Low Temperature Hydrothermal Synthesis of $\text{BaMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$ Sols and Powders

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Perovskite $\text{BaMg}_{1/3}\text{Ta}_{2/3}\text{O}_3$ sol-derived powders have been produced by hydrothermal synthesis at low temperatures of 160°C - 350°C. The particles in these powders tend to be irregular shaped, ultra-fine and magnesium-deficient. Methods have been found for producing near-stoichiometric particles and these have more rounded morphologies and larger sizes. Thus, a clear link has been established between the stoichiometry and morphology of the powder particles which suggests that the particle growth mechanisms under hydrothermal conditions are affected strongly by stoichiometry. [hydrothermal synthesis, ceramic, microwave dielectric, perovskite]

1. Introduction

In recent years, much work has been performed on ceramics based on $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (BMT) and $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (BZT) for use in microwave dielectric resonators. These materials have moderate dielectric constants (20-30), very high Q values ($Q \cdot f > 100$ THz at around 10 GHz) and near zero values of τ_f , the temperature coefficient of the resonant frequency. In particular, ultra-high Q values have been achieved for some BMT based materials with $Q \cdot f$ in the range 200 to 400 THz [1,2,3,4].

Most published studies of BMT-based materials have used powders prepared by the conventional mixed oxide route and have shown the need for very high sintering temperatures [2,3,4] ($\geq 1600^\circ\text{C}$) for reasonable times, or very long times at lower temperatures [1] (≈ 100 hours at 1450°C). Such firing conditions are required in order to give time for atomic-level homogeneity to be achieved by diffusion, as well as to obtain a high degree of atomic ordering on the B sites in the structure.

It is often found that the use of chemically prepared powders leads to improved sintering since such powders can usually be produced with better control of particle size and morphology, as well as improved purity and homogeneity, than can mixed oxide powders. For this reason, a number of studies have been carried out on the production of BMT powders and films using the sol-gel method [5,6,7]. It was found, however, that despite the powders showing good sinterability, the microwave Q values of these ceramics were much lower than for mixed-oxide route ceramics, even when sintered at comparable temperatures. No reason has yet been found for this effect, although the authors of one paper [5] suggested that possible reasons could include the presence of dopant ions in the mixed-oxide materials, and/or grain size effects or non-stoichiometry in the sol-gel materials.

It may be expected that other chemical methods could also be used for the preparation of perovskite BMT. In particular, hydrothermal synthesis has been useful in the preparation of other barium based materials such as barium titanate [8] and barium hexaferrite [9]. Thus, in this paper we describe the application of hydrothermal synthesis to the production of perovskite BMT. Attempts to produce a powder with improved particle morphology, size and stoichiometry by adjusting parameters such as the precursor sol composition and synthesis temperature are then described. This work has been reported more fully elsewhere [10].

2. Experimental Method

Precursor sols were produced from barium and magnesium acetates and hydrated tantalum oxide (derived from tantalum oxalate) in highly alkaline conditions. Alkaline conditions were provided by the organic base tetramethylammonium hydroxide (TMAH), sodium hydroxide (NaOH) or potassium hydroxide (KOH). These precursor sols were then autoclaved at temperatures of 160°C - 350°C for 2 hours, and powders were filtered off, washed and dried. Characterisation of the powders was then performed using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Identification of the crystalline phases in the powders was performed by comparison of XRD traces with JCPDS (now ICDD) standards.

3. Results and Discussion

Fig. 1 shows an XRD trace for a typical powder synthesised at 200°C using TMAH, with the main perovskite peaks indicated. This shows that the perovskite phase has been formed at a temperature as low as 200°C. The peaks are somewhat broadened, however, suggesting that the particle size is ultra-fine (i.e. a few nm). A pair of peaks is also noted at $2\theta \approx 24^\circ$; these are the largest peaks for BaCO_3 (JCPDS 44-1487), and other peaks for this phase may be noted in the region of $2\theta = 34^\circ$.

Fig. 1. XRD trace for a powder synthesised hydrothermally at 200°C using TMAH with the main perovskite peaks indicated.

Fig. 2 shows a TEM image of a similar powder (actually produced at 160°C) and the reason for this peak broadening may be seen clearly: most particles are clusters of irregular-shaped,

ultra-fine crystallites (smallest dimensions typically ≈ 10 nm). TEM EDX analysis of these clusters shows that they are usually 30 - 50 % deficient in magnesium as compared with the stoichiometric composition, and are sometimes deficient in barium as well. In addition to these clusters, there are also thin platelets, often having a hexagonal morphology; examples of which may be seen in Fig. 2. EDX analysis of these platelets shows peaks for Mg and O and it was assumed that they were magnesium hydroxide since this compound often displays a hexagonal platelet morphology [11,12]. Thus, it seems that some of the Mg is precipitated separately as the hydroxide, rather than reacting fully with the other metal ions. Any unreacted barium is likely to have remained in solution as has been observed previously for the hydrothermal synthesis of BaTiO₃ [13].

Fig. 2. TEM image of particles in a powder synthesised hydrothermally at 160°C using TMAH.

Since hydrothermal synthesis at low temperatures using TMAH in an aqueous reaction medium resulted in the formation of magnesium-deficient particles and the separate precipitation of magnesium hydroxide, methods were sought to overcome this undesirable event. Two such methods are described below.

Fig. 3. XRD trace from a powder hydrothermally synthesised at 350°C using NaOH. The main perovskite peaks are indicated.

Firstly, higher temperatures were used (300°C - 380°C) with NaOH or KOH. Fig. 3 shows an XRD pattern for a powder produced at 350°C using NaOH, with the main perovskite peaks indicated. The main feature of this trace is the presence of sharp peaks corresponding to the perovskite phase indicating that the perovskite particles have somewhat larger dimensions than those produced using TMAH at 200°C or less. Large peaks for BaCO₃ (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.

Fig. 4. TEM image of particles in a powder synthesised hydrothermally at 350°C using NaOH.

Fig. 4 is a TEM image of this powder and the reason for the sharper XRD peaks can be seen clearly: the particles are larger, with dimensions in the range of 10 to 100 nm. The particles also have more rounded morphologies than those produced by the low temperature method but they tend to be elongated in one direction with a range of aspect ratios between 1 and 9. The chemical composition of such particles in a number of powders 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 atom % of total metal-ion content. One of the most highly elongated particles was found, however, to have much higher levels of Na (≈ 20 at. %). Such Na-rich particles may have a different crystal structure and this could explain the presence of the unidentified peaks on the XRD traces.

Such a high level of contamination would almost certainly affect the dielectric properties of the ceramic. Whilst Na or K ions adsorbed on the particle surfaces could probably be removed by washing, it seems likely from these results that some of the Na ions have become incorporated within the particles. Such Na or K ions would be extremely difficult to remove, and thus, this method was not investigated further.

A second method was developed in an attempt to improve the reaction of magnesium with the other ions using TMAH in an organo-aqueous reaction medium at temperatures close to 200°C. A XRD trace for one powder produced using this route is shown in Fig. 5, with the main perovskite peaks indicated. All the main peaks are those for the perovskite phase and the only

indication of any impurity is a small BaCO_3 peak at $2\theta \approx 23.9^\circ$. Moreover, the perovskite peaks are sharper than those for powders prepared by the standard TMAH method thus indicating a larger particle size.

Fig. 5. XRD trace for a powder synthesised at 190°C using TMAH in an organo-aqueous solution. The main perovskite peaks are indicated.

Fig. 6. TEM image of particles in a powder synthesised at 190°C using TMAH in an organo-aqueous solution.

A TEM image of this powder is shown in Fig. 6 and it can be seen clearly that most particles have dimensions of the order of 30 nm and a rounded morphology. There are, however, some clusters of irregular shaped particles similar to those found in powders made by the standard TMAH method, as well as a few magnesium hydroxide platelets. The particles were studied by selected area diffraction on the TEM and it was found that both the rounded particles and the clusters of irregular shaped particles had the perovskite structure [14]. Quantitative EDX analysis on the TEM was then used to study particles in this powder. It was found that the rounded particles had near-stoichiometric compositions whereas the clusters of irregular shaped particles were typically 50 % deficient in magnesium [14].

It is clear, then, that there is a strong link between the composition of the perovskite particles and their morphology. Magnesium-deficient particles always appear to adopt irregular morphologies and ultra-fine sizes, whereas near-stoichiometric

particles adopt more rounded morphologies and larger sizes. In addition to this, the presence of Na or K ions seems to result in the growth of more elongated particles. Thus, it is evident that the way in which particles grow under hydrothermal conditions is affected strongly by the composition of the particles.

Despite the inhomogeneity displayed by the organo-aqueous derived powder, it represents useful progress towards synthesising a stoichiometric, homogeneous powder although further work is required in order to realise this aim fully.

4. Conclusions

It has been shown that perovskite BMT powders can be made by hydrothermal synthesis at low temperatures of $\leq 200^\circ\text{C}$.

The resulting perovskite particles are magnesium-deficient with the separate precipitation of magnesium hydroxide.

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

A clear link has been found between the stoichiometry and morphology of powder particles suggesting that the particle growth-mode is affected strongly by stoichiometry.

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