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Low temperature hydrothermal synthesis of $Ba(Mg_{1/3}Ta_{2/3})O_3$ sol-derived powders

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Powders of the microwave dielectric material barium magnesium tantalate $Ba(Mg_{1/3}Ta_{2/3})O_3$ have been produced by hydrothermal synthesis at moderately low temperatures (160 to 350 °C). It was found that while it is relatively straightforward to produce the material in the desired perovskite phase at or below 200 °C, the powder particles tend to be highly irregular in morphology with extremely small dimensions (of the order of 10 nm) and deficient in magnesium (with some precipitation of the excess magnesium as the hydroxide). The effects of both higher synthesis temperatures and different feedstock preparation were thus investigated with the aim of improving the precipitation of magnesium under hydrothermal conditions in order to produce a more homogeneous, stoichiometric powder and significant progress was made. It was found that when near-stoichiometric particles are formed, they adopt rounded morphologies and exhibit larger particle sizes (around 30–50 nm). These results show that the hydrothermal feedstock and the synthesis temperature used have a profound effect on particle stoichiometry, which in turn affects the growth morphology of the particles.

1. Introduction

The increasing demand for microwave communications and the continuing miniaturization of electronic circuitry has resulted in a need for smaller microwave resonators with good frequency selectivity and temperature stability. These are usually constructed using a dielectric ceramic material with a moderately high dielectric constant, a low loss at microwave frequencies (usually expressed as a high Q value) and a near-zero value of the temperature coefficient of the resonant frequency, τ_f. Since the discovery of the excellent microwave dielectric properties exhibited by $Ba(Zn_{1/3}Nb_{2/3})O_3$–$Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics with the complex perovskite structure [1], there has been much research into a variety of similar materials. Such materials have a perovskite structure with the general formula of $Ba(X'_{1/3}X''_{2/3})O_3$ (where X' is Zn, Mg, Ni or other metallic elements which form a divalent ion and X'' is Ta or Nb). In particular, materials based on $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) have shown great promise and Q_f values (a useful figure of merit) of between 200 and 400 THz have been measured by some workers [2–5] at frequencies close to 10 GHz, together with τ_f values close to zero.

These properties were all achieved using ceramics synthesized by the mixed oxide route with the addition of various dopants and required the use of extremely high sintering temperatures [3–5] ($\geqslant$1600 °C) or very long sintering times at lower temperatures [2] ($\approx$100 h at 1450 °C). Chemically synthesized ceramic powders often possess better chemical homogeneity and a finer particle size together with better control of particle morphology than those produced by the mixed oxide route; these features often result in improved sinterability. Thus, a number of workers have investigated the production of BMT powders by the sol–gel method [6–8]. These powders did, indeed, display high sinterability with relative densities of $>96\%$ of theoretical being achieved at sintering temperatures of between 1300 °C and 1400 °C for times as short as 2 h. In addition to this, one study found that complete atomic ordering into the hexagonal perovskite structure (JCPDS card 18-176) had occurred after 5 h sintering at 1400 °C [6]. Despite this, microwave measurements on ceramics produced from sol–gel powders showed unexpectedly low values of Q_f [6, 7] of between 30 and 105 THz, even when sintered at 1600 °C for a long time of 64 h. No reason has yet been found for this effect, although a number of possibilities have been suggested, including the effects of dopant ions in mixed-oxide produced ceramics, and grain size and non-stoichiometry in sol–gel derived ceramics [6].

Another technique for the chemical synthesis of ceramics which has shown particular promise in recent years is the hydrothermal method. In this method, ceramic sols are produced by chemical reactions in an aqueous or organo-aqueous solution under the simultaneous application of heat and pressure (the pressure being normally autogenous), usually in the presence of an alkali or acid which has a pseudo-catalytic effect upon the reaction. This has been shown to be useful for the preparation of a wide variety of ceramic materials including other barium based

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materials such as barium titanate ($BaTiO_3$) [9] and barium hexaferrite [10]. Moreover, this technique has some significant advantages over other chemical synthesis techniques. Firstly, simple salts such as acetates and nitrates can often be used instead of the expensive alkoxides usually required for the sol–gel method. Secondly, many materials can be produced directly in the desired crystalline phase at relatively low temperatures ($\leqslant 350\,^\circ C$), thus eliminating any need for a calcination treatment prior to sintering. Finally, since the particles are produced in a sol form, these sols can be used directly in the production of green ceramic bodies via techniques such as extrusion, injection moulding, viscous processing or pressure filtration without requiring prior conversion to a dry powder. Such methods may result in reduced particle agglomeration or the formation of softer, more deformable agglomerates as compared to the use of dry powder routes, leading to improved sintering behaviour and reduced flaw sizes; and, consequently, dense ceramics with better mechanical properties than those prepared by conventional routes.

In this paper, we describe the first reported hydrothermal synthesis of a perovskite barium magnesium tantalate powder. Attempts to produce a powder with improved particle morphology, size and stoichiometry by adjusting processing parameters such as the precursor sol composition and synthesis temperature are then described.

2. Experimental Method

The raw materials were barium acetate, $Ba(CH_3COO)_2$, and magnesium acetate, $Mg(CH_3COO)_2 4H_2O$, (both from Aldrich Chemical Co., Gillingham, UK), and tantalum oxalate solution (from H. C. Starck Ltd., Goslar, Germany). (Tantalum oxalate solution does not have a simple chemical formula but the concentration of oxalate ions and tantalum (as Ta_2O_5) in solution is specified by the manufacturers.) Oxalate ions were found to be detrimental to the synthesis of the perovskite phase, so the tantalum oxalate solution was treated in the following manner to remove them: the solution was added dropwise to ammonia solution with stirring resulting in the precipitation of a hydrated tantalum oxide and the retention in solution of the oxalate ions; the precipitate was then filtered out and washed free of oxalate ions.

Precursor sols for the hydrothermal synthesis were produced using barium and magnesium acetates and the hydrated tantalum oxide in aqueous-based, alkaline solutions. Alkaline conditions were used since barium and magnesium are both alkaline metals, rendering them soluble in acidic or neutral conditions, and so requiring strongly alkaline conditions to ensure their complete precipitation. Moreover, strongly alkaline conditions have been shown to be necessary in the hydrothermal synthesis of other barium-containing compounds such as barium titanate [9] and barium hexaferrite [10]. A variety of bases were used including the strong organic base, tetramethylammonium hydroxide, $(CH_3)_4NOH$, hereafter referred to as TMAH; ammonia solution ($NH_3(aq)$); sodium hydroxide (NaOH); or potassium hydroxide (KOH). TMAH was preferred to NaOH or KOH at low temperatures since the latter bases may leave behind sodium or potassium ions in the ceramic. It is, however, limited to use at or below 200 °C since it undergoes partial decomposition to trimethylamine, $(CH_3)_3N$, at temperatures between 100 and 200 °C with the decomposition being almost complete above 200 °C. Thus, for the experiments at higher temperatures inorganic bases had to be used.

The precursor sols were treated hydrothermally in either a 250 cm^3 polytetrafluoroethylene (PTFE)-lined Berghof autoclave or a 4 l Baskerville autoclave constructed from the corrosion resistant nickel-based alloy, Hastelloy C276. Hydrothermal synthesis was carried out at temperatures of between 160 and 350 °C for a period of 2 h at the desired temperature, usually with stirring. The synthesized sols were vacuum filtered and the resulting powder cake was then washed with water, followed by acetone. The powder cake was then dried at room temperature for several days and was then powdered using a porcelain pestle and mortar. These powders were then investigated using X-ray diffraction (XRD) and transmission electron microscopy (TEM).

As regards the XRD characterization of the perovskite phase of BMT, it should be noted that JCPDS standards exist for both $Ba(Mg_{1/3}Ta_{2/3})O_3$ (18-176) and $Ba(Zn_{1/3}Ta_{2/3})O_3$ (18-201 and 29-203), which have the same crystal structure. The synthesized BMT powders usually matched the newer $Ba(Zn_{1/3}Ta_{2/3})O_3$ standard (29-203) more closely than the older $Ba(Mg_{1/3}Ta_{2/3})O_3$ standard (18-176). In particular, the peak intensities matched those of the former much better than those of the latter. In the light of this, the original papers upon which these standards are based were examined carefully. It was found that the earlier standards (18-176 and 18-201) are based on a general survey of a number of compounds with the same structure [11], whereas the later $Ba(Zn_{1/3}Ta_{2/3})O_3$ standard (29-203) is based on a detailed XRD and neutron diffraction study of the structure of this material [12]. Thus, it was concluded that this was a more reliable standard, although the unit cell parameters may be shifted slightly from those for $Ba(Mg_{1/3}Ta_{2/3})O_3$.

3. Results

Fig. 1 shows the XRD pattern for a powder produced at 200 °C using TMAH, with the main peaks for the $Ba(Zn_{1/3}Ta_{2/3})O_3$ standard (29-203) indicated. The peaks match those for the standard well, thus showing that the perovskite phase has been formed at a temperature as low as 200 °C. The peaks, however, are somewhat broadened, suggesting that the particle size is extremely fine (i.e. of the order of a few nanometres). A pair of peaks is also noted at around $2\theta = 24^\circ$; these are the largest peaks for $BaCO_3$ (JCPDS 44-1487), and some other peaks for this phase may be noted in the region of $2\theta = 34^\circ$. A TEM image of a similar powder which was produced at 160 °C is shown in

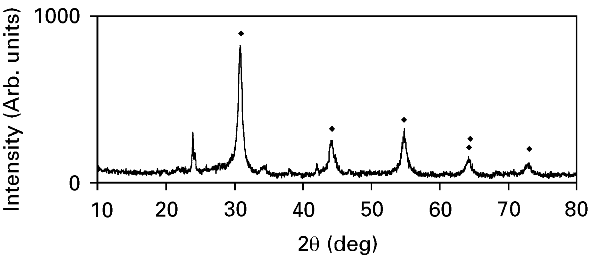

Figure 1 XRD trace for a BMT powder synthesised at 200 °C for 2 h using TMAH with the positions of the main peaks for the BZT standard (JCPDS 29-203) indicated (◆).

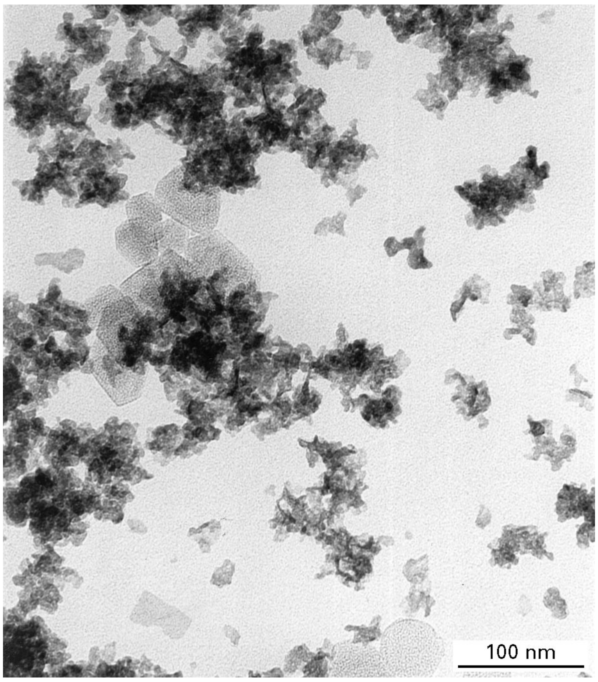

Figure 2 TEM image of a BMT powder synthesised using TMAH at 160 °C for 2 h.

Fig. 2 and the reason for the XRD peak-broadening may be seen clearly: most particles are clusters of irregularly shaped crystallites with extremely small dimensions (typically with the smallest dimensions being of the order of 10 nm). Energy dispersive X-ray (EDX) analysis on the TEM showed that these particles were usually deficient in magnesium (and sometimes barium). Some thin hexagonal platelets may also be observed in Fig. 2; EDX analysis of these platelets showed peaks for magnesium and oxygen. Magnesium hydroxide has a hexagonal crystal structure (JCPDS 44-1482) and is often found as hexagonal platelets [13, 14]; thus it was assumed that these platelets consisted of magnesium hydroxide. It seems likely, therefore, that at least some of the magnesium not incorporated within the perovskite particles was precipitated out as the hydroxide. It is also probable that any excess barium has remained in solution, as has been observed previously for the hydrothermal synthesis of barium titanate [15].

Fig. 3 shows the XRD traces for powders produced at temperatures of 200 and 350 °C, respectively, using ammonia solution to provide alkaline conditions. For the powder produced at 200 °C, the main feature is

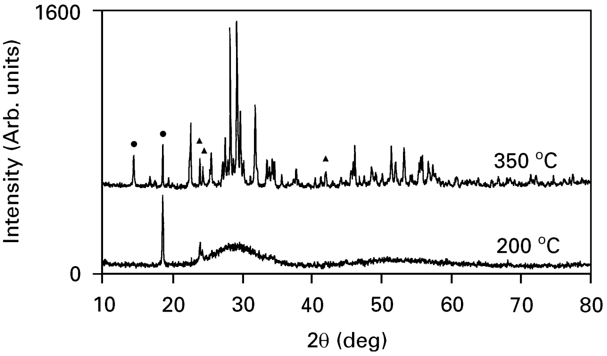

Figure 3 XRD traces for BMT powders synthesized using ammonia for 2 h at 200 and 350 °C, respectively. Peaks that can definitely be attributed to $BaCO_3$ (JCPDS 44-1487) and two unidentified peaks are marked (▲ and ●, respectively), the remaining peaks can be attributed to two $BaTa_2O_6$ phases (JCPDS 20-821 and 20-147).

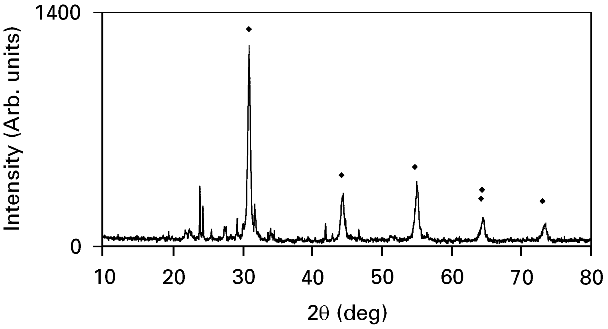

Figure 4 XRD trace for a BMT powder synthesized at 350 °C for 2 h using NaOH with the positions of the main peaks for the BZT standard (JCPDS 29-203) indicated (◆).

a broad hump centered on $2\theta = 29°$ which is probably related to the presence of amorphous material; the only evidence of any crystallinity are the $BaCO_3$ peaks at around $2\theta = 24°$ and an unidentified peak close to $2\theta = 19°$. For the powder produced at 350 °C, however, sharp peaks are observed, which match well to a $BaTa_2O_6$ phase (JCPDS 20-0821); there are also some unidentified peaks in this trace. It is clear, therefore, that crystallization is retarded when ammonia is used to provide basic conditions and that when crystallization occurs, it is to a phase which is significantly deficient in Ba and Mg with respect to the desired perovskite phase.

Clearly, whilst the desired perovskite phase can be formed by hydrothermal synthesis in sufficiently alkaline conditions, achievement of the desired stoichiometry is more difficult. In particular, a method must be found to ensure the complete reaction of the magnesium with the other components in order to produce a homogeneous BMT powder and avoid the co-precipitation of magnesium hydroxide. The results of two methods that were used in an attempt to achieve this aim are described below.

Firstly, higher temperatures (300–380 °C) were used with NaOH and KOH as the base. A XRD trace for one of the powders produced using NaOH is shown in Fig. 4 with the main perovskite peaks indicated. The main feature of this trace is the presence of sharp peaks corresponding to the perovskite phase, indicating

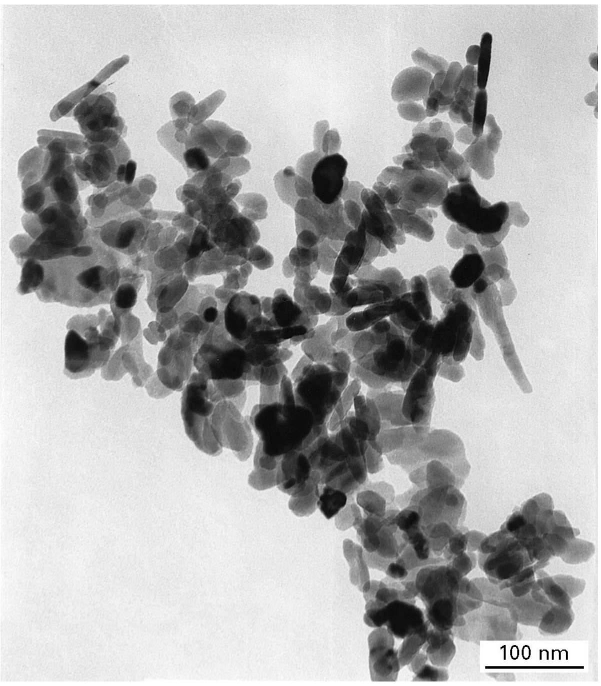

Figure 5 TEM image of particles in a BMT powder synthesized at 350 °C for 2 h using NaOH.

that the perovskite particles have somewhat larger dimensions than those produced using TMAH at 200 °C or less. Large peaks for $BaCO_3$ (i.e. a pair close to $2\theta = 24^\circ$ and a group around $2\theta = 34^\circ$), as well as some unidentified peaks, are also present. A TEM micrograph of this powder is shown in Fig. 5 and it may be seen that the particles have a rounded morphology with a tendency to be elongated in one direction, having aspect ratios of between 1 and 9. In addition to this, most particles are larger than those produced by the low temperature method, with the dimensions of most particles being in the range of 10–100 nm. The chemical composition of particles was studied by EDX and, in most cases, the relative amounts of Ba, Mg and Ta were found to be close to stoichiometry but there was contamination of most particles by Na or K at a level of 3 to 5 at % of total metal-ion content. One of the most highly elongated particles was found to have much higher levels of Na ($\approx$ 20 at %), however. Such Na-rich particles may have a different crystal structure and this could explain the presence of the unidentified peaks on the XRD traces.

This level of contamination by Na or K would almost certainly affect the dielectric properties of a sintered material. Whilst it is probable that some washing solutions could be effective for removing Na or K from particle surfaces, removing Na or K ions that have been incorporated into the crystalline structure of the particles would be much more difficult. Unfortunately, it seems likely from the results detailed above, that a certain proportion of the Na ions in the runs with NaOH have been incorporated within the particles. Thus, the use of NaOH (and possibly KOH as well) for the hydrothermal synthesis of BMT is likely to result in unacceptable levels of Na or K ions within the material which cannot be removed easily.

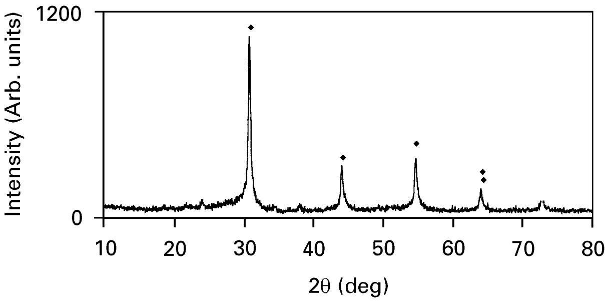

Figure 6 XRD trace for a BMT powder synthesized at 200 °C for 2 h using a modified TMAH method with the positions of the main peaks for the BZT standard (JCPDS 29-203) indicated (♦).

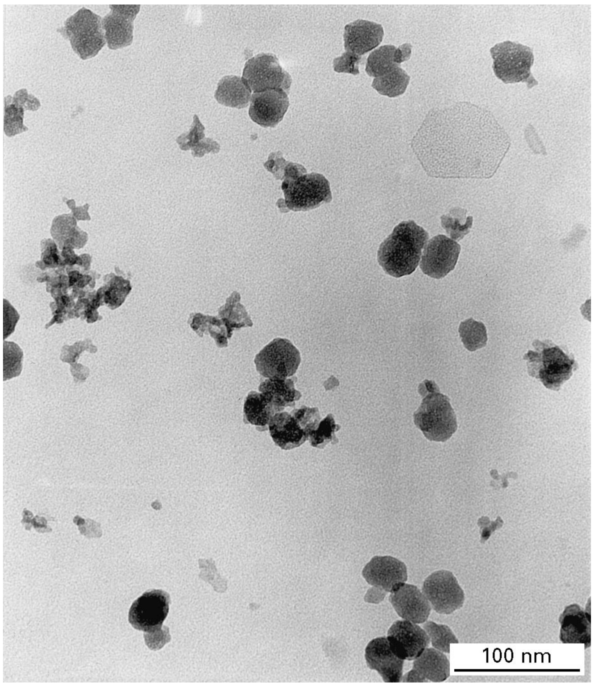

Figure 7 TEM image of a BMT powder synthesized at 200 °C for 2 h using a modified TMAH method.

A modified method was developed using TMAH at temperatures close to 200 °C in an organo-aqueous solution. A XRD trace for one of the resulting powders is shown in Fig. 6, with the main peaks for the perovskite phase indicated. All the principal peaks on this trace are those for the perovskite phase, and the only indication of any impurity is a small $BaCO_3$ peak at $2\theta \approx 23.9^\circ$. The peaks are also sharper than those for materials produced at 200 °C by the standard TMAH method, suggesting that a more desirable particle size has been achieved. This is confirmed by TEM, as shown in Fig. 7, which shows that this powder is dominated by rounded particles with dimensions of about 30 nm. In addition to these rounded particles, however, there are particle clusters similar to those produced at 200 °C by the standard TMAH method, consisting of ultrafine irregularly shaped particles, and a few magnesium hydroxide platelets. In view of this morphological inhomogeneity, the powders were studied by EDX analysis and electron diffraction in the TEM in order to ascertain the reason for the difference in morphology between the two types of BMT particle. It was found that whilst both types of particle exhibited the perovskite crystal structure, the rounded particles had compositions close to the stoichiometric composition, whereas the agglomerates of irregular particles were significantly deficient in magnesium. Thus, a clear link has been established between the stoichiometry of the BMT particles and their morphology.

4. Discussion

It has been shown that, while perovskite barium magnesium tantalate may be produced readily by hydrothermal synthesis given sufficiently alkaline conditions, achievement of the desired stoichiometry and homogeneity is more difficult. It seems likely that where magnesium deficiencies occur, the magnesium does not react fully with the other ions at the synthesis temperature leaving some excess magnesium in solution as the hydroxide. This magnesium hydroxide is most probably precipitated out on cooling of the sol after hydrothermal processing as the hexagonal platelets which were observed in many samples. Thus, it seems that the key to the production of a homogeneous powder consisting of stoichiometric BMT particles is to ensure that the magnesium reacts fully with the barium and tantalum ions. The two methods that were investigated in this study both showed some promise but significantly more work is required in order to achieve the desired goal of producing a homogeneous powder consisting of stoichiometric particles with rounded morphologies and sizes of less than 100 nm.

It is interesting to see that there is a very clear link between the stoichiometry of particles and the morphology that they adopt. In every case studied, it has been seen clearly that those particles which are significantly deficient in magnesium have highly irregular shapes (often with the smallest dimensions being in the region of 5–10 nm), while still having the perovskite crystal structure, whereas those perovskite particles with a near-stoichiometric composition have larger particle sizes (30–50 nm) and rounded morphologies. Thus, the degree of reaction of magnesium with the other ions at the synthesis temperature affects significantly the way in which perovskite particles grow after nucleation.

It is also interesting to consider the way in which the presence of sodium ions affects the particle morphology. It seems likely that the tendency for particles to adopt an elongated morphology is caused by the presence of a certain amount of Na ions in the crystal structure, although the reason for this effect has not yet been determined. It could be, however, that the Na ions have aided the formation of the ordered hexagonal perovskite structure of BMT rather than the disordered cubic perovskite structure which might normally be expected to form at these low temperatures [6]. If this hexagonal structure was formed, then different particle growth rates would be expected along the *c*-direction and perpendicular to the *c*-direction. This could, in some circumstances, lead to the production of elongated particles like those observed in this powder. In order to determine whether the ordered hexagonal phase has been formed, detailed XRD measurements would have to be performed on the powders by looking for the presence of both peak splittings at high angles and small superlattice reflections at a variety of angles; this has not been done at present.

Finally, it is clear that the hydrothermal synthesis of this triple cation ceramic oxide presents more complications than the synthesis of dual cation ceramics such as barium titanate [16] since there is much more scope for non-stoichiometry, and this, in turn, has a marked effect upon the particle size and morphology. Overcoming such difficulties, however, would give significant benefits not only for synthesis of this material but would also give useful insights concerning the synthesis of many similar multi-cation ceramic materials including microwave dielectric ceramics based on $Ba(Zn_{1/3}Ta_{2/3})O_3$.

5. Conclusions

Barium magnesium tantalate, $Ba(Mg_{1/3}Ta_{2/3})O_3$, has been produced in the perovskite phase by hydrothermal synthesis at moderately low temperatures (160 to 350 °C) for 2 h from relatively inexpensive non-alkoxide precursors.

Significant progress has been made towards producing a homogeneous, stoichiometric powder with a rounded particle morphology and sub-100 nm particle size.

It has been found that the composition of the starting sol and the hydrothermal synthesis temperature have a profound influence upon the particle stoichiometry, which in turn has a strong effect upon the morphology of the perovskite particles.

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