Journal of Materials Science & Technology xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Materials Science & Technology

journal homepage: www.jmst.org

Recent progress in molten salt synthesis of low-dimensional perovskite oxide nanostructures, structural characterization, properties, and functional applications: A review

Piaojie Xue, Heng Wu, Yao Lu, Xinhua Zhu*

National Laboratory of Solid State Microstructures, School of Physics, Nanjing University, Nanjing 210093, China

ARTICLE INFO

Article history:
Received 11 April 2017
Received in revised form 30 June 2017
Accepted 5 July 2017
Available online xxx

Keywords:
Low-dimensional perovskite nanostructures
Molten salt synthesis
Structural characterization
Physical properties
Functional applications

ABSTRACT

Molten salt synthesis (MSS) method has advantages of the simplicity in the process equipment, versatile and large-scale synthesis, and friendly environment, which provides an excellent approach to synthesize high pure oxide powders with controllable compositions and morphologies. Among these oxides, perovskite oxides with a composition of ABO3 exhibit a broad spectrum of physical properties and functions (e.g. ferroelectric, piezoelectric, magnetic, photovoltaic and photocatalytic properties). The downscaling of the spatial geometry of perovskite oxides into nanometers result in novel properties that are different from the bulk and film counterparts. Recent interest in nanoscience and nanotechnology has led to great efforts focusing on the synthesis of low-dimensional perovskite oxide nanostructures (PONs) to better understand their novel physical properties at nanoscale. Therefore, the low-dimensional PONs such as perovskite nanoparticles, nanowires, nanorods, nanotubes, nanofibers, nanobelts, and two dimensional oxide nanostructures, play an important role in developing the next generation of oxide electronics. In the past few years, much effort has been made on the synthesis of PONs by MSS method and their structural characterizations. The functional applications of PONs are also explored in the fields of storage memory, energy harvesting, and solar energy conversion. This review summarizes the recent progress in the synthesis of low-dimensional PONs by MSS method and its modified ways. Their structural characterization and physical properties are also scrutinized. The potential applications of low-dimensional PONs in different fields such as data memory and storage, energy harvesting, solar energy conversion, are highlighted. Perspectives concerning the future research trends and challenges of low-dimensional PONs are also outlined.

1. Introduction

MSS method is a simple, versatile, and environmental-friendly approach, which has been widely used to synthesize high purity and nanoscale inorganic oxides with controllable compositions and morphologies. In this approach, inorganic molten salt is served as the reaction medium to enhance the reaction rate and to reduce the reaction temperature of the reactant oxides. Thanks to the short diffusion distances and large mobilities of the reactant oxides in the molten salts, the whole solid-state reactions are easily carried out at moderate temperatures (600–800 °C) in a short soaking time (less one hour) [1,2]. Besides the low formation temperature, molten salts also promote to stabilize the specific morphology of the final products [1–3]. Furthermore, the morphology of the final products can be well controlled by adjusting the processing parameters (e.g. the types and quantities of the used molten salts, different reactant oxides, heating temperature and duration, and heating/cooling rates) in the MSS reactions [4–7]. Up to date, a wide range of inorganic oxide materials with tunable morphology has been synthesized by MSS method [8–11]. For examples, perovskite ceramic powders of $BaTiO_3$ [12,13], $BaZrO_3$ [14], $SrTiO_3$ [15], $Ca_{1-x}Sr_xTiO_3$ [16,17], $Pb(ZrTi)O_3$ [18], and lead-based relaxors with a $A(B'B'')O_3$ perovskite structure have been synthesized by the MSS method [1,19–21]. In addition, pristine $BaTiO_3$ nanostructures (including nanowires) with diameters of 50–80 nm and aspect ratios from 1 to over 25, as well as single-crystalline $SrTiO_3$ nanocubes with an average edge length of 80 nm have been synthesized [22]. The evolution of $BaZrO_3$ particle morphology from predominantly cubes to

* Corresponding author.
E-mail address: xhzhu@nju.edu.cn (X. Zhu).

https://doi.org/10.1016/j.jmst.2017.10.005
1005-0302/

a mixture of cubes and spheres and finally to solely spheres is also documented by increasing the annealing/reaction times at selected annealing temperatures [16,17]. Recently, the MSS method has been used to synthesize one-dimensional (1D) perovskite $MTiO_3$ (M = Pb, Ba, Sr elements) nanostripes by using the mixed chlorides (NaCl/KCl = 1:1) as molten salt media [23].

Generally, in the process of MSS method, two fundamental reaction mechanisms are involved during the formation of the final products. The first one is all the reactant oxides are fully dissolved within the molten salt and they diffuse to react in a short time. One model example is the Bi_2WO_6 system [24], in which Bi_2WO_6 particles are formed through complete dissolution of the constituent oxides (WO_3 and Bi_2O_3) in an equimolar mixed KCl-NaCl chlorides heated at 650 °C for 1 h and complete reaction between WO_3 and Bi_2O_3. The second one is that some reactants are much more soluble within the molten salt than the other components, so they diffuse onto the surfaces of the other components and react with them, forming the final products with a similar morphology as the less soluble reactants. A model example is template-free fabrication of pure single-crystalline $BaTiO_3$ nanorods by MSS method at relatively high temperature and large ratios of the salt to the precursors [25]. Since barium oxide has higher solubility in the molten NaCl/KCl salts as compared with the titanium oxide, therefore, much amount of barium oxide is dissolved in the molten salt whereas the insoluble titanium oxide particles have a chance to reunite into rods-like particles in the molten salt environment, acting as templates for further growth. As a consequence, the dissolved barium oxide particles can diffuse to the surfaces of rod-like titanium oxide and react with it *in situ* to form $BaTiO_3$ rod-like nanostructure. Here, the relative dissolution is a key factor in the reaction process, and the morphology of the less soluble reactants is finally inherited during the formation of final products. During the particle growth stage, the total surface areas are reduced, thus, finally the surfaces with high energy disappear, and the morphology of the final product is composed of the crystallographic planes with lowest surface energy, reaching the equilibrium state. Details about the fundamental reaction mechanisms of MSS reactions can be found in the previous reviews [1,5,26].

The main processing stages of the MSS method for synthesis of perovskite oxide powders are schematically illustrated in Fig. 1. At stage I, the reactant oxides and/or other appropriate precursors corresponding to the desired compound are mixed with either the desired salts (e.g., NaCl, KCl) or an eutectic mixture of the salts (e.g., NaCl - KCl, NaOH - KOH, $NaNO_3$ - KNO_3, Na_2SO_4 - K_2SO_4, Li_2SO_4-Na_2SO_4). At stage II, the mixture is heated at a temperature above the melting point of the salt medium to form a molten flux. At this temperature, precursor molecules disperse, dissociate, rearrange, and then diffuse rapidly throughout the salt. At stage III, the product particles start to nucleate and grow up *via* the solution-precipitation process. The characteristics of the product powder are controlled by selecting the temperature and duration of the heating. The reacted mass is cooled to room temperature and washed with an appropriate solvent (water usually used) to remove the salt. The complex perovskite oxide powders can be obtained after drying, and they have several unique characteristics as compared to those obtained by other methods such as solid-state reactions [27,28], combustion synthesis [29,30], and sol-gel method [31,32]. Such unique features are determined mainly by the chemical and crystallographic constraints given by the salts [33,34], which are especially distinguishable in the case of strongly anisotropic perovskite oxides. It is believed that the features are related to the surface and interface energies between the constituents and the salts, resulting in a tendency to minimize the energies by forming a specific morphology. The environments during the development of the morphology of perovskite oxides can be controlled by the

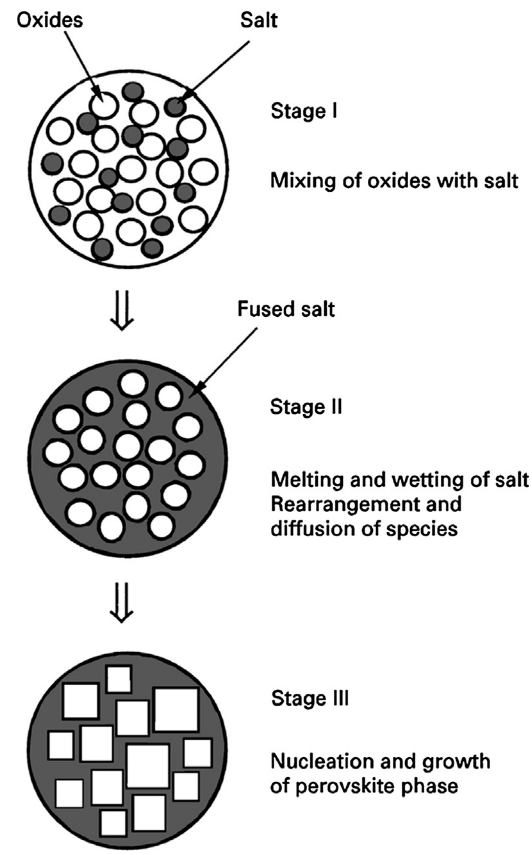

Fig. 1. Schematic illustration of the main processing stages of the MSS method for synthesis of perovskite oxide powders.

selected salts. Therefore, the selection of the molten salts is critical in obtaining desirable powder characteristics.

Nanostructured oxide materials exhibit novel phenomena because of the size effects that appear during the downscaling of the spatial geometry of oxide materials. Compared with the bulk counterparts, nanostructured oxide materials possess some specific surfaces and have lots of surface atoms and higher levels of surface energy. Up to date, nanostructured oxide materials including zero-dimensional (0D), 1D, and two-dimensional (2D) oxide nanostructures, have attracted much attention due to their unique geometries and novel properties, which make them as key building blocks to construct various oxide nanodevices [35–37]. However, it is found that the synthesis of 1D or 2D oxide nanostructures by the traditional MSS method is much difficult due to the nature of equiaxial growth for the oxide particles. To achieve the anisotropic growth of oxide particles in MSS process, selection of suitable templates with specific morphology is crucible to promote the process [39–41]. The template method is an efficient and mild way to prepare pure 1D or 2D oxide nanostructures with controllable morphology at moderate reaction conditions [40–42].

Among the inorganic oxides, perovskite oxides with a composition of ABO_3 are one of the most important functional materials due to their rich physical properties (e.g. dielectric, ferroelectric, piezoelectric, magnetic, multiferroic properties) [35]. Generally, in the ABO_3 perovskite structure A-site is occupied by alkaline earth ions or rare-earth ions, and B-site is occupied by transition metal ions. Many physical properties of perovskite oxides are resulted from B-site cations while tuned by A-site cations [43,44]. Over the past few years, many low-dimensional PONs (e.g. nanoparticles, nanowires, nanorods, nanotubes, nanofibers, nanobelts, and 2D-nanostructures) have been synthesized by MSS method. Their process-structure-property relations are intensively investigated.