Micron 44 (2013) 21–44

Contents lists available at SciVerse ScienceDirect

Micron

journal homepage: www.elsevier.com/locate/micron

Invited review

Microscopical and physical characterization of microwave and microwave-hydrothermal synthesis products

X.H. Zhu*, Q.M. Hang

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

ARTICLE INFO

Article history:
Received 1 May 2012
Received in revised form 7 June 2012
Accepted 8 June 2012

Keywords:
Microwave processing
Microwave-hydrothermal process
Oxides
Nanomaterials
Microscopical and physical characterization

ABSTRACT

Application of microwave energy for materials processing is emerging as an innovative technology with many advantages over the conventional processing, and the rapid progress in this field suggests that microwave material processing (e.g., microwave and microwave-hydrothermal process) will play an outstanding role in the broad field of nanoscience and nanotechnology. This review article gives an up-to-date overview of the current microscopical and physical characterization of the products synthesized by microwave and microwave-hydrothermal process, particularly for oxide nanomaterials because they are indispensable for nanotechnological innovations due to their combinations of infinite variety of structural motifs and properties with manifold morphological features. Basic principles, advantages, and limitations of microwave and microwave-hydrothermal processes are first introduced, and then their recent applications in the synthesis of different classes of functional materials especially for oxide nanomaterials are critically reviewed. Next, the recent progress on the structural and physical characterizations is summarized and discussed. Finally, prospects for future researches within this field are elaborated.

Contents

* Corresponding author. Tel.: +86 25 83592772; fax: +86 25 83595535.
E-mail address: xhzhu@nju.edu.cn (X.H. Zhu).

0968-4328/$ – see front matter
http://dx.doi.org/10.1016/j.micron.2012.06.005

1. Introduction

As one form of electromagnetic energy with the frequency range from 300 MHz to 300 GHz (corresponding the wavelengths from 1 mm to 1 m), microwaves have longer wavelengths and lower available energy quanta than other forms of electromagnetic energy such as visible, ultraviolet or infrared light. In the microwave heating process materials couple with microwaves and absorb the electromagnetic energy volumetrically, transforming them into heat. Therefore, the heat is generated from inside the material, in contrast with the conventional heating where the heat is transferred from outside to inside via heat conduction. Compared with the conventional heating manner, microwave heating has several advantages such as rapid heating rates, reduced processing time, energy efficiency, which provides finer microstructures leading enhanced product quality. In recent years the application of microwave as an energy source in material processing has been extensively investigated, such as in the fields of ceramics, semiconductors, polymeric materials (Chandrasekaran et al., 2011; Oghbaei and Mirzaee, 2010; Agrawal, 2010, 2005, 1998; Clark et al., 2000; Das et al., 2009; Agrawal et al., 2004; Thostenson and Chou, 1999; Clark and Sutton, 1996; Sutton, 1989).

Recently, low-dimensional oxide nanomaterials have attracted much attention due to their distinctive geometries, novel physical and chemical properties, which make them have potential applications in nanodevices (Rørvik et al., 2011; Patzke et al., 2011; Zhu et al., 2010a,b; Zhu, 2009; Bae et al., 2008; Kuchibhatla et al., 2007). For example, oxide nanowires with high aspect ratios, are ideal initial building blocks for fabricating nanodevices, due to their special geometry and anisotropic physical properties. Over the past years hydrothermal process has proven to be effective route for the synthesis of low-dimensional oxide nanomaterials due to their simple and variable setup, low-cost and "green chemistry" features (Patzke et al., 2011; Yoshimura and Byrappa, 2008; Cushing et al., 2004). However, the convenient operation of hydrothermal reactions also has some disadvantages. The most obvious one is its long initial heating period that may result in inhomogeneous temperature profiles within the autoclave. To overcome this problem, microwave is introduced to the hydrothermal processes, to heat the reaction mixture rapidly and homogenously to the desired temperatures. As a consequence, microwave-heating opens up a new option for energy- and cost-saving approaches towards low-dimensional nanomaterials' production (Baghbanzadeh et al., 2011; Bilecka and Niederberger, 2010). In addition, this state-of-the-art technique is also time-saving through dramatically increased crystallization kinetics, and it provides access to novel or otherwise metastable phases. Large number of scientific publications covers this subject, and the literatures are growing too rapidly to cite all the major contributions. In this article, we do not intend to provide an exhaustive overview, instead we focus on overview of the current microscopical and physical characterizations of the selected materials synthesized by microwave and microwave-hydrothermal (M-H) process, particularly for the low-dimensional oxide nanomaterials, because they are invaluable for fabricating nanodevices due to their combinations of infinite variety of structural motifs and properties with manifold morphological features. This review is organized as follows: it begins with a short description of the principles, advantages, and limitations of microwave and M-H processes, and then followed a critical review on their recent applications in the synthesis of different functional materials, especially for low-dimensional oxide nanomaterials. Next, the research progresses on the microstructural and physical characterization of the products synthesized by microwave and M-H processes, are summarized and discussed. Finally, this review elaborates the main benefits of microwave and M-H processes for the synthesis of nanomaterials, and their prospects in the future researches are also presented.

2. Principles of microwave irradiation

2.1. Microwave and M-H process: basic principles

As a novel technology microwave processing of materials can provide the material processor with a powerful and significantly different tool to process materials that may not be amenable to conventional means of processing. In microwave heating, the continuous electromagnetic waves are produced in the magnetron and transmitted through a hollow metallic tube into a resonant cavity where the materials are to be processed (Oghbaei and Mirzaee, 2010; Agrawal, 2010; Clark et al., 2000; Das et al., 2009). Materials are heated due to their molecular frictions caused by alternating polarization of molecules, which involves two main processes, namely dipolar polarization and ionic conduction. Since the electromagnetic radiation can produce an oscillating field, which results in alignments of the dipoles or ions of the samples along the direction of electric field. Due to the time scales of the orientation and disorientation phenomena relative to the frequency of the microwave irradiation, different amounts of heat are produced through the molecular friction and dielectric loss. As the rotation frequencies of many polar molecules in the liquid begin to lag behind the frequency of electric field oscillations, a resistive heating begins to be produced within the medium. This is named as dielectric loss, which is the portion of the energy of an alternating electrical field in a dielectric medium that is converted into heat and lost in the sample. In the case of ionic conduction the dissolved charged particles oscillate back and forth under the influence of the microwave irradiation, collide with neighboring molecules, and thus generate heat. It is important to note that the ionic conduction mechanism represents a much stronger effect than the dipolar polarization with respect to the heat-generating capacity, and this has of course great consequences for the synthesis of nanoparticles in ionic liquids. However, due to the complexity of microwave interactions with materials, in order to heat the sample efficiently in microwave oven, experimental parameters (e.g., irradiation power, reaction temperature and pressure inside the vessel) must be controlled precisely.

Over the past years hydrothermal synthesis as a well-established and promising approach, has been used to synthesize oxide nanomaterials, starting from binary oxides (e.g., ZnO, CuO, MgO, TiO_2, SnO_2) to ternary oxides (e.g., $BaTiO_3$, $PbTiO_3$, $BiFeO_3$, $KNbO_3$), and then to more complex compounds (e.g., $Ba_{1-x}Sr_xTiO_3$, $La_{0.5}Ca_{0.5}MnO_3$, $La_{0.325}Pr_{0.300}Ca_{0.375}MnO_3$) (Patzke et al., 2011). The advantage of this approach is its low synthesized temperature compared with the traditional solid-state and vapor-phase reactions, and also the hydrothermal process gives rise to the crystalline products without any further post-annealing treatment (e.g., calcination required after sol–gel process) (Yoshimura and Byrappa, 2008). However, the conventional heating in hydrothermal process relies on thermal conduction of black-body radiation to drive chemical reactions, whereby the reaction vessel serves as an intermediary for energy transfer from heating source to the solvent, and finally to the reactant molecules. So, this heating manner inevitably suffers from several disadvantages especially at low temperatures, such as the long initial heating period that may result in inhomogeneous temperature profiles within the autoclave and slow reaction kinetics, leading to poor nucleation and broad size distributions of the products. To address the problem of heating inhomogeneity, and to enhance the crystallization kinetics of hydrothermal process, M-H process was developed and coined by Komarneni et al. (1992), which has been received much attention due to its many distinct advantages over the conventional hydrothermal process. For example, in the M-H process, the microwave radiation couples with the reaction mixture, and the electromagnetic energy is converted into thermal energy, which is absorbed by the reaction mixture. Therefore, the heat generated inside the reaction mixture