Journal of Alloys and Compounds 678 (2016) 290–296

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Synthesis and sintering of nano-sized forsterite prepared by short mechanochemical activation process

Mohammad Sadegh Abdi Maghsoudlou [a, *], Touradj Ebadzadeh [b], Zahra Sharafi [a], Marziyeh Arabi [a], Karim Rostami Zahabi [a]

[a] Materials and Metallurgical Department, Engineering Faculty, Malayer University, Malayer, Iran
[b] Ceramic Division, Materials and Energy Research Centre, Alborz, Iran

ARTICLE INFO

Article history:
Received 27 October 2015
Received in revised form
30 January 2016
Accepted 2 February 2016
Available online 10 March 2016

Keywords:
Mechanochemical processing
Nanostructured materials
Oxide materials
Sintering
X-ray diffraction
Microstructure

ABSTRACT

The findings reported in this *paper offer* an affordable technique for the synthesis of nano-sized pure forsterite from magnesium chloride hexahydrate, sodium metasilicate nonahydrate and sodium hydroxide as precursors. The stoichiometric mixture of reagents was manually mixed and subjected to high-energy ball milling for a short time (~10 min). The monitoring of as-milled powder by x-ray diffraction method confirmed that the solid-state displacement reactions occur during high-energy ball milling. After washing and drying, the resulting precursor was subjected to heat treatments in air at various temperatures ranging from 500 to 1100 °C for studying forsterite development. The heat-treated powders were characterized by XRD, STA, FTIR, BET, FE-SEM and TEM techniques. The results revealed that the hydrated compounds formed at room-temperature completely dissociate into periclase and forsterite from 600 °C. The more forsterite phase was generated by the increase of temperature from 600 to 800 °C by the consumption of periclase and amorphous silica present in precursor and finally single-phase forsterite was yielded at 900 °C/2 h. The TEM and FE-SEM results demonstrated that the as-prepared powder consists of separate particles with nearly spherical morphology, 20–60 nm mean particle size and 15.4 m^2/g specific surface area. Sample sintered at 1500 °C/2 h had 89.5% theoretical density and homogeneous single-phase microstructure.

1. Introduction

Bringing materials to the nano-scale can change substantially theirs chemical and physical properties. Therefore, the advanced materials based on such nanoparticles commonly display superior combinations of physical, mechanical, and magnetic properties in comparison with micron-sized materials. These size-dependent properties make nanostructures of various compounds surprisingly valuable for use in structural and device applications in which superior mechanical and physical characteristics are obligatory.

Forsterite (Mg_2SiO_4) is an intermediate compound in the MgO-SiO_2 system, recognized as a technically important material with unique properties owing to high refractoriness (≥1890 °C), low dielectric constant, excellent thermal insulation, low thermal expansion coefficient and good chemical stability [1–4]. Such promising characteristics make forsterite and M-doped forsterite (M = Co, Ni, Cr, Eu) ceramics an appropriate candidate for engineers and designers to use them in the fabrication of numerous technical components such as refractory materials [5,6], dielectric substrates [7,8], solid oxide fuel cells (SOFC) [9,10], optical devices [3,11], pigments [12], biomaterials [1,13,14], composite materials [5,15,16], etc. The most common method for synthesis of this compound is solid-state sintering in which the various mixtures of MgO-SiO_2-bearing compounds such as oxides, hydroxides, carbonates and other chemical compounds powders have been used as the starting precursors. Heating the mixture of raw materials at elevated temperatures (≥1300 °C) in this method is a requisite for yielding forsterite powder and consequently, the majority of powders prepared by solid-state technique lies in micron-sized scale and commonly suffers from agglomeration, low surface area, unreacted particles (free silica and MgO) and impurity phase like $MgSiO_3$ [2,9,10].

In order to solve these problems and prepare high-purity forsterite powders for advanced applications, a wide variety of

* Corresponding author.
E-mail addresses: msabdim@gmail.com, msabdi@malayeru.ac.ir (M.S. Abdi Maghsoudlou).

http://dx.doi.org/10.1016/j.jallcom.2016.02.020
0925-8388/

approaches has been offered by researchers, including sol–gel method [10,12,17–19], geopolymer technique [20], chemical vapor deposition [21], molten salt technique [3], flame spray pyrolysis [11], mechanochemistry and mechanical activation routines with a subsequent heat treatment [9,22–24], etc. Among mentioned methods, mechanochemistry processing is a very popular technique in materials science and engineering and provides numerous benefits for the synthesis of advanced materials because of its simplicity, low-cost process, low agglomeration, the high-proficiency and the applicability to fundamentally all classes of materials [25,26]. In this technique, the final products can be synthesized either directly during mechanical milling or subsequently heat-treatment at low temperatures in compared with the ceramic method [26,27]. The different mixture of raw materials, including zeolite and MgO [9], talc and magnesium carbonate [23] or MgO [28], magnesium carbonate and amorphous silica with and without the presence of mineralizer ion [24,29] and MgO and silica [30] subjected to high-energy ball milling for different milling times to synthesize mechanochemically forsterite powder. Tavangarian et al. [23] indicated that the nano-sized Mg_2SiO_4 powder could be synthesized through long-time milling of reagents ($t \geq 10$ h) encompassing talc ($Mg_3Si_4O_{10}(OH)_2$) and magnesium carbonate ($MgCO_3$) powders followed by a high temperature ($T \geq 1000$ °C) heat treatment. Results published by Fathi et al. [24] demonstrated a combined process of long-term ball milling ($t \geq 10$ h) and subsequent thermal heating (≥1000 °C) is essential for synthesizing nanostructure forsterite from the mixture of amorphous SiO_2 (99.9%) and $MgCO_3$, while the findings of Cheng et al. [30] revealed that 30 h high-energy ball milling is required for converting of $MgO–SiO_2$ mixture into nano-forsterite powder at 850 °C. Although the prolonged high-energy ball milling of initial precursors could be widely used for particle reduction purposes and consequently, for successful synthesis of nano-sized Mg_2SiO_4, this method is not a preferred option for some of the applications because it will wear the milling media rapidly and also result in an increase in production cost and probability of the contaminations in the synthesized powder. The presence of contaminations such as Fe and Cr resulting from milling medium can create problems in impurity-sensitive applications, especially electrical ones. Furthermore, it is generally accepted that powders activated for a long time are prone to grain growth phenomena in compared with non-activated powders at any temperature due to high surface energy.

According to reported works [22,31,32], the use of soft and hydrated precursors that contain the structural water or hydroxyl groups can cause a decline in the milling time and increase in the reactivity and homogeneity of the milled powders rather than a reduction in the particle size during mechanochemical processing. The factors mentioned above can provide new intermediate bounds between particles and subsequently, result in an increase in the occurrence of mechanochemical reactions and consequently the formation of the desired phase occurs at lower temperatures [27]. For instance, the synthesis of forsterite occurred at a low temperature of 900 °C after heat treatment of powder mixtures milled in less than 1 h by the use of soft materials such as $Mg(OH)_2$ (as a source of MgO) and silicic acid (as a source of silica) [22].

So far, little attention has been paid to the effect of short-time high-energy ball milling on the preparation of nanostructured forsterite from soft hydrated materials in literature. Additionally, little data has been published on the features, morphology and sintering behavior of nano-sized forsterite synthesized by using soft materials. Thus, the purpose of the present work is to investigate the synthesis of Mg_2SiO_4 from $MgCl_2.6H_2O$, $Na_2SiO_3.9H_2O$ and NaOH. The mixture of precursors was exposed to high-energy ball milling for 10 min. The characterization of synthesized powders was carried out by means of XRD, FTIR, STA, BET, FESEM and TEM techniques. The sintering behavior of as-prepared forsterite powder was also evaluated. The obtained results revealed that the nano-forsterite powder can be used as suitable nanoparticles for manufacturing advanced components.

2. Experimental procedures

Magnesium chloride hexahydrate ($MgCl_2.6H2O$; 99.9% purity, Merck, Germany), sodium metasilicate nonahydrate ($Na_2SiO_3.9H_2O$; GR grade with 99.9% purity, Shantou Xilong Chemical Co, China) and sodium hydroxide (NaOH; 99.9% purity, Merck, Germany) were used as the starting reagents. These materials were manually blended at the molar ratio of 2:1:2 respectively and then poured into zirconia pots and subjected to high-energy ball milling (Retsch planetary ball mill type PM 400) for a short time (~10 min). The 250 ml Zirconia pots altogether with Zirconia balls with the diameter of 10 mm were used as the milling media. Milling speed and ball to powder weight ratio were fixed at 300 rpm and 10:1, respectively. The as-milled powders was washed by the deionized water for several times to remove the resulted soluble salts. The as-milled and washed powders were dried in an electric oven at 80 °C for 48 h and then identified by x-ray diffraction analysis (X'Pert Pro MPD, Panalytical) with CuKα radiation ($\lambda = 0.154$ nm) in ranging from 10 to 70.

In order to synthesize the forsterite powder, the milled powders were washed and dried and finally exposed to heat treatment at temperature of 500–1100 °C. All runs of synthesis and sintering process in this study were carried out with a ramp rate of 10 °C/min for 2 h in a tube electrical furnace in air atmosphere. The mean crystallite size of obtained forsterite powder was determined by the Scherrer equation (Eq. (1)) [12].

$$D = 0.9\lambda/(\beta\cos(\theta)) \quad (1)$$

Where λ is the wavelength of X-ray radiation (0.15406 nm), θ is the Bragg angle and D is the mean crystallite size in nm and also β is the revised half-width of the diffraction peaks in radians. Four diffraction peaks (031), (131), (211) and (400) and two ones (200) and (220) were considered to determine the mean crystallite size of as-synthesized forsterite and periclase, respectively.

The morphology and particle size of the synthesized powder were exanimated by the use of a transmission electron microscopy (TEM) (EM10C, Zeiss) operating at an acceleration voltage of 80 kV. For TEM observations, the resulted powder was dispersed in ultrapure water by sonication and then was dropped onto a carbon-coated copper grid (200–300 mesh). A Fourier transform infrared spectroscopy (RXI spectrometer, Perkin Elmer) was applied to record the FTIR graph of all samples in the frequency range of 400–4000 cm^{-1}. Thermal analysis of the precursor was accomplished by a thermal analyzer (STA 1640, polymer laboratories). The specific surface area of obtained powder was determined by BET method using the equipment Gemini 2360 of Micrometrics.

In order to evaluate the sinterability of synthesized powder, the powder calcined at 900 °C was grounded into fine powders using mortar and pestle. After mixing of powder with 5 wt.% of a solution containing 8 wt.% PVA as a binder, the mixture was aged for 24 h, passed through a 40-mesh screen to form granules. The granulated powder was pressed at 100 MPa in a steel die with the diameter of 1 cm. The specimens were dried in an electric oven at 110 °C for 48 h, and then fired between 1100 and 1550 °C. The bulk density and porosity of sintered samples were determined by Archimedes' method. Emission scanning electron microscopy (FE-SEM, Tescan, Mira3) was employed for the microstructure examination of the sample sintered at 1500 °C/2 h, which was polished after thermal etching at 1420 °C for 20 min.