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Research Article

Rapid Synthesis of Dittmarite by Microwave-Assisted Hydrothermal Method

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Dittmarite was obtained using MgO and $(NH_4)_2HPO_4$ as raw materials via microwave-assisted hydrothermal method for 3 min at 120°C. The resulting samples were investigated by X-ray powder diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy, and thermogravimetry-differential thermal analysis. The results indicate that dittmarite can be rapidly synthesized by microwave-assisted hydrothermal method. With higher temperature and longer reaction time, highly crystallized dittmarite can be obtained. Pure dittmarite can be synthesized for 3 min at 120°C, which is faster than with the use of any other reported methods.

1. Introduction

Dittmarite was first discovered at Skipton Caves by MacIvor in Australia [1]. The mineral has gained interest because of its strongly defined layered crystal structures. Many researchers have studied a series of compounds, $M_IM_{II}PO_4 \cdot H_2O$ (M_I = NH_4, K; M_{II} = Mn, Fe, Co, Ni), related to dittmarite for their synthesis [2] and application in shape-selective redox catalysts, ionic exchange, ionic conductivity, magnetic properties, and so on [3–6].

The present study focuses on the rapid synthesis of pure dittmarite via microwave-assisted hydrothermal method. MgO was used as the source of magnesium and $(NH_4)_2HPO_4$ was used as the source of phosphate and ammonium. The phases of the samples were identified by X-ray powder diffraction (XRD). The microstructure, infrared spectrum, and thermal properties of the samples were measured by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy, and thermogravimetry-differential thermal analysis (TG-DTA), respectively.

2. Experiment

The $MgNH_4PO_4 \cdot H_2O$ compound was prepared by a microwave-assisted hydrothermal method using Ethos A (Milestone, Italy). Analytical reagents MgO and $(NH_4)_2HPO_4$ were added in a half-filled Teflon container, keeping the solution pH by adding KOH at approximately 8. The solutions were microwaved for 3, 5, and 10 min at 50, 80, and 120°C. The resulting precipitate was separated by filtration, washed with deionized water and ethanol, and then dried for 24 h at 80°C.

The as-prepared samples were identified by XRD analysis on D/max-RB diffractometer (Rigaku, Japan) using CuKα radiation (λ = 1.5418 Å) in the 2θ range of 5° to 70°. Differential thermal analysis and thermogravimetry were traced using STA 449 C Jupiter (NETZSCH, Germany). Using TM-1000 (HITACHI, Japan), the SEM images of the samples were visualized. The infrared absorption spectrum of the sample was measured by a Thermo Scientific Nicolet 380 FT-IR spectrometer (Thermo Fisher Scientific, USA).

3. Results and Discussion

Figure 1 shows the powder XRD patterns of the synthetic samples with various temperatures and reaction times. Figure 1(a) illustrates the XRD patterns of samples prepared under 50°C for 3, 5, and 10 min. The main phase is MgO, but many reflections with lower intensity which represent

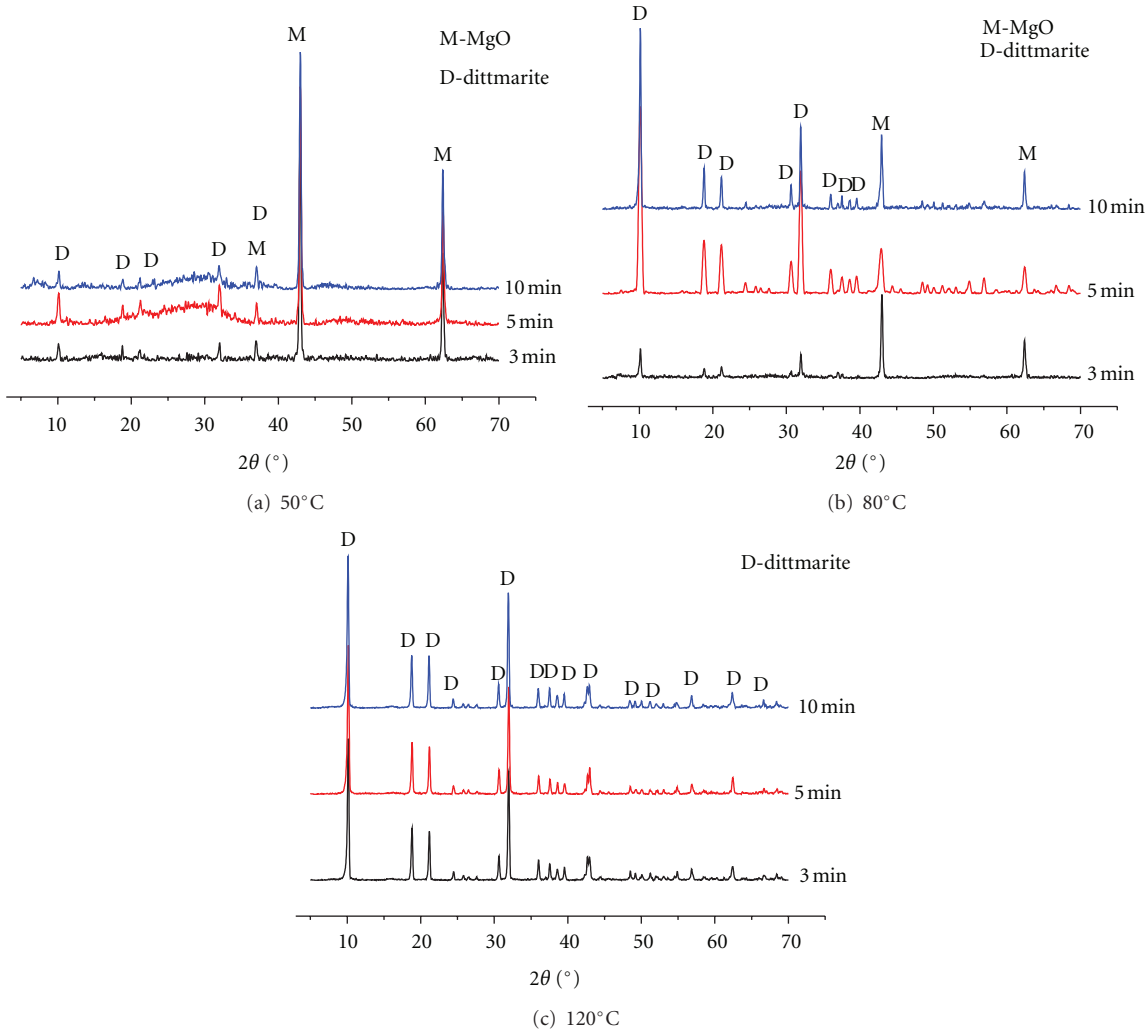

Figure 1: XRD patterns of the samples.

dittmarite can also be found. In Figure 1(b), dittmarite and MgO still coexist in the samples, but the peak intensity of dittmarite increases with longer reaction times. Meanwhile, the peak intensity of MgO decreases with longer reaction times. The XRD patterns shown in Figure 1(c) match closely with the published pattern for dittmarite (JCPDF 36-1491). Thus, they are considered as single-phase materials. This result indicates that dittmarite can be easily synthesized by microwave-assisted hydrothermal method under 120°C within a 3 min reaction time.

The SEM micrograph of dittmarite is shown in Figure 2. The sample is mainly composed of plate-like dittmarite. The particles of dittmarite are in agglomeration state with a flower-like shape, the result is similar with the SEM morphgraph of dittmarite-type compound $KMnPO_4 \cdot H_2O$ prepared by Koleva et al. [7].

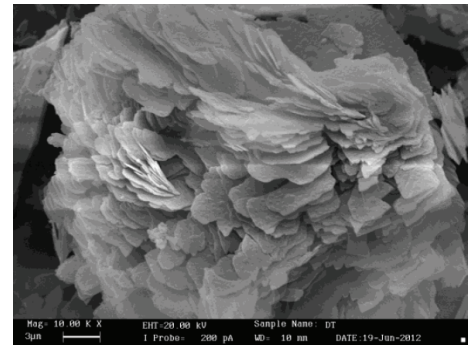

Figure 2: SEM morphgraph of dittmarite.

The FT-IR absorption spectrum for dittmarite is shown in Figure 3. The phosphate ion vibrations are at about 1,061, 979, and 576 cm^{-1}. All the bands between 3250 and 2400 cm^{-1} belong to the NH_4^+ stretching modes The bands at 3500 and 1641 cm^{-1} appear as a result of the stretching and bending H_2O vibrations, respectively, and around 1470 cm^{-1} belong to the NH_4^+ bending vibrations. The H_2O bending mode band is expected to appear at ~1500 cm^{-1} whereas the vibration at 633 cm^{-1} represents the Mg–O bond. This spectrum is in accordance with previous studies [8–10].

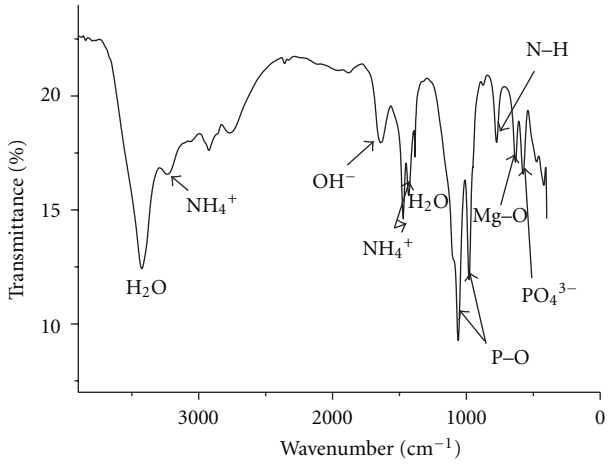

Figure 3: FT-IR spectrum of the as-prepared dittmarite.

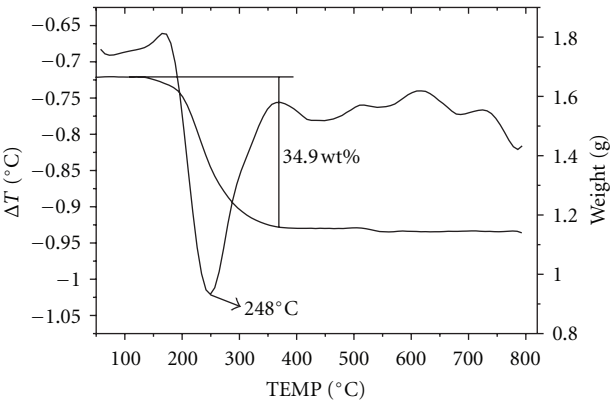

Figure 4: TG-DTA curves for the as-prepared dittmarite.

The TG and DTA curves of the obtained dittmarite at a rate of 10°C/min from ambient temperature to 800°C are presented in Figure 4. The thermal decomposition study shows the endothermic steps in the temperature range from 165°C to 370°C, and the experiment value is 34.9 wt%, which corresponds to the mass loss of water and ammonia molecules present in the structure.

Based on the above results, the formation mechanism of dittmarite can be discussed as follows. Due to heating by microwave irradiation, the samples result in homogeneous nucleation within a very short time and the nucleation and crystal growth occur simultaneously. For the past few years, many researchers have posited that the kinetics of material synthesis may be significantly accelerated using microwave-assisted hydrothermal methods [11–14]. In the current study, the rapid synthesis of dittmarite by microwave-assisted hydrothermal methods was found to have the potential for saving energy and cost of production.

4. Conclusions

In the current paper, dittmarite was rapidly synthesized by microwave-assisted hydrothermal methods at 120°C for 3 min using MgO and $(NH_4)_2HPO_4$ as raw materials. Microwave irradiation can significantly accelerate the reaction. The anticipated materials can be prepared at lower temperature and shorter reaction time using microwave heating.

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