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Hydrothermal synthesis and formation mechanism of tetragonal barium titanate in a highly concentrated alkaline solution

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ABSTRACT

Tetragonal cube-shaped barium titanate ($BaTiO_3$) was produced by the hydrothermal treatment of a peroxo-hydroxide precursor, a single-source amorphous barium titanate precursor, in a highly concentrated sodium hydroxide solution. Phase pure barium titanate with cube-shaped morphology and particle-sizes in the 0.2–0.5 μm range were formed at temperatures above 80 °C. Also, the cube-shaped morphology of the $BaTiO_3$ product was preceded by spherical- and plate-like morphologies with, respectively, a Ti-excess and Ba-excess. Coinciding with these morphological observations, changes in the reaction product were also observed. The formation of crystalline $BaTiO_3$ proceeded alongside secondary $BaTi_2O_5$ and Ba_2TiO_4 phases. These secondary phases disappeared as the reaction time was increased leaving only $BaTiO_3$ as the sole reaction product. Kinetic analysis of the formation of hydrothermal $BaTiO_3$ crystallization by the Johnson-Mehl-Avrami method showed that $BaTiO_3$ crystallization is a homogeneous dissolution-precipitation reaction. The mechanism is governed by nucleation and growth in the beginning of the reaction and dissolution-precipitation dominating throughout the hydrothermal reaction process.

1. Introduction

Barium titanate ($BaTiO_3$) is the most widely investigated perovskite material due to its piezoelectric and ferroelectric properties [1–3]. Various synthesis methods were developed for perovskite-type materials over the years. In the conventional solid-state method the powdered reactants are mixed by grinding the powders, and sometimes pressed into pellets, and reacted at elevated temperatures [4]. The conventional solid-state reaction can produce large quantities of powder. Drawbacks of this method are the relatively high synthesis temperature (> 700 °C), the difficulty in controlling the powder particle-size, formation of secondary phases and the presence of hard agglomerates due to high processing temperatures [5–8]. The resulting ceramic powder needs to be milled in order to break hard agglomerates and sequential high-temperature treatments could be necessary so that unreacted reagents can react further into the reaction product. Coating of $BaCO_3$ with amorphous titania, for example, has enabled researchers to lower the synthesis temperature of $BaTiO_3$ to around 600 °C. However, the process is not straight forward and is time consuming [8]. The molten-salt is a solid-state synthesis in the presence of a salt or a eutectic salt mixture, but also requires elevated temperatures for the synthesis of $BaTiO_3$ [9,10]. Sol–gel processes enable a better control of the end-product with respect to stoichiometry, homogeneity and purity. Disadvantages, from an environmental perspective, are the use of hazardous chemicals [8,11].

The hydrothermal process has several advantages over other conventional processes such as energy saving, simplicity, better nucleation control, higher rate of reaction, better shape control, etc. Most important is that the chemical environment can be suitably tailored. Although the process involves slightly a longer reaction time, it provides highly crystalline particles with a better control over its size and shape [12,13]. Reports on the hydrothermal synthesis of barium titanate, and perovskite materials in general, exist in great numbers [13,14]. The synthesis processes differ in the precursor used (crystalline TiO_2 [15–17], Ti-alkoxide [16,18–20], and titanium (IV) chloride ($TiCl_4$) [21–24]), the solution medium (aqueous/non-aqueous) [18,19,24,25] and the use of templates in topotactical reactions [26–29].

According to Lencka et al. [30], barium titanate is stable in alkaline environments between pH 9 and 14. Thermodynamically speaking, the lower the feedstock concentration the higher the pH needs to be in order to precipitate pure and stable crystalline barium titanate. Not only the pH of the solution, but also other conditions such as the reaction temperature is important for

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producing stable barium titanate. Moon et al. [31,32] reported that alkaline reagents such as KOH and NaOH, which provide a highly alkaline solution, facilitate the transformation from hydrous oxide gel into the perovskite material, instead of forming individual regions of titanium, respectively, barium hydrous oxide gel.

A single-source precursor is a homogeneous, single-phase, amorphous precursor material that contains all the required cations in the correct ratio [4]. This method offers the advantage of producing homogeneous multi-component ceramics where the materials are mixed at the molecule level. Many functional ceramics have been prepared with single-source precursors over the years [11]. Single-source precursors can also be made from inorganic oxides and hydroxides by adjusting the pH to form polymeric, multi-cation oxyhydroxyl species. The charge-pH diagram of inorganic oxides and hydroxides are given by Livage et al [33]. The distribution of the various titanium species as a function of pH and the calculated stability diagram of aqueous titanium species was reported by Lencka et al. [30].

This work is a continuation of the published work by Özen et al. [22] and is part of a research project which aims the fabrication of textured ceramic materials in a strong magnetic field: see Özen et al. [34], Vriami et al. [35] and Özen et al. [36]. The hydrothermal synthesis, characterization and formation mechanism of tetragonal barium titanate is described in this work.

For the current experiments varying concentrations (0–10 M) of aqueous sodium hydroxide (NaOH) solutions were used. Several reaction parameters will be discussed. Sodium hydroxide was chosen as the alkaline medium due to its strong basic properties. The hydrothermal temperature and the reaction time were varied.

Various studies were done over the years to elaborate the formation mechanism of hydrothermal barium titanate formation [31,37–43]. In order to clarify the formation process of hydrothermal $BaTiO_3$ crystallization a kinetic study was also done. For the kinetic evaluation of hydrothermal $BaTiO_3$ crystallization the precursor solution was hydrothermally treated in a 10 M NaOH solution for varying reaction times at different temperatures: 100 °C, 150 °C, and 200 °C. The hydrothermal products were also washed with diluted acetic acid solutions with the purpose of removing the unwanted barium carbonate ($BaCO_3$) reaction by-product.

2. Materials and methods

2.1. Synthesis of the barium-titanium-peroxo-hydroxide precursor

The peroxo-hydroxide method produces a single-source precursor whereby the barium and titanium ions are mixed in a 1:1 ratio [21,22]. The general reaction process of peroxo-hydroxide reactions can be described as follows. $TiCl_4$ is a highly reactive reagent which is hydrolyzed into titanium hydroxyl species in water. By adding $TiCl_4$ to water the solution is made acidic whereby all Ti-species are hydroxo-aquo ($[Ti(OH)_2(OH_2)_4]^{2+}$) complexes, condensation reactions can begin as soon as one hydroxo ligand appears in the coordination sphere which infers moving to the hydroxo-domain. To initiate condensation hydrogen peroxide is added in excess resulting in a titanium-peroxo-hydroxide complex with the formula $Ti(O_2)(OH)_{N-2}^{4-N+}$ (water molecules not shown):

$$Ti(OH)_{2(aq)}^{2+} + H_2O_{2(aq),excess} \rightleftharpoons Ti(O_2)(OH)_{N-2(aq)}^{4-N+} + NH_{(aq)}^{+} \tag{1}$$

where N denotes the number of hydrogen ions which are liberated when the peroxo complex is produced from the titanium-aquo ion and H_2O_2 [44]. The hydroxide ions are the result of deprotonation from water molecules in complexation with the metal ion. Below pH 1 the mononuclear $Ti(O_2)OH^+$ titanium-peroxo-hydroxide complex is formed. Schwarzenbach et al. [44] concluded that the titanium-peroxo-hydroxide complex is actually dinuclear ($Ti_2O_5{}^{2+}$) in nature and that the mononuclear nature of the Ti-peroxo-hydroxide complex at pH < 1 is due to the lower stability of the dinuclear complex at extremely low pH. Further deprotonation by increasing the pH of the solution, by addition of an alkaline base or ammonium hydroxide for example, will give different Ti-peroxo-hydroxide complexes (water molecules not shown):

$$\begin{gathered}
\text{pH} < 1: \\
2\,Ti(O_2)(OH)_{(aq)}^{+} \\
1 < \text{pH} < 3: \\
Ti_2O_5(OH)_{(aq)}^{+} \rightleftharpoons Ti_2O_5(OH)_{2\,(aq)} \\
3 < \text{pH} < 9: \\
Ti_2O_5(OH)_{3\,(aq)}^{-} \rightleftharpoons Ti_2O_5(OH)_{4\,(aq)}^{2-} \rightleftharpoons Ti_2O_5(OH)_{5\,(aq)}^{3-} \rightleftharpoons Ti_2O_5(OH)_{6\,(aq)}^{4-}
\end{gathered} \tag{2}$$

Hence, by increasing the pH of the titanium-peroxo-hydroxide solution anionic species are formed which will condense by forming hydroxy-bridges between the metal atoms. It should be mentioned that condensation products which are only dinuclear are considered to be rare in hydrolysis of metal-aquo ions [44].

A titanium-peroxo-hydroxide reaction in the presence of excess barium ions will give the barium-titanium-peroxo-hydroxide complex at relatively high pH. The overall reaction equation is given in the following reaction equations (pH ≥ 9):

$$Ba_{(aq),excess}^{2+} + Ti(OH)_{2(aq)}^{2+} + H_2O_{2(aq),excess}\left(\rightleftharpoons Ba_{(aq),excess}^{2+} + Ti_2O_5(OH)_{6(aq)}^{4-}\right) \rightleftharpoons Ba_2Ti_2O_5(OH)_{6(s)} \tag{3}$$

The barium-titanium precursor was produced according to the method described in [22] The barium reagent ($BaCl_2 \cdot 2H_2O$, ≥ 99.0%, Fluka) was added to demineralized water and $TiCl_4$ (99.9%, Acros) was added to the barium solution with a syringe, to minimize contact with air, under vigorous stirring so that the dissolution of $TiCl_4$ proceeded in a minimum amount of time. The barium and titanium concentrations were adjusted so that the barium to titanium ratio amounted to 2. The total barium and titanium concentration was fixed at 0.05 M. Immediately after having added $TiCl_4$ to the barium solution, hydrogen peroxide (H_2O_2, 35%, Acros) was added dropwise to the solution (pH = 1.2). The H_2O_2 to titanium ratio was fixed at 3. The complexation reaction was visible by the formation of a clear dark red colored solution. The excess hydrogen peroxide ensures the deprotonation of the titanium hydroxo-aquo complex. The overall reaction is given by Eq.(3) (water molecules are not shown) [44].

The solution was then stirred for an additional half hour. Co-precipitation of metal-hydroxides in aqueous solutions is initiated by solubility change depending on pH [33]. Therefore, the precursor solution was precipitated by the dropwise addition of NH_4OH (28–30%, Acros) till pH 10.1 ± 0.2 which was accompanied by a color change of the suspension from dark red to non-transparent milky pale green. By the addition of the alkaline reagent a polymerization reaction was initiated which resulted in the cross-linked network of Ti–O–Ti bonds with Ba^{2+}ions located in the 'cavities' of the cross-linked structure. The barium-titanium-peroxo-hydroxide complex solution was stirred for 2 h. Afterwards, the metal coprecipitate was filtrated with a Buchner funnel and washed three times with demineralized water. The coprecipitate was then dried overnight at room temperature and crushed to fine powder with a ceramic mortar.