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# Elucidating the effects of high temperature mixing method under hydrothermal condition (HTMM) on grain refinements and assembling structures

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ABSTRACT

Crystal size and microstructure are of great importance in determining the physical and chemical properties of functional materials, and refine powders, especially their assembled porous structures have potential application in ceramic fabrication, absorption, catalysts and drug delivery, due to their characters of high activity and large specific surface area. Herein, high temperature mixing method under hydrothermal condition (HTMM) was adapted to synthesize barium strontium titanate [(Ba, Sr)$TiO_3$, BST] powders with various Ba/Sr ratios ($x$ = 0.5, 1.0, 3.0 and 4.0). In comparison with conventional hydrothermal synthesis (CHS), the effects of HTMM on grain refinement and porous structure formation were exclusively investigated. XRD and SEM results indicated that, in the given condition, BST powders prepared by HTMM were much smaller than that by CHS, especially at a lower Ba/Sr ratio. Additionally, assembled porous architectures were constructed by HTMM. It's believed that the high temperature mixing process and continuous rotation contributed to the grain refinement and assembled porous structure, respectively. The assumption was further confirmed through the synthesis of sodium niobate ($NaNbO_3$) powders by HTMM. It's demonstrated that HTMM is advantageous in preparation of refine powders and porous assembled architectures.



## 1. Introduction

Both crystal size and microstructure are of great importance in determining the physical and chemical properties of functional materials [1,2]. It's notable that there exists a critical grain size, below which the materials will display significantly enhanced performance due to the unique characters of large surface areas, affluent surface atoms and extremely high activation [3]. The preparations for micro- or/and nanoparticles are mainly divided into two categories, *i.e.* top-down [4] and bottom-up [5]. Among them, the bottom-up methods, like co-precipitation [6,7], solvothermal [8], sol-hydrothermal [9,10] and microemulsion [11], show evident advantages in nanomaterial production, due to their low reaction temperature, compositional homogeneity and controllability, especially in comparison to the solid state reaction. As the representative bottom-up method, the facile hydrothermal syntheses have been employed to synthesize kinds of advanced materials. Although selective synthesis can be achieved by tuning the hydrothermal process parameters, including pH, raw material ratio, temperature and duration [12–14], one prominent issue is that the crystallization process occurs inevitably at certain temperature during the elevating period; the earlier formed crystals will suffer from a longer crystal growth process than the later ones, thus the final products would be lack of homogeneity in size distribution, and some large grains may disperse in small particles randomly.

To obtain the size-uniform nanoparticle, several novel strategies have been designed deliberately. For instance, Friderichs et al. proposed a two-phase oil/water solvothermal environment method to prepare monodisperse $SrTi_{1-x}Zr_xO_3$ nanocubes with an edge length of 10 nm [15]. Most remarkably, the size and shape of the nanoparticles depended on neither the Zr content nor reaction time. It's believed that oleate ion surfactants played a vital role in prohibiting the grain growth [15]. Another common approach is the introduction of organic capping-agents to prevent the crystal facets growth [16–18].

It's well-known that nucleation and crystal growth is the two key parts controlling the final grain size and distribution. However, previous works were mainly involved in the management of crystal growth process. Herein, we paid our special attention toward the nucleation process, and developed a high temperature mixing method under hydrothermal conditions (HTMM) to refine the grain size and modify

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its uniformity. In our previous work, HTMM was primarily designed to circumvent the intermediate phase, aiming to obtain the pure targets [19]. During this process, the self-designed double-chambered Teflon-linear enables the raw materials located separately, and the chemical reaction is triggered as it reaches the preset temperature. Actually, it's demonstrated that HTMM had unique advantages in circumventing the intermediate impurities, thereby improving the purity of final products [20].

$ABO_3$-type perovskite structure compounds, barium strontium titanate [(Ba, Sr)$TiO_3$, BST] and sodium niobate ($NaNbO_3$), are widely investigated environmental-friendly piezoelectric and catalytic materials [21–24]. For example, BST nanopowders with an average grain size of 475 nm were prepared by a high-energy ball-milling method [25]. Taking the syntheses of BST and $NaNbO_3$ as case study, in this work, we will elucidate the effects of HTMM on the grain refinement and morphology controlling from the view point of nucleation and crystal growth. The proposed HTMM would be a prevalent strategy to synthesize nanomaterials.

## 2. Experimental procedures

### 2.1. Chemicals

Potassium hydroxide (KOH, 99.0% min) and titanium dioxide ($TiO_2$, 99.0% min) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Barium chloride($BaCl_2$, 99.5% min) was purchased from Nanjing Reagent Co., Ltd. Strontium nitrate ($Sr(NO_3)_2$, 99.5% min) was purchased from Shanghai Xinbao Fine Chemical Factory. Tetrabutyl titanate ($Ti(C_4H_9O)_4$, 98.0% min) was purchased from Shanghai Zhanyun Chemical Reagent Co., Ltd. Nitric acid ($HNO_3$, 65% min) was purchased from Guangdong Guanghua Sci-Tech Co., Ltd. Absolute ethyl alcohol ($C_2H_5OH$, 99.7% min) was purchased from Nanjing Ningshi Chemical Reagent Co., Ltd. Sodium hydroxide (NaOH, 96% min) and niobium oxide ($Nb_2O_5$, 99.5% min) was purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were of analytical grade and used as received without further purification.

### 2.2. Conventional hydrothermal syntheses (CHS)

In the typical hydrothermal synthesis of BST powders, $TiO_2$ was used as starting materials. Firstly, $TiO_2$ (0.04 M) and $BaCl_2$ (0.16 M) were added into 55 ml KOH (0.6 M) aqueous solution. After stirring for 30 min, different amount of $Sr(NO_3)_2$, depending on the ratios of Ba/Sr ($x = 0.5, 1.0, 3.0, 4.0$) were dissolved in the mixture. Subsequently, the prepared precursors were transferred into Teflon-lined autoclave and kept at 200 °C for 10 h. And then, the resultant was naturally cooled to room temperature. The product was rinsed with de-ionized water and then anhydrous alcohol, and precipitated with centrifugation for 10 min at 3000 rpm to yield a white powder. Rinsing was repeated thrice to remove excess ions from the final product, and the precursor was dried at 80 °C overnight.

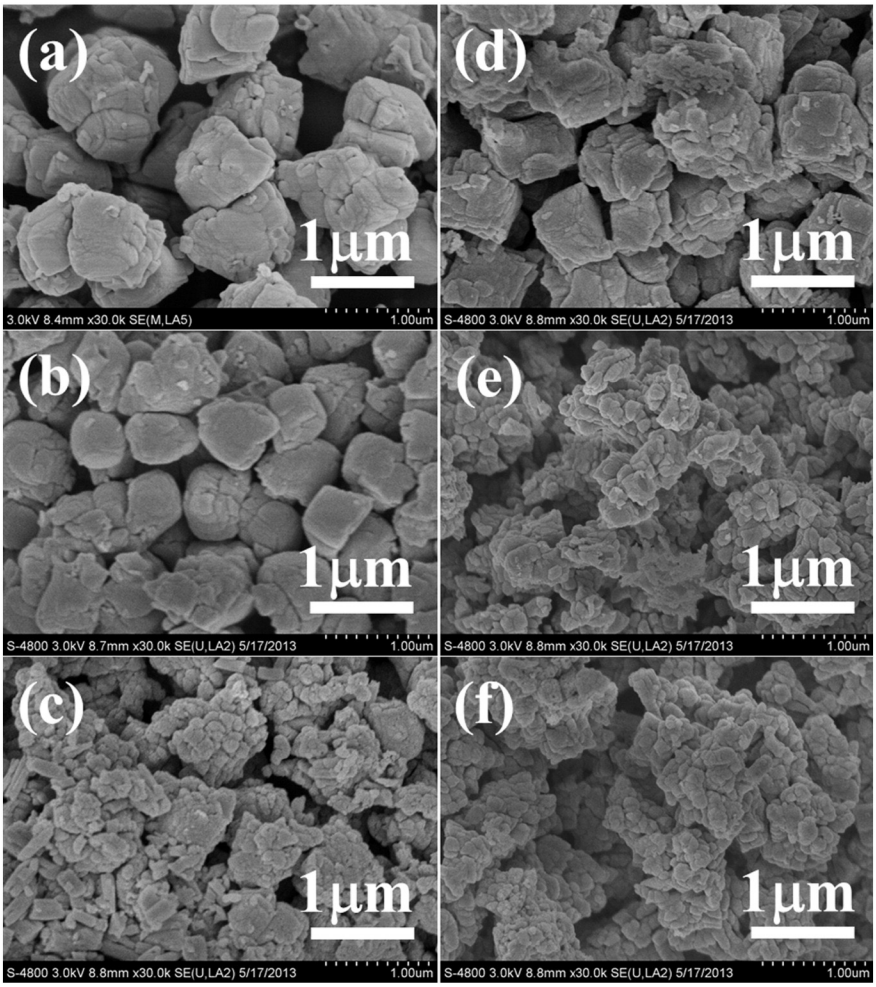


**Fig. 1.** FE-SEM images of BST powders synthesized by (a-c) CHS and (d-f) HTMM with different Ba/Sr ratios: (a) $x = 0.5$; (b) $x = 3.0$; (c) $x = 4.0$; (d) $x = 0.5$; (e) $x = 3.0$; (f) $x = 4.0$.