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Synthesis and characterization of crystalline nanosized MgF_2 powder via microemulsion route

Ali Saberi *, Zahra Negahdari, Sofiane Bouazza, Monika Willert-Porada

Chair of Materials Processing, Faculty of Engineering Science, University of Bayreuth, 95440 Bayreuth, Germany

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ABSTRACT

Nanosized MgF_2 was synthesized by precipitation in microemulsions of water in cyclohexane stabilized by polyethylene glycol tert-octylphenyl ether. The synthesized MgF_2 powder was characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), BET specific surface area, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), and X-ray diffraction (XRD). The results showed that the synthesized powder was a MgF_2 powder with a crystallite size in the range of 9–11 nm and a specific surface area of 190 m^2/g.

1. Introduction

Metal fluoride nanoparticles (i.e., powders with a particle diameter smaller than 100 nm) have received intense research attention during the past few years because of their potential applications in optics, optoelectronics, biological labelling, catalysis fields, etc. [1–4]. Magnesium (II) fluoride (MgF_2) is one of the most interesting metal fluorides due to its low chemical reactivity even at elevated temperatures, low refractive index (1.38), high corrosion resistance, high thermal stability, and significant hardness [5–8]. MgF_2 has a rutile structure where Mg^{2+} ions are surrounded by six F^- ions and each F^- ion by three Mg^{2+} ions [9]. It has been extensively used as an antireflective and protective coating on glass optics because of its low refractive index. In addition, due to the large band gap of MgF_2 (about 12.8 eV), it can be used as a promising UV transparent material [10–12]. Also since it possesses a relatively chemically inert surface and hosts Lewis acidic centers on its surface, MgF_2 is widely used as a catalyst support [4,9].

The traditional approaches to synthesize metal fluorides are thermal decomposition and fluorination of adequate starting substances with reactive fluorinating agents at elevated temperatures. The synthesized metal fluorides via these techniques have large particle size and low specific surface area (<100 m^2/g) [13,14]. Recently synthesis of nanosized MgF_2 on the basis of soft chemical methods has been investigated. Murthy et al. [15] applied sol–gel fluorination process to synthesize an amorphous MgF_2 with a high surface area in the range of 150–350 m^2/g for catalytic applications. Herein an amorphous MgF_2 formed from the reaction between $Mg(OCH_3)_2$ and HF in a non-aqueous solvent (MeOH or ether). The obtained powder had carbonaceous residue and needed further fluorination with N_2-diluted gaseous HF or CCl_2F_2 or $CHClF_2$ at 250 °C to obtain a fine white MgF_2 powder [8,15]. Later on, Krüger et al. [16] used the non-aqueous sol–gel technique [15] as a simple and cheap procedure instead of the common PVD method which requires high temperatures and corrosive gases such as HF and F_2 to develop a low refractive index MgF_2 film on a glass substrate by means of spin coating at temperatures as low as 300 °C. Sermon and Badheka [17] synthesized a MgF_2 xerogel with a BET surface area about 820 m^2/g via reaction of magnesium methoxide ($Mg(OCH_3)_2$ with methanolic solution of HF in a N_2 glovebox. XPS characterization showed that the presence of carbon and oxygen in the xerogel resulted from residue organics and also a lower surface atomic Mg:F ratio than the stoichiometric MgF_2 (1:1.4). Although the aforementioned attempts are based on the non-aqueous sol–gel method which results in mainly amorphous MgF_2 with high surface area, high-temperature processing, further purification and fluorination with gaseous HF and specific synthetic equipment are required in most cases, which restrict their application. Amorphous MgF_2 with high surface area is suitable as a support of catalytically active phases. Other researchers have tried to synthesize nanosized crystalline MgF_2 powders via precipitation route which has the potential to be used as a unique matrix for optical applications.

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* Corresponding author. Tel.: +49 0921 557207; fax: +49 0921 557205.
E-mail addresses: Ali.Saberi@Uni-Bayreuth.de, Ali_Saberi@yahoo.com (A. Saberi).

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Sevonkaev and Matijevi [18] synthesized MgF_2 with different morphologies (cubic, prismatic, platelet-like, and spherical) by precipitation in aqueous solutions of NaF and $MgCl_2$ at 80 °C at different pHs. The prepared MgF_2 had a particle size in the range of 50–100 nm. Nandiyanto et al. [12] also followed the previous method and could change the shape and the size of particles by varying the molar ratio of $MgCl_2$ to NH_4F to obtain either an amorphous nanosized MgF_2 with cubic morphology at a size of 6 nm or a crystalline one at a size of 100–300 nm. Skapin et al. [13] synthesized partially crystalline MgF_2 with a medium range surface area of 70 m^2/g via oxidative decomposition of magnesium nitrate hydrate, $Mg(NO_3)_2{\cdot}2H_2O$, with F_2 in liquid HF. Despite the fact that the synthesis of MgF_2 via direct precipitation from aqueous solution is more suitable for scaling up, the obtained powder has bigger crystallites. Wu et al. [19] expressed that the crystallite size of synthesized metal fluoride is mainly controlled by the solubility product constant ($K_{sp,0}$). According to the solubility product constant of MgF_2 ($K_{sp,0} = 6.5 \times 10^{-9}$), the crystallite size in the range of 30–100 nm for synthesized MgF_2 via the direct precipitation method has been predicted. Therefore it is necessary to confine the growth space to synthesize nanosized MgF_2 via precipitation route.

The aim of this study was the synthesis of a crystalline nanosized MgF_2 via the reaction of magnesium salt and aqueous HF in inverse micelles (water-in-oil inverse microemulsion) at relatively low temperatures.

2. Experimental procedures

All reagent materials were used without further purification. Magnesium nitrate (99.9%, $Mg(NO_3)_2{\cdot}6H_2O$), Triton X-100 (polyethylene glycol tert-octylphenyl ether, MW. 625), cyclohexane (≥99%, C_6H_{12}), 1-hexanol (≥99%, $C_6H_{14}O$), and aqueous hydrofluoric acid (≥40%, HF) were purchased from Sigma–Aldrich Chemical Co. In a typical synthesis, 24 mmol of Triton X-100 and 48 mmol of 1-hexanol were added to a reaction vessel, a 250 ml PTFE round bottom flask containing 1.8 mol of cyclohexane. The mixture was stirred at 40 °C for 30 min. Triton X-100 and 1-hexanol were respectively chosen as the surfactant and co-surfactant. The basic concept of the microemulsion process is dispersion of the water phase as tiny drops into the oil phase using a surfactant and a co-surfactant in order to confine the growth of particles precipitating within [20]. In addition, 64 mmol of $Mg(NO_3)_2{\cdot}6H_2O$ was separately dissolved in 0.5 mol of distilled water and added to the previous solution while stirring. After 30 min mixing, 128 mmol of 40% HF aqueous solution was introduced drop-wise into the respective solution. The resulting microemulsion solution was stirred vigorously at 80 °C under reflux for 3 h on a magnetic hot plate stirrer. The resulting opaque suspension was allowed to cool down to room temperature and subsequently washed using centrifugation at 3000 rpm for 20 min for several times with a mixture of water and methanol (volume ratio of 1:1) to remove non-polar solvent and surfactants. Due to non agglomeration of synthesized particles or the small difference in reflective indexes of the synthesized particles and the media (H_2O/methanol mixture), the obtained solution was clear. Afterward the clear solution was dried at 80 °C for 24 h in atmospheric condition and subsequently for 6 h at 50 mbar. While drying, the solution changed to a transparent colorless soft agglomerated mass. The mass was easily ground using an agate pestle and mortar to a fine white powder and characterized with a Philips (PW-3040) X-ray diffractometer (XRD) with Cu-K_α radiation. JCPDF card No. 006-0290 was used as a reference for the identification of MgF_2. The crystallite size was determined by Rietveld refinement [21] and using PANalytical X'Pert HighScore Plus software version 2.2.0. A field emission scanning electron microscope (LEO® 1530, FE-SEM) and transmission electron microscope (Zeiss CEM 902, TEM) were utilized to determine the particle morphology and to assess the size of the primary particles and the nature/extent of aggregation. Attenuated total reflection (ATR) investigation was carried out using a using a Bruker Vertex 70 FTIR spectrometer equipped with a diamond crystal Harrick MVP-Pro^{TM} accessory. The spectrum was recorded in attenuated total reflection between 4000 and 400 cm^{-1} with a spectral resolution of 2 cm^{-1}.

3. Results and discussion

The product of synthesis resembled transparent agglomerates after drying. These millimetre-sized agglomerates were absolutely ground to a fine, white powder. The XRD pattern of the synthesized powder is illustrated in Fig. 1. The XRD pattern corresponds to MgF_2 and confirms the obtained powder was crystalline. The width of the peaks corresponds to the small particle size. The crystallite size of magnesium fluoride powder determined from Rietveld refinement was about 8.6 nm, where R_{exp} (R expected), R_{wp} (R weighted pattern), and S (goodness of fit) were respectively 3.29, 4.22, and 1.28. The goodness-of-fit value (S) of 1.3 or less is usually considered to be quite satisfactory [22,23].

The morphology and particle size of the synthesized magnesium fluoride were examined by FE-SEM (Fig. 2). The SEM micrograph indicated that the synthesized powder had a spherical morphology with a particle size smaller than 12 nm. A mono-size distribution of the particles confirms mono-size formation of micelles in cyclohexane while processing.

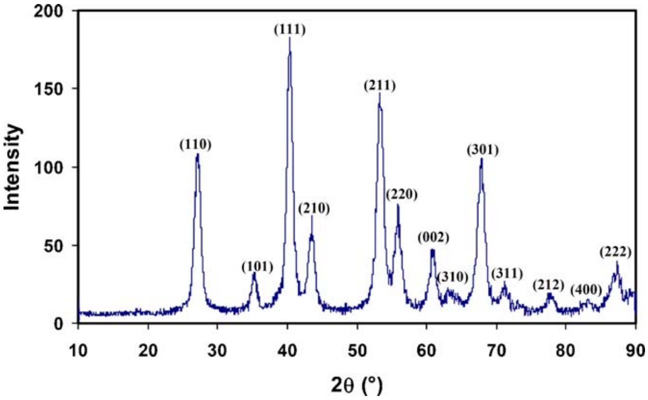

Fig. 1. XRD pattern of synthesized magnesium fluoride.

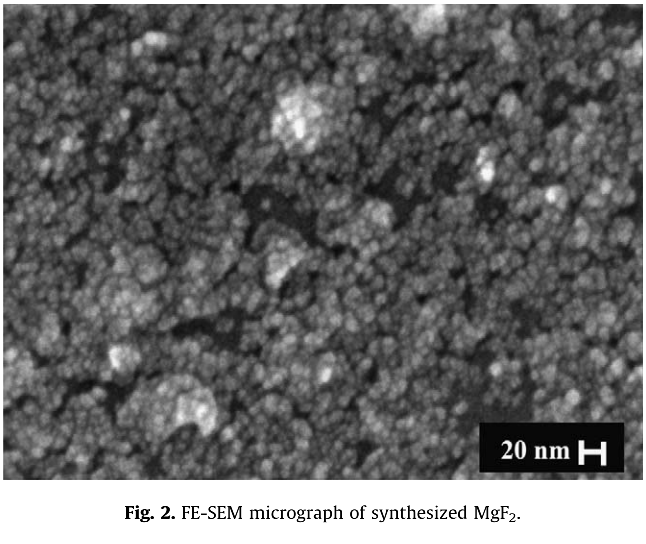

Fig. 2. FE-SEM micrograph of synthesized MgF_2.

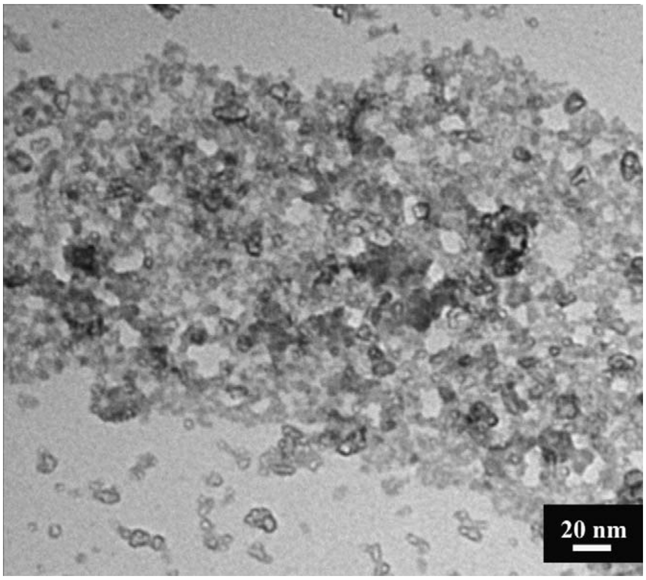

Fig. 3. BF-TEM micrograph of synthesized MgF_2.

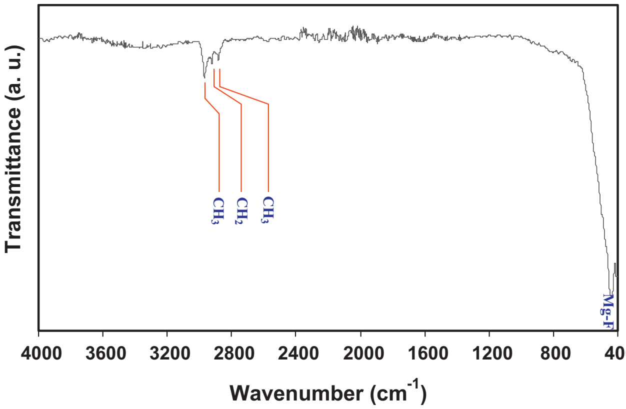

Fig. 4. ATR-FTIR spectrum of synthesized MgF_2.

Fig. 3 shows a bright field TEM (BF-TEM) image of the synthesized MgF_2 particles. The TEM micrograph depicted that the most of the non-agglomerated particles were single crystals with a crystallite size in the range of 9–11 nm. The size and morphology of particles were in good agreement with the XRD and SEM results. The microscopic observations proved that the microemulsion method could successfully confine the growth of precipitated MgF_2 particles within the tiny water drops in the oil phase.

Although the synthesized MgF_2 was a white powder, its purity was further examined by means of FT-IR spectrometry. The peak at 432 cm^{-1} in the FT-IR spectrum in Fig. 4 was assigned to the Mg–F stretching vibration of MgF_2. Other researchers have assigned a broader band at 435 cm^{-1} to the stretching vibration of Mg–F [24,25]. Although the synthesized MgF_2 was washed several times with the mixture of methanol and water, the characteristic bands of the remaining surfactant groups were observed in the FT-IR spectrum. The 2964, 2920 and 2880 cm^{-1} transmission bands were assigned to the asymmetric stretching vibrations of $-CH_3$ and $-CH_2$, and the symmetric stretching vibrations of $-CH_3$ groups from the residue surfactant, respectively. Despite the fact that the applied procedure was capable of synthesizing nanosized crystalline MgF_2 powder, the synthesized powder had a trace amount of organic residue (Triton X-100). The residue surfactant might be beneficial for better dispersion of the synthesized powder in aqueous media.

BET results showed that the synthesized powder had a specific surface area of 190 m^2/g, which was significantly higher than those of the crystalline MgF_2 powders reported by Wojciechowska et al. (1–44 m^2/g) [9]. The specific surface area of the synthesized crystalline powder is comparable with that of the amorphous MgF_2 powders synthesized via a sol–gel route (150–350 m^2/g) [15].

4. Conclusions

A crystalline magnesium fluoride powder with spherical morphology was successfully synthesized via microemulsion route at 80 °C. The synthesized MgF_2 was a partially agglomerated powder with crystallite size smaller than 11 nm. The specific surface area of the synthesized MgF_2 was about 190 m^2/g. The synthesized MgF_2 powder has the potential to be used as a proper matrix for up- and down-conversion applications.

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