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Short communication

Synthesis and characterization of nanocrystalline forsterite through citrate–nitrate route

Ali Saberi [a], Zahra Negahdari [b,*], Babak Alinejad [c], Farhad Golestani-Fard [c]

[a] Department of Material Science and Engineering, Faculty of Mechanical Engineering, University of Tabriz, Tabriz, Iran
[b] Materials Processing, University of Bayreuth, Bayreuth, Germany
[c] Department of Materials Engineering, Iran University of Science & Technology, Tehran, Iran

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Abstract

Nanocrystalline forsterite, Mg_2SiO_4, powder was synthesized according to the citrate–nitrate technique using an aqueous solution of magnesium nitrate, colloidal silica, citric acid, and ammonia. The dried precursor and the powders calcined at different temperatures were characterized by X-ray diffraction (XRD), simultaneous thermal analysis (STA), field emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM). The initial crystallization temperature of forsterite was around 770 °C while fully crystallized forsterite was obtained at 860 °C with a crystallite size of about 30 nm.

Keywords: A. Powders: chemical preparation; B. Electron microscopy; B. X-ray methods; Nanostructures

1. Introduction

Forsterite is a crystalline magnesium silicate with the chemical formula Mg_2SiO_4, named after the German scientist Johann Forster, in the magnesia–silica system which belongs to the group of olivines. The extremely low electrical conductivity of forsterite makes it an ideal material for tunable laser. It shows also good refractoriness due to high melting point (≈1890 °C), low thermal expansion, good chemical stability and excellent insulation properties even at high temperatures, as well [1–4].

Forsterite is widely synthesized via a solid-state reaction method. The high temperature and long reaction time needed, the low chemical homogeneity and large crystallite size of synthesized powder via this technique make solution-based techniques more preferable in the synthesis of forsterite powder. One of these non-conventional techniques is the citrate–nitrate method which has been used to synthesize oxides [5–8].

A redox reaction between nitrate ions as an oxidising agent and citrate ions as a fuel agent liberates the required energy for the synthesis of oxide powders at lower temperatures which results in a powder with a relatively smaller crystallite size [9].

The simplicity of the experimental set-up, cheapness, and good chemical homogeneity of the synthesized powder are the other advantages of this method [10] which form the basis of the present study on the synthesis of nanocrystalline forsterite powder via a citrate–nitrate route.

2. Experimental procedure

Magnesium nitrate ($Mg(NO_3)_2{\cdot}6H_2O$), citric acid ($C_6H_8O_7{\cdot}H_2O$), ammonia solution (NH_4OH, 30%) (all supplied by Merck Co., Germany), and colloidal silica with a particle size smaller than 14 nm (26 wt.% solid fraction, Mitsubishi Monsanto Chemical Co., Japan) were used as starting materials.

To prepare a transparent sol, 0.0142 mol (3.639 g) magnesium nitrate was dissolved in 50 ml distilled water. Then 0.0071 mol (1.642 g) colloidal silica was introduced into the solution to set the MgO/SiO_2 molar ratio to the stoichiometric amount of 2. Afterwards citric acid as the chelating-fuel agent was added to the solution. The molar ratio of citrate to Mg^{2+} cations in the solution was maintained at 1:1. The solution was agitated using a magnetic stirrer at room temperature for 1 h. The pH of the solution was adjusted to 6 by adding ammonia drop-wisely. The sol was heated using a hot plate up to 120 °C to get a viscose yellowish gel. As the sol heats up, the chelating agent, citric acid, binds to the metal

* Corresponding author. Tel.: +49 921 55 7207; fax: +49 921 55 7205.
E-mail address: Zahra.Negahdari@Uni-Bayreuthr.de (Z. Negahdari).

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ions and forms metal–citrate complexes. By further heating polymerization occurs and most of the excess water is removed [9]. Thus the gel was heated at 180 °C in an electric oven to get a brownish mass. The obtained mass, hereinafter referred to as the precursor, was ground into a powder by a pestle and mortar and subsequently heat-treated in an atmospherically controlled furnace at various temperatures for 1 h with a heating rate of 10 °C/min and 50 ml/min dry air flow rate.

Differential scanning calorimetry and thermogravimetric analyses of precursor were carried out using a Netzsch STA-449C with a heating rate of 10 °C/min in a continuous air flow (50 ml/min).

Phase evaluation of the calcined precursor at different temperatures was studied using a Philips (PW-3040) diffractometer with Cu Kα radiation. JCPDS cards 34-0189, 45-0946, and 47-0867 were used for identification of forsterite, periclase, and ammonium nitrate, respectively. The crystallite size was determined using the following Scherrer equation:

$$L = \frac{k\lambda}{\beta(2\theta)\cos\theta_0} \quad (1)$$

where λ is the wavelength of X-ray (=0.15406 nm), θ_0 is the Bragg angle, k is a constant (=0.9), and L is the crystallite size. The half-width of the diffraction line β (in radians for 2θ) was taken as the experimental half-width (β_{exp}) and corrected for experimental broading (β_{instr}) according to the following equation [11]:

$$\beta(2\theta) = (\beta_{exp}^2 - \beta_{instr}^2)^{1/2} \quad (2)$$

β_{instr} was measured experimentally using a silicon sample.

Further, a field emission scanning electron microscope (LEO® 1530, FE-SEM) and transmission electron microscope (LIBRA® 200, TEM) were used for microstructural observations. Specific surface area of the synthesized powder was measured by a Micromeritics ASAP 2010 instrument according to the BET technique.

3. Results and discussion

The simultaneous thermal analysis (DSC–TG) of the precursor is shown in Fig. 1. The small endothermic peak at 110 °C in the DSC plot accounted for 9 wt.% of the initial weight loss in the TG, is assigned to the dehydration of the precursor. Although it has been dried at 180 °C the presence of the water in large quantities is due to the hygroscopic nature of the dried precursor which causes absorbing water vapor present in the atmosphere during the storage period. An outstanding and sharp exothermic peak observed at about 250 °C with a corresponding 45 wt.% weight loss is due to the explosive decomposition of ammonium nitrate as well as the combustion of citrates. According to the literature [12–14], ammonium nitrate which has been formed by the reaction of ammonium cations (NH_4^+) with nitrates (NO_3^-) during the preparation of the sol as an oxidising agent participates in a redox reaction with citrate ions as a reductant. During the redox reaction, ammonium nitrate is mainly decomposed and the reactions of ammonium nitrate decomposition are accompanied with heat generation (exothermic reactions). The liberated heat (enthalpy) decreases the synthesis temperature of forsterite. The second exothermic peak (360 °C) may be caused by the formation of periclase. The third exothermic peak in the temperature range of 450–550 °C is due to the oxidation of carbonaceous residues. Further heating produces a small and broad exothermic peak around 760 °C, which corresponds to the crystallization of forsterite.

The X-ray diffraction (XRD) patterns of the precursor and the calcined powders are shown in Fig. 2. According to the XRD results, the precursor is a mixture of an amorphous matrix and crystalline ammonium nitrate (NH_4NO_3) (Fig. 2a). The XRD pattern shows disappearance of the related peaks to ammonium nitrate and formation of periclase (MgO) at 360 °C. Forsterite has been formed above 770 °C according to heterogeneous reaction between periclase and amorphous silica provided by colloidal silica. Up to 800 °C, apart from the forsterite related peaks, periclase reflections can be detected in samples. As the temperature rises from 800 to 860 °C, the intensity of forsterite lines increases, the intensity of periclase lines decreases and forsterite is developed completely at 860 °C. Based on experimental observations [15], the crystallization of the amorphous silica occurs at temperatures above 900 °C. Since the highest temperature for

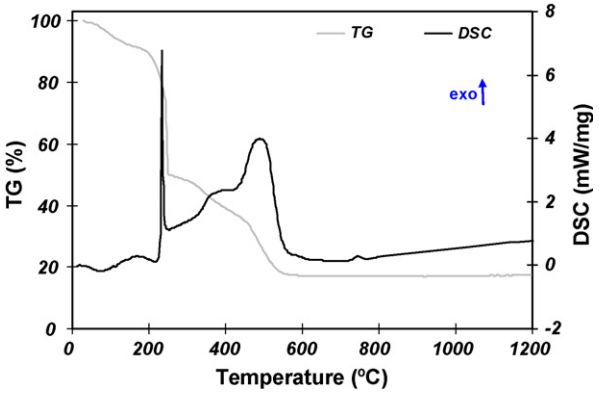

Fig. 1. DSC–TG curves of forsterite precursor (dry air flow = 50 ml/min, heating rate = 10 °C/min).

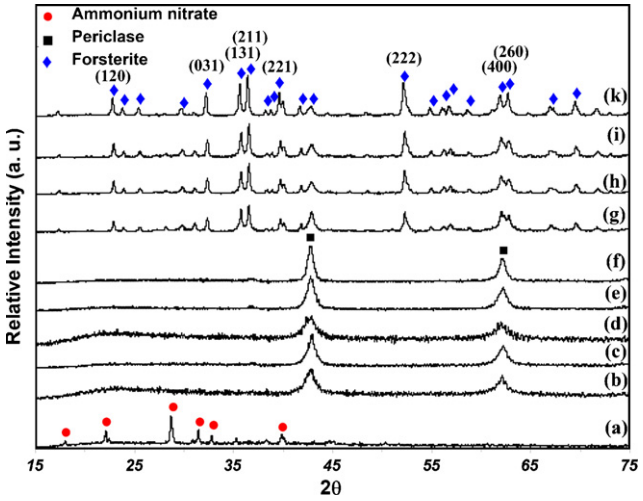

Fig. 2. X-ray diffraction patterns of the precursor (a) and the calcined precursor at different temperatures for 1 h, 360 °C (b), 480 °C (c), 530 °C (d), 650 °C (e), 750 °C (f), 775 °C (g), 800 °C (h), 830 °C (i), and 860 °C (k).

Table 1
The approximate crystallite size, D, of the forsterite powder calcined at different temperatures for 1 h.

T (°C)	d_{211} (Å)	D (nm)	d_{120} (Å)	D (nm)	d_{400} (Å)	D (nm)
775	2.453	15	3.874	17	1.493	14
800	2.454	18	3.876	21	1.494	16
830	2.454	22	3.876	25	1.495	21
860	2.456	27	3.881	31	1.497	26

formation of forsterite is 860 °C, the β-cristobalite crystalline phase will not be developed and detected beside periclase during phase transformation sequences of forsterite formation.

Table 1 presents the approximate crystallite size and characteristics of the forsterite powders calcined at different temperatures. Three diffraction peaks (2 1 1), (1 2 0), and (4 0 0) were chosen to measure the crystallite size. As the calcination temperature was increased, a gradual increase in peak intensities accompanied by sharpening of the peaks was observed, which indicates the crystallite size of forsterite was rising. The average crystallite size of calcined forsterite at 860 °C is in the range of 27–30 nm.

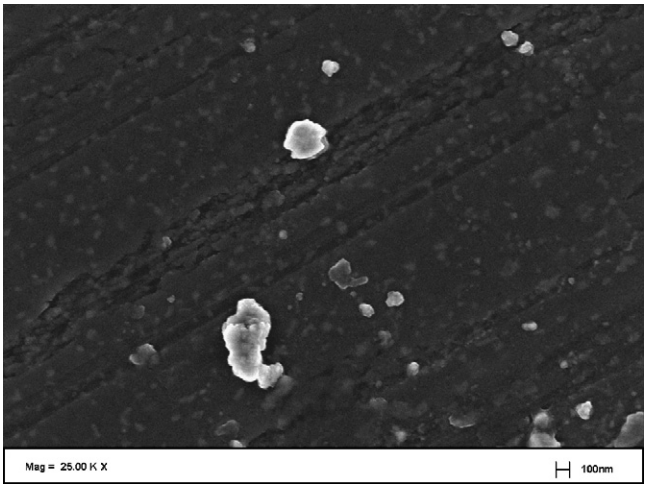

Fig. 3. FE-SEM micrograph of forsterite powder synthesized at 860 °C.

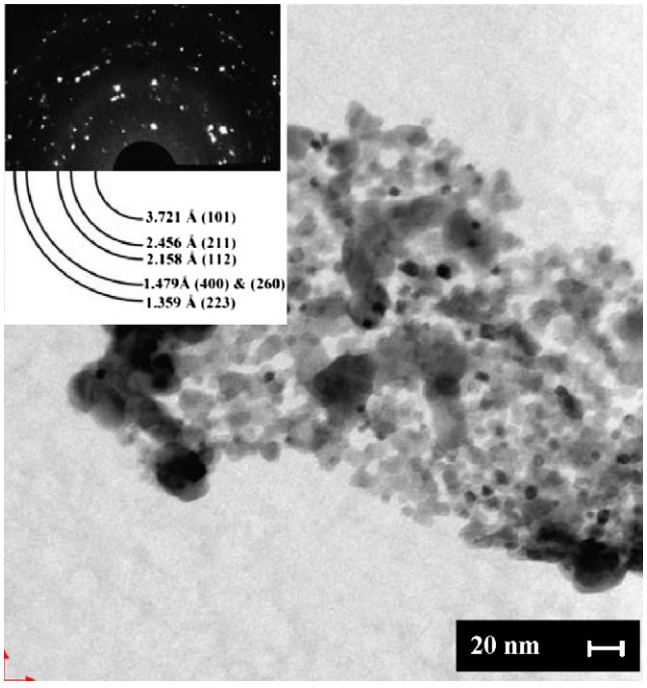

Fig. 4. Bright field TEM micrograph and SAED pattern of Mg_2SiO_4 forsterite powder calcined at 860 °C.

A FE-SEM micrograph (Fig. 3) shows the morphology of the calcined powder at 860 °C. In spite of partial agglomeration, the size of agglomerated powder is in the range of 50–300 nm. Forsterite powder resulting from the combustion reactions was characterized by TEM, as well (Fig. 4). The bright field TEM image and selected area electron diffraction (SAED) pattern of synthesized powder at 860 °C show that the synthesized forsterite is polycrystalline with a crystallite size distribution in the range of 18–30 nm. The synthesized powder has irregular shapes with a bimodal nanocrystallite size distribution which is due to a multi-step decomposition of the precursor with the citrate to Mg^{2+} molar ratio of 1:1 during auto-ignition [16]. The specific surface area of synthesized powder at 860 °C is 14.95 m^2/g.

4. Conclusion

Nanocrystalline forsterite (Mg_2SiO_4) was synthesized by an auto-ignition process using magnesium nitrate, colloidal silica, citric acid, and ammonia at relatively low temperatures. The initial crystallization temperature of Mg_2SiO_4 was 770 °C, whereas fully crystallized forsterite was obtained at temperatures above 860 °C. The crystallite size of powder calcined at 860 °C was in the range of 27–30 nm, and its agglomerated particle size was smaller than 300 nm.

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