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SYNTHESIS OF NANOCRYSTALLINE BARIUM TITANATE: EFFECT OF MICROWAVE POWER ON PHASE EVOLUTION

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Abstract

Nanocrystalline BaTiO₃ (BT) powder was synthesised using a polymer precursor route and the influence of conventional, microwave and combined hybrid heating methods on phase formation was investigated. A single-phase tetragonal BT (t-BT) nanocrystalline powder of about 20 nm primary particle size and decreased agglomeration were formed when high levels of microwave energy were used. This was accomplished at a lower processing condition of 700°C for 30 min compared to conventional processing, which required 900°C for 5 h, resulting in potential savings in time and energy. During the nano BT synthesis, the role of microwaves was determined by subjecting the samples to identical thermal histories, i.e. exactly the same time-temperature profiles, while using a range of different levels of microwave power. Significant reduction in the activation energy for the formation of the tetragonal phase was observed with increasing levels of microwave power and the results are explained in terms of a possible non-thermal mechanism. Furthermore, under otherwise identical thermodynamic conditions of temperature, time and (atmospheric) pressure, the co-occurrence of hexagonal crystal structure at < 200 W of additional microwave power along with formation of tetragonal

crystal structure at ≥ 200 W and single phase tetragonal crystal structure at ~ 1200 W was observed, demonstrating a new method of controlling the phase evolution during the synthesis of nanostructured barium titanate powder. The methodology could be applied to synthesise a variety of functional ceramic powders with tailored levels of crystallographic phases.

Graphical abstract:

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Introduction

The trend in electronics engineering are towards the utilization of ecologically green materials and process techniques [1]. The development and use of Pb-free titanates for electronic applications has been the subject of intense investigation over recent years with a view to meeting regulatory demands [2]. Barium titanate, BaTiO_3 (BT), stands out as the most promising candidate material since it possesses excellent dielectric, piezoelectric and ferroelectric properties and hence BT-based compositions are widely used in multilayer capacitors, thermistors and optoelectronic devices [3]. Since the use of nanocrystalline BT formulations improves the reactivity [4], enhances the dielectric properties and enables device miniaturization [5], many researchers have worked on different methods for synthesizing BT nanopowders. Traditional solid-state synthesis [6], soft chemistry methods such as sol gel [7], co precipitation [8] and hydrothermal [9] have all been investigated, each providing different benefits and challenges. While most of these methods yield stoichiometric nanocrystalline powders, the formation of agglomerates is very difficult to elude [10]. It is possible to avoid the formation of bi- or multi modal grain size distribution by removing these agglomerates before sintering in the green processing stage, only then can the potential benefits of nanostructures be fully utilised.[11]. In addition, these procedures requires a further calcination stage to form the required final compound from the as-prepared precursor. Since traditional processing depends on heat transfer across the isolated precursor powder bed, it demands a extended soaking time at a higher temperature, resulting in substantial particle growth and turns to hard agglomerates making it difficult to be eliminated[12].

Thus, there is a need to develop more efficient processing methodologies for the synthesis of nanopowders with reduced and softer agglomeration.

During material synthesis, microwaves can be used as a complementary source of energy [13]. The interaction of the microwave radiation with a dielectrically lossy material induces the localised heating of volumetric nature. This enhances the reaction kinetics and therefore helps to lower the processing conditions such as temperature and/or time [13]. During the early years of microwave processing, uncertainties prevailed related to the accuracy of the temperature measurements. These could include the formation of localized hot-spots, the field-focusing effect of thermocouples and non-uniform thermal distribution due to 'inside-out' heating effects [14]. The use of microwave transparent optical fibre thermometers (OFTs) and hybrid microwave / radiation heating can overcome some of these issues [15,16]. In addition, it has often been demonstrated that microwave heating can enhance the kinetics of a range of processes, including synthesis mechanisms, sintering, grain growth and densification of a range of materials [13,17,18]. Both experimental and theoretical modelling results have shown that microwave heating can lower the activation energy and/or pre-exponential factor, which, in turn, enhances the mass diffusion and reaction kinetics [19,20]. For instance, reports on BaTiO₃'s microwave assisted solid state synthesis showed that the activation energy for BT formation is reduced to 42 – 58 kJ mol⁻¹ under microwave irradiation [21,22], which compares favourably to the 105 – 128 kJ mol⁻¹ measured when the powder is synthesised conventionally through solid state synthesis [23–25], though it should be noted that a similar reduction in activation energy has been

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5 reported via use of the hydrothermal synthesis route [26–28] that involves the use of
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7 high pressure. The use of non-stoichiometric precursors has also been found to enhance
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9 the reaction kinetics significantly due to the excellent microwave coupling of the
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11 reactants[29]. There are also a few reports on the microwave-assisted wet chemical
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13 synthesis of nanocrystalline BaTiO₃ involving precipitation[30], solvothermal[31] and
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15 hydrothermal[32] processes. Notably, it is important to have at least one of the reactants
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17 with good microwave absorption characteristics to make full use of the benefits of
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19 microwave processing[13] and these are dictated by the dielectric properties (relative
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21 permittivity, ϵ_r , and loss tangent, $\tan \delta$) of the materials involved.
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27 Therefore, a simple polymeric precursor route was used in the present work for the
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29 synthesis of nano BT powders as it would provide a homogeneous mixture of the
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31 constituents and a soft, porous, amorphous carbon based precursors that can quickly
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33 couple with microwaves, resulting in efficient and volumetric heating.
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38 39 Experimental

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41 The fundamental procedure was adapted from previous work by one of the authors [33].
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43 The titanium ion solution was produced by mixing titanium tetra-isopropoxide (98%,
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45 Aldrich, Steinheim, Germany) with citric acid, CA (99.5%, Acros Organics, New
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47 Jersey, U.S.A) and ethylene glycol, EG (98%, Fluka, Steinheim, Germany). The molar
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49 ratio of CA : EG was maintained at 1 : 4. Afterwards, the necessary BaCO₃ (99%,
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51 Fluka, Steinheim, Germany) powders was added to the titanium solution to get 1:1 ratio
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53 of Ba: Ti. In order to promote polymerization and remove solvents, the prepared
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55 solution was maintained at 200°C for 5 h in an oven, resulting in dark brown, solid.
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5 glassy resin. On further charring in a furnace at 400°C for 2 h it yielded a soft, fragile
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7 solid, that was crushed using an pestle and mortar, referred to as ‘the precursor’, figure
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10 1. Alternative barium sources of barium hydroxide, BaOH.9H₂O (99.99%, Sigma
11 Aldrich, U.K) and barium acetate, C₄H₆BaO₄ (99.99%, Sigma Aldrich, U.K) were also
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13 investigated for the production of the precursor.
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18 Thermal analysis was undertaken using a simultaneous TGA/DSC thermal analyzer
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20 (SDT 2960, TA instruments, UK Ltd) at 10°C min⁻¹ ramp rate in air. Using Universal
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22 Analysis, TA Instruments software, the enthalpies of formation of the various BT
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24 phases were calculated using the area below the peak for the weight-corrected heat flow
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26 versus temperature curve. Certain features including calculation of the particle size of
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28 the powders were measured using transmission electron microscopy (JEOL JEM
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30 2000FX, JEOL Ltd. Tokyo, Japan).
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36 Most of the experiments were undertaken using a hybrid furnace merging microwave
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38 and radiation type heating, figure 2. The latter was able to operate in radiation,
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40 microwave or radiation / microwave hybrid mode, with a microwave frequency of
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42 2.45 GHz and up to 2 kW of microwave power if required. [15,16]. In the hybrid
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44 furnace heating facility, the microwave and radiation energy input could be varied
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46 independently whilst keeping the temperature and time profiles, the amount of reactants
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48 and the experimental arrangement all consistent allowed determination of whether the
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50 use of microwaves and different microwave power levels resulted in any changes to the
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52 reaction process or resulting phase evolution.
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The precursor was placed in silica crucibles inside the hybrid furnace and the crucible top was covered using a thin layer of high purity alumina thermal insulation wool with a central hole for inserting top control probe to reduce the heat loss as shown in the figure 2 [34]. From figure 3, it is evident that there was no BT formation at temperatures below 600°C using purely radiation heating, therefore in order to achieve thermal equilibrium; the precursors were kept at 500°C for 30 min at the start of all calcinations and to minimize any temperature gradients across the sample. Following some initial experiments, a calcination temperature of 700°C with a hold time of 30 min and a heating rate 15°C min⁻¹ was chosen for each calcination experiment. The microwave power level was fixed in increments of 200 W at a given value between 0 and 1000 W, and the radiation heating power varied to provide the required, and identical, temperature / time profile; continuously monitoring the input power for radiation heating, forward and reflected microwave power. This enabled an exact comparison of the microwave field effect on the reaction enhancement and crystallization. Temperature was measured and monitored with the control probe being located at the centre of the sample throughout the research using optical fibre thermometry, OFT (M10 and M100, Luxtron, U.S.A) whilst a second OFT probe measured the temperature at one end of the sample [16], thus the temperature variation across each sample was monitored. To minimise the influence of optical radiation from the heating elements, the OFTs were protected using a low loss quartz tube. The OFT was calibrated using a distinct set of experiments evaluating the melting point of vanadium pentoxide and the

accuracy was found to be $\pm 3^{\circ}\text{C}$ [35]. Furthermore, an infrared camera was also used to determine the average distribution of temperature through each sample.

To allow activation energy calculations to be undertaken, the same amount of precursors were calcined using the same experimental arrangement and varying the temperature between 500 and 700°C for times between 5 and 120 min whilst using 0, 600 and 1000 W of microwave power. The amount of tetragonal BT phase formation for each processing conditions were analysed using powder X-ray diffractometry, XRD, using Cu K α radiation (Bruker D8 model diffractometer, Bruker AXS GmbH, Karlsruhe, Germany) and micro-Raman spectroscopy (Horiba Yvon Raman LabramHR spectrometer, Horiba Jobin Yvon SAS, Villeneuve d'Ascq, France) [36]. The characteristic tetragonal peak at 307 cm⁻¹ from respective Raman spectra's [36] were used to calculate the percentage of the tetragonal phase in the calcined BT powders, for the respective processing condition. The analysis involved initially normalising the Raman curves to 100, subsequent peak smoothening and creating the base line [36]. The peak height and the area under the peak were computed using the integration method [36]. References for the ability to obtain pure tetragonal BT were obtained from the integrated peak area of the precursor calcined at 700°C for 30 min using microwave-only heating and 900°C for 5 h using radiative-only heating respectively. The former conditions were determined following experiments using a second microwave facility, a multimode cavity capable of proving an adjustable, continuous output power up to a maximum of 6 kW at an operating frequency of 2.45 GHz and; the use of 1300 W was found to be sufficient for achieving the required temperature. The processing

temperature was varied between 550 – 700°C at 50°C intervals and the samples were held at each temperature for 30 or 60 min. The sample temperature during microwave heating was measured using an optical pyrometer (Minolta/Land Cyclops 152, Land Infrared, Sheffield, UK) along with a thermal imaging camera (FLIR Systems, ThermoVision™ A40, Boston, USA) described elsewhere [15,16]. Determining the conditions required to generate pure tetragonal phase using radiation heating only required the precursor to be calcined between 600-900°C for 5 h in a silicon carbide heating element muffle furnace (Laboratory chamber furnace-ELF 1100, Carbolite Ltd., U.K). The temperature of the sample was measured using a thermocouple of type K; in this case, the temperature variation across the sample was not measured as it was presumed to be homogeneous given the duration of the calcinations.

Under the assumption that the conditions for t-BT crystallization were based on isothermal, random nucleation and driven more by temperature and less by time dependence, a Johnson-Mehl-Avrami kinetic model analysis was derived. Such models are often used to extract kinetic information from isothermally crystallised samples [37,38]. The model describes that the nucleation sites consistently emerge in the reactant mixtures from which crystal growth occurs [37,38]. Hence, the approach is widely used for wet chemical approaches including sol gel [7], hydrothermal [26] and polymer-based synthesis routes [39]. In order to separate the effect of microwave heating alone, the same amount of BT precursors were used in the hybrid furnace experimental facility and calcined at different temperatures, time and microwave power levels. Although it is a common practice to use XRD data for quantification in such

calculations, the latter is not reliable for distinguishing phases with similar lattice parameters. In contrast, Raman data is sensitive to the nature of the molecules, chemical bonds and has small spatial resolution and can therefore be used for samples that are non-crystalline, partially reacted or have similar lattice parameters. Therefore, the degree of tetragonal BT formation was determined by analysing the Raman spectra of the calcined powders across the range 100 – 1100 cm^{-1} and the correlation value, α (which is an indication of the degree of tetragonal BT crystallization)[26], was calculated using a reference spectrum obtained from the conventionally calcined BT powders at 900°C/ 5h, figure 4.

Results and Discussion

As shown in Figure 3 & Table 1, the decomposition of the precursors takes place in multiple steps that was completed at ~655°C. Both the barium carbonate and hydroxide sources showed a similar weight loss of ~40%, with an associated exothermic peak at 440 – 460°C, corresponding to the formation of an intermediate phase from the precursor. Whereas, the barium acetate source exhibited a smaller weight loss of only ~15% and intermediate phase formation occurred at the lower temperature of 387°C. All three precursors formed showed a second exothermic peak at 580°C, which could be attributed to the formation of the BaTiO_3 [40] and another endothermic reaction peak at ~655°C that matched the tetragonal BT phase transformation [40]. Since the final tetragonal BT formation temperature of ~655°C and its total enthalpy of formation of ~115±10 J mol^{-1} was broadly similar for all the precursors, BaCO_3 was used to prepare the precursor that was used throughout the rest of the work reported here.

The XRD results of the precursor powder, figure 4, show that complete transformation to tetragonal BT required 5 hrs at 900°C when using radiation heating only, whilst when microwave-only heating was used, figure 5, well crystallized single-phase t-BT could be formed after only 30 min at 700°C. Lesser conditions in both cases yielded the residual presence of unreacted intermediate phases. The lattice parameters calculated using the XRD peak position for the calcined BT powders using different heating sources are shown in Table 2; they both match well with the standard JCPDS card, no: 081-2196, for t-BT. However, given that the maximum peak for the cubic phase occurs at $2\theta = 31.530^\circ$ (JCPDS 89-2475), whilst those for the tetragonal phase occur at 31.505° and 31.602° , it was very difficult to be certain that only pure tetragonal BT had been formed and, hence, Raman spectroscopy was also used and the results are shown in figures 6 & 7. Although, theoretically, the cubic symmetry does not produce any Raman active modes, this polymorph shows only a broad band at around 290 and 520 cm^{-1} . This could be associated with the local disordered positioning of Ti atoms [36,41,42]. The evident bands at 260, 306, 520 and 721 cm^{-1} are the characteristic peaks of tetragonal BaTiO_3 [36,41,42]. The appearance of the 306 cm^{-1} peak indicates, at least on the local scale, an asymmetric TiO_6 octahedral existing within the BT unit cell structure whilst the sharper band at 1064 cm^{-1} corresponds to the symmetric stretching mode of CO_3^{2-} in the BaCO_3 [40,43,44]. Comparing the Raman spectra of the powders calcined using different heating sources under different conditions; figures 6 & 7, the tetragonal phase nucleation can be clearly seen to start at a lower temperature when microwave heating

was used. As expected, the degree of tetragonal phase formation was found to increase with an increase in processing temperature.

Appearance of the small peak at 640 cm^{-1} in the BT powders calcined in radiation heating only at 700°C for 5 h, figure 6, suggests the presence of a small amount of the high temperature hexagonal phase within the reaction product, which, in turn, could have arisen because the particles contain planar defects in the stacking sequence [40,43,44]. The fact that the peak is not present under any experimental conditions in microwave-only calcined powders investigated, figure 7, could be due to some defects that are commonly introduced during particle growth [45]. The use of microwaves may enhance bulk phase nucleation [46] and the resulting shorter heating times required will provide less time for particle growth; this argument is supported by the TEM results, figure 8, in which it can be seen that the microwave-calcined BT powder particles are smaller. Interestingly, despite this (and the fact that this means that they will have had greater surface areas) they also appear to be less agglomerated; the particle size and agglomerates sizes were measured using both TEM and particle size analysis and the results were similar.

Figure 9 shows the temperature variation across the samples collected from infra-red thermal imaging camera and they are moderately uniform at each stage of the hybrid-heated calcinations, implying that any t-BT phase formation enhancement seen with hybrid heating is not due to the development of local temperature gradients, at least on a macroscale.

Figure 10 shows the Raman spectra of the BT powders processed at 700°C for 30 min using varying microwave power levels. There is no characteristic tetragonal peaks at 306 and 720 cm^{-1} for the radiation only only processed BT powders; rather the sample contained unreacted BaCO_3 and TiO_2 – though the latter peaks appeared for all samples, albeit with decreasing intensity with increasing microwave power. It may be seen that the tetragonal phase started to form when just 200 W of microwaves were used and the amount increased with increasing microwave power. Single phase tetragonal BT nanopowders was synthesized when using 1300 W of microwave power during the microwave-assisted hybrid heating trials, which compares very favourably with the 900°C for 5 h required during the conventional radiant heating experiments. It is interesting to note that the microwave power input required for achieving completion of the reaction using hybrid heating matched well with the microwave-only heating experiments using the second microwave facility. In addition, the peak drop at 180 cm^{-1} further verified the presence of long-range symmetry in the nano BT powder prepared using higher microwave power levels, whilst no evidence for the hexagonal phase was observed for any of the hybrid-heated samples. Table 3 summarises the different phases identified during various heating conditions.

The above results show clear evidence that the use of microwave heating accelerates the formation of the tetragonal BT phase, with more microwave power increasing the extent of the reaction, even when all other factors are kept as similar as possible. Finally, comparing the time-temperature profile for single-phase t-BT synthesis in conventional radiation heating and pure microwave heating, Figure 11, clearly signifies that the

microwave process requires only $1/10^{\text{th}}$ of the total energy for a conventional radiation type heating cycle, a feature that could be quite useful for process scale-up.

As indicated in the experimental, to understand the extent of the reaction, a JMA kinetic model was derived from the % tetragonal BT crystallization calculated from the Raman data. The JMA plots of both conventional and microwave assisted heating, while

calcining in hybrid facility, generated a typical S-curves as shown in Figure 12. Figure

13 depicts the Avrami plot analysed according to the JMA transformation, equation (1),

$$\ln[-\ln(1-\alpha)] = n\ln(K) + n\ln(t - t_0) \dots \dots \dots \text{Equation 1}$$

Amongst the various interpretations of Avrami equations, the most notable are [37,38], as described in the model, the calculated n values signifies the crystallization mechanism taking place such as rate of nucleation and/or particle growth.

During conventional radiation heating there was a single regime at both 700°C and 800°C with the Avrami exponent value, n, being high at ~4.5 at the lower temperature, which represents an interface-controlled three dimensional nucleation rate. Interestingly, increasing the temperature to 800°C resulted in an n value of <1, which, as indicated above, was interpreted as meaning that there was a no obvious nucleation or it was very slow and mostly dominated by growth of the pre-existing nuclei sites. In contrast, under the microwave calcination there were two clear regimes. At 600°C the Avrami exponent was ~2 in the first regime, suggesting a slow nucleation rate, whilst $n \approx 6.5$ in the second regime suggested a slower reaction kinetics for the formation of a well crystallised t-BT [47]. At higher temperatures of 700°C and 800°C, the Avrami

exponent was very high, between ~7.5 and 8 in the first regime respectively, indicating a rapid particle nucleation and growth rate, whilst the value of 0.5 in the second regime infers that the rate of particle nucleation and growth are very slow. Consequently, it is evident from kinetic model evaluation that compared to conventional radiation type heating, where the nucleation and growth coexists; the nucleation rate in microwave heating is rapid and more dominant than the subsequent growth.

With the chemical reactions being repeated at different reaction temperatures, it was possible to obtain the rate constant, K ; it was expected to follow an Arrhenius behaviour during the BT formation. The tetragonal BT formation using different heating sources are also indicated for comparison in [figure 14](#). The data shows clearly that the t-BT phase conversion was enhanced significantly when microwaves were used, especially at lower temperatures. The degree of differences means that the change in the observed reaction kinetics cannot simply be due to temperature gradients or inaccuracy of the measurement. The data also satisfies the classic parabolic model, which indicates that the diffusion of the ions during the BT formation is the rate controlling mechanism and is governed by:

$$\text{Degree of reaction} = (\% \text{ tetragonal}) = (t_{\text{react}})^{1/2} \dots\dots\dots \text{Equation 2}$$

Considering the Arrhenius equation with a view to elucidating the origin of the enhanced reaction kinetics:

$$k = A \exp\left(\frac{-Q}{RT}\right) \dots\dots\dots \text{Equation 3}$$

where, k is the diffusion rate constant, Q the activation energy; T the absolute temperature, R the universal gas constant (8.314 J/mol K) and A is the pre-exponential factor.

Since equation 3 is similar to that for a straight line, $y = mx + c$, taking logarithms on both sides of the equation means that the slope corresponds to $-Q/R$ and the ordinate to the pre exponential factor, A :

$$\ln k = A - \frac{Q}{RT} \quad \text{.....Equation 4}$$

The activation energy Q was determined from the plot of $\ln k$ versus $1000/T$ in figure 15 for the different microwave power level and the results are shown in table 4.

The activation energy (E_a) for the microwave assisted synthesis was determined to be 40 ± 2 kJ / mol using 1000 W of microwave power, whereas the value for the conventional radiation heating situation was measured as 92 ± 1 kJ / mol, i.e. the activation energy was decreased to half whilst using microwave power. These results match with values from the literature [23–25]. Interestingly, the calculated E_a for the microwave assisted tetragonal BT synthesis were broadly comparable with E_a reported for hydrothermal synthesis of BT [26–28] and, in addition, there was a slight variation in the pre-exponential factor observed compared to the literature. The pre- exponential factor is governed by the collision frequency [48] and depends on materials factors such as γ , a geometric factor, λ the jump distance and Γ the jump frequency. It is given by [49]:

$$A = \gamma \lambda^2 \Gamma \quad \text{.....Equation 5}$$

where the jump frequency (Γ) is described by:

$$\Gamma = \nu \exp\left(\frac{-\Delta G^+}{kT}\right) \dots \dots \dots \text{Equation 6}$$

where ν is the natural vibration frequency of the atoms and ΔG is the Gibbs free energy:

$$\Delta G = \Delta H - T\Delta S \dots \dots \dots \text{Equation 7}$$

where $\Delta H = Q - RT$ is the change in enthalpy of the reaction and ΔS is the change in entropy of the system. For a spontaneous chemical reaction the Gibbs free energy of the system must decrease, which is temperature dependent. Thus in order to proceed non-thermally, either the enthalpy and/or entropy of the system has to change. From Equation 6, the jump frequency is also influenced by the activation energy of the reaction system and thus changes in the activation energy, Q , have a greater impact on lowering the enthalpy of the chemical reaction (H), and hence the net free energy (G), compared to changes in the pre-exponential factor. Therefore the enhancement in reaction kinetics of tetragonal BT nucleation in the present system could be attributed to the combination of change in the activation energy, which in turn changes the pre exponential factor and hence the Gibbs free energy, of the system, favouring the reaction going towards completion.

Previous work based on densification, e.g. [41,50], found that the greatest effect associated with the use of hybrid microwave / conventional radiation heating occurs during the early stages of sintering, with the effect declining as densification increased. Similar results were obtained using computational modelling based on changes in the

densification and contribution of the ponderomotive effect [51]; it was also more pronounced in the initial stages of sintering and decreased towards the end of the sintering process. One explanation for these effects comes from calculations of the dynamics of stable neck growth during microwave sintering, which have demonstrated that the dominant diffusion mechanism transforms from boundary to surface diffusion and then on to volume diffusion as sintering progresses from the early to final stages of densification [51]. It would seem logical that something similar is happening here. As most chemical reactions are diffusion controlled, it would seem that microwaves provide an additional driving force for diffusion, which is of non-thermal nature [52] and directly influences the transport phenomena [50] along with achieving effective utilization of the reaction enthalpies [13,53] and bulk volumetric nucleation [13,46].

Although it has previously been shown that the use of relatively low microwave power levels, e.g. ≥ 300 W, during hydrothermal synthesis that involve the use of high pressures can yield tetragonal barium titanate [54,55], the results from the present work have demonstrated that power levels as low as ~ 200 W at atmospheric pressure can allow the nucleation of nano tetragonal barium titanate that also benefits from reduced agglomeration. Therefore, the powder is better and the energy required to produce it is lower. Finally, it is believed that this approach could be used to synthesise a variety of functional ceramic powders that require tailored levels of specific crystallographic phases.

Conclusions

Single-phase tetragonal BaTiO₃ (BT) fine nanopowders with reduced agglomeration compared to coarser nanopowders that are conventionally synthesized were prepared using the microwave-assisted polymeric precursor method. They were also produced using less demanding processing conditions, viz. just 700°C for 30 min, in contrast to those required with radiative heating, 900°C for 5 h, thereby reducing the time, temperature and in turn the energy needed. Use of a hybrid heating furnace that could vary the required input power supply of radiation heating and microwave heating whilst maintaining otherwise identical processing conditions and utilising exactly the same temperature measurement and experimental system has indicated that the results are genuine and cannot be explained simply by measurement errors. Rather, the activation energy required for the tetragonal BT formation was observed to be approximately halved, to 40 kJ/mol, compared to the apparent 92 kJ/mol when using conventional radiation type heating. It is believed that the non-thermal nature of the enhanced reaction kinetics during the microwave-assisted reactions forming nanocrystalline barium titanate powders could be due to accelerated surface diffusion and bulk nucleation together with effective utilization of reaction enthalpies. Thus, the benefits of microwave heating have been demonstrated to be genuine and to provide a new way of controlling the phase evolution during nanoceramic synthesis, a trait that is expected to be applicable to other ceramic systems.

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Barium Source	% Total weight loss	Intermediate phase formation		BaTiO ₃ formation		Tetragonal phase conversion	
		T / °C	ΔH / Jmol ⁻¹	T / °C	ΔH / Jmol ⁻¹	T / °C	ΔH / Jmol ⁻¹
Barium carbonate	40%	437-462	83 ± 5	580	113 ± 5	655	25 ± 3
Barium hydroxide	40%	438	81 ± 5	580	115 ± 5	655	30 ± 3
Barium acetate	15%	386	20 ± 10	580	102 ± 10	655	73 ± 5

Table 1: Temperature and enthalpy of BT formation for different precursors obtained from the TG/DTA results.

Calcination method	a / nm	c / nm	c/a ratio
Standard JCPDS	0.4006	0.4017	1.003
Conventional only	0.4005 ± 0.0004	0.4018 ± 0.0004	1.003
Microwave only	0.4007 ± 0.0003	0.4017 ± 0.0003	1.003
Hybrid	0.4007 ± 0.0004	0.4017 ± 0.0004	1.003

Table 2: Lattice parameters of the tetragonal BT powders calcined using different heating conditions calculated using the XRD results.

	Pure conventional	Hybrid heating	Pure microwave
Hexagonal coexistence	700°C, 5 h	<200 W at 700°C, 30 min	
Tetragonal nucleation	800°C, 5 h	≥200 W at 700°C, 30 min	550°C, 1 h using 900 W
Single phase tetragonal	900°C, 5 h	1300 W at 700°C, 30 min	700°C, 30 min using 1300 W

Table 3: Phase evolution during nano BaTiO₃ synthesis under conventional, microwave and hybrid heating conditions obtained from the Raman results.

Input microwave power	0 W	600 W	1000 W
Activation energy / kJ mol ⁻¹	92 ± 1	48 ± 3	40 ± 2
Pre exponential factor	13 ± 1	10 ± 3	9 ± 2

Table 4: The activation energy and pre exponential factor for different microwave power for t-BT formation under hybrid heating.

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