3$O$_7$ nanotubes firstly aggregates together due to nano-size effect. After that, they transferred to BaTiO$_3$ species on the surface of the Na$_2$Ti$_3$O$_7$ tubes in the presence of OH$^-$ due to the increased interfacial activity under relatively higher hydrothermal temperature, followed with direct in site fusion of the BaTiO$_3$ species. It can be known from this transformation that low dielectric constant of hydrothermal medium could possibly decrease the interfacial
energy of BaTiO₃ crystals, and thus limit the growth of the particles due to more easily saturated hydrothermal medium.

In addition, it is well agreed that alkali is a prerequisite for conversion of H₂Ti₃O₇ precursor into BaTiO₃. Except for that, it may also play a role in adjusting the size evenness of BaTiO₃ nanoparticles, as illustrated in figure 7(b). In spite of the difficult solubility of BaTiO₃ in hydrothermal medium, strong alkaline environment made TiO³⁻ ions continually re-dissolve and separate from the surface of the formed BaTiO₃ particles, and then re-precipitate onto other BaTiO₃ particles until a balanced size distribution of the particles was reached due to energy minimum principle, as illustrated in figure 7(c).

3.6. Microwave absorption property

The microwave absorption property of the BaTiO₃ with different sizes was then investigated. As microwave absorber, the absorption performance is well agreed to be dependent on its complex permittivity and permeability. The real part ε′ and μ′ of the complex permittivity and permeability represent the storage of electric and magnetic energies, while the imaginary part ε″ and μ″ indicate the loss and dissipation of the two types of energies. Figure 8 represents the real and imaginary parts of the complex permittivity and permeability in the frequency range of 0.1–16 GHz for different sizes of BaTiO₃ particles with 50% weight percent in paraffin and 2 mm thickness. It can be seen from figure 8(a) that real permittivity parts of all the samples gradually decreased with increasing frequency. This is possibly due to the dielectric relaxation (e.g., dipole relaxation), and unmaintainable electric polarizations that cannot keep up with more and more frequent electromagnetic variation. What is more, as the size of BaTiO₃ nanoparticles decreased, the real permittivity increased. As seen in figure 8(a), the BaTiO₃ with the average size of approximately 21 nm exhibited highest permittivity property. As for the reason, smaller BaTiO₃ nanoparticles, which have higher specific surface area, may result in more efficient interfacial polarization and intensive dielectric relaxation. The higher interfacial polarization and dielectric relaxation, which was caused by smaller particle size effect, also improved the dielectric loss of the BaTiO₃ nanoparticles, as can be seen in figure 8(b). This indicated that the particle size of BaTiO₃ plays an important role in improving and optimizing the dielectric ability.

Figures 8(c) and (d) represent the real and imaginary parts of the complex permeability for the BaTiO₃ particles with different particle sizes. It can be seen from figure 8(c) that BaTiO₃ particles with smaller size gave higher permeability particularly in high frequency band (10–16 GHz). This is possibly because of the increased specific surface area. At the same time, as seen from figure 8(d), the imaginary part of the permeability also increased with decreased BaTiO₃ size. This implies more magnetic loss. Furthermore, in the two frequency bands of 2–8 GHz and 10–16 GHz, more obvious magnetic loss could be observed. This increase in magnetic loss is considered to promote microwave absorption.
To understand the intrinsic reasons of BaTiO₃ particles with different sizes for microwave absorption, their dielectric loss factor (\( \delta \varepsilon \)) and magnetic loss factor (\( \delta \mu \)) were calculated. As known, the permittivity and permeability change with different electromagnetic field. This accompanies with the movement of electrons or ions. \( \delta \varepsilon \) and \( \delta \mu \) represent absorber’s attenuation ability under per unit permittivity and permeability for incident electromagnetic wave. The two loss factors were calculated based on the equations as below:

\[
\delta \varepsilon = \frac{\varepsilon''}{\varepsilon'} \\
\delta \mu = \frac{\mu''}{\mu'}
\]

Figure 9 presents the \( \delta \varepsilon \) and \( \delta \mu \) curves of the BaTiO₃ particles with different sizes. Both \( \delta \varepsilon \) and \( \delta \mu \) contribute to microwave absorption abilities. In other words, the higher the \( \delta \varepsilon \) and \( \delta \mu \) are, the higher absorption efficiency the samples could possess. \( \delta \varepsilon \) comes about through damping forces acting on polarized atoms and molecules. In figure 9(a), the \( \delta \varepsilon \) at low frequency with little change is considered to be determined by the leak conductance, while the \( \delta \varepsilon \) at high frequency with obvious increase mainly results from the relaxation polarization and electric conductance \[15, 37\]. In addition, the \( \delta \varepsilon \) has no obvious difference in the frequency range of 0–16 GHz especially for the BaTiO₃ particles decreasing below approximately 100 nm. This is possibly owing to similar crystallization formation of those different BaTiO₃ particles and little change in tetragonality structure, which therefore made the damping force for incident microwave not influenced by the size change of the BaTiO₃ particles.

Figure 9(b) shows the magnetic loss factor (\( \delta \mu \)) of the BaTiO₃ particles with different sizes. \( \delta \mu \) increases with increasing electromagnetic frequency. This is due to more frequent magnetization and demagnetization of the BaTiO₃ particles, thus leading to more magnetic loss. As the size of the BaTiO₃ particles decreases, magnetic loss factor could be observed especially in the frequency range of 3–8 GHz. One possible reason is because of the increased specific surface area with the decreased BaTiO₃ particles. Convincible mechanism for the effect of BaTiO₃ size on the magnetic loss requires further experimental analysis and demonstration.

To further investigate the microwave absorption properties of the BaTiO₃ samples with different sizes, reflection loss (R.L.) was used to indicate the microwave absorption ability. It was calculated according to the transmission line theory, as represented in following equation:

\[
\text{R.L.} = 20 \log \left| \frac{Z_{\text{in}} - 1}{Z_{\text{in}} + 1} \right|
\]

where the normalized input impedance (\( Z_{\text{in}} \)) is given by equation:

\[
Z_{\text{in}} = \sqrt{\frac{\mu'}{\varepsilon'}} \tanh \left( j \frac{2\pi fd}{c} \sqrt{\mu'\varepsilon'} \right)
\]

where \( \varepsilon' = \varepsilon' - j\varepsilon'' \), \( \mu' = \mu' - j\mu'' \), \( f \) is the microwave frequency (Hz), \( d \) is the thickness of the absorber (m), and \( c \) is the velocity of light in free space (m/s). The reflection loss of the BaTiO₃ samples with 2 mm thickness and 50% weight percentage in paraffin was calculated in the frequency range of 0.1–16 GHz, and the results were shown in figure 10(a). With increasing frequency, all BaTiO₃ samples showed increased reflection loss. This is due to higher sensitivity of BaTiO₃ for high frequency band, which thus resulted in more dielectric and magnetic losses, as shown in figures 8(b) and (d). As the size of BaTiO₃ particles decreased, the reflection showed an increased trend. One possible reason is that the increase of the specific surface area enhanced the dielectric and
magnetic losses. The maximum value of the reflection loss in the test frequency range (0.1–16 GHz) reached approximately 5 dB. This value is not high as expected, which is attributed to insufficient BaTiO$_3$ content in paraffin and low test thickness.

Then, the reflection loss under higher thickness (2–8 mm) was calculated and the result was shown in figure 10(b). It can be seen that increasing thickness led to larger reflection loss at high frequency band (10–16 GHz). At the same time, a resonance peak appeared at low frequency range. With increasing thickness, this resonance peak shifted to lower frequency range. As a matter of fact, the area of the reflection loss between 10–16 GHz is also the part of a larger resonance peak, and its maximum peak value is considered to be shifting to lower frequency band with increasing thickness. This shift of the reflection loss with increasing thickness implies the adjustability for desired microwave absorption band. In order to intuitively understand the microwave absorption performance of the BaTiO$_3$ samples with different sizes, the absorptivity (A) of the BaTiO$_3$ samples was calculated based on reflection loss according to the equation as below:

$$ A = (1 - \frac{RL}{10}) \times 100\% $$ (10)

The absorptivity result was presented in figure 10(c). The maximum absorptivity could reach up to approximately 98.7% when at 8 mm thickness. Furthermore, it can be seen that the range above the absorptivity of 80% gradually increased with increasing thickness. This makes it possible for adjustment in desired microwave absorption band.

4. Conclusion

In summary, different BaTiO$_3$ nanoparticles with the average sizes of approximately 21, 53, 104, 284, and 512 nm were hydrothermally prepared from BaCl$_2$ and TiO$_2$ in alkaline medium with or without the presence of EtOH. It is found that strong alkaline environment possibly played a role in tuning the size evenness of BaTiO$_3$ nanoparticles through the re-dissolution of BaTiO$_3$ and re-precipitation of TiO$_3^{2-}$ ions. The addition of EtOH led to easier formation of BaTiO$_3$ nanoparticles due to decreased solution polarity. In the absence of EtOH, higher hydrothermal temperature was required in order to increase activation energy for conversion of Na$_2$Ti$_3$O$_7$ intermediate into BaTiO$_3$. In the presence of EtOH, the formation of BaTiO$_3$ could occur at a mild temperature, but at the same time the size would be limited due to lowered interfacial activity of the BaTiO$_3$ nanoparticles. Through the adjustment of hydrothermal alkalinity, polarity, and temperature, more different and controlled sizes of the perovskite BaTiO$_3$ nanoparticles could be expected. According to microwave
absorption evaluation, the decreased BaTiO$_3$ size increased the reflection loss. This is possibly because the
decreased BaTiO$_3$ size led to the increased specific surface area of the BaTiO$_3$ nanoparticles.

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