Sonochemical Synthesis of Dolomite from Removed-K Bittern for Color-Tunable Phosphor Applications

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Abstract

This study determines a method for the synthesis of carbonates from removed-K bitterns using ultrasonic cavitation. The results suggest that dolomite (CaMg(CO₃)₂) nanoparticles can be easily synthesized by irradiating ultrasonic waves for 20 min using a removed-K bittern adjusted to a Ca/Mg molar ratio of 0.5. In addition, the immersion method was used to convert dolomite, which emits green or red light, into a phosphor. By changing the mixing ratio of the green- and red-emitting phosphor, it was possible to produce dolomite phosphors with control over emission colors such as green, yellow-green, yellow, orange, and red. These phosphors can be applied as guide lights and interior lights.

Key Words: Sonochemistry, Dolomite, Phosphor, Removed-K bittern, Nanoparticles

1. Introduction

More than 99.9% of the total dissolved salt content in seawater comprise anions, such as chloride, sulfate, bicarbonate, bromide, boric acid, and fluoride, as well as cations such as sodium, magnesium, calcium, potassium, and strontium. Most cations in seawater are constituent elements of functional ceramic materials. In addition, these ceramics may be synthesized using seawater as a source of raw materials. For instance, as calcium-based materials, limestone (calcium carbonate) and gypsum (calcium sulfate) are used as infrastructure materials. Moreover, they are also used as biomaterials (calcium phosphate) or functional materials (calcium silicate). These materials would be beneficial for a wide range of industrial applications. Manufacture of useful materials from seawater is possible. This study proposes a novel method for the synthesis of inorganic materials from seawater. The hydrothermal reactions commonly used for synthesizing functional ceramic materials require unfavorable reaction conditions, such as high temperatures and pressures, and long reaction times. Some ceramic materials from seawater derivatives using hydrothermal reactions have been reported. However, these materials can be easily synthesized in a short span using ultrasonic cavitation generated by irradiating a liquid, such as water with waves of frequency 20 kHz or higher. Chemical reactions (hot spots) in extreme conditions, such as high temperature and pressure, and high-speed agitation, are instantaneously caused by the crushing of minute bubbles generated in the solution.

There are reports on the synthesis of simple and composite oxides using the sonochemical method. Moreover, some materials with sonochemical synthesis have been reported. The synthesis of functional materials by ultrasonic irradiation was considered using seawater as a source of raw material. We focused on using double salt, dolomite (CaMg(CO₃)₂) in which calcium carbonate (CaCO₃) and magnesium carbonate (MgCO₃) are often combined in a molar ratio of 1:1. Fig. 1 shows Local crystal structure of dolomite. (Blue circle: Ca, Orange circle: Mg, Red circle: O, Brown circle: C)
conventional hydrothermal synthesis says that calcium ions (blue) in the calcite structure of calcium carbonate are replaced with magnesium ions (orange) as shown in Fig. 1, and dolomite was formed via an intermediate called magnesium calcite. In general, double salts have better physical and chemical properties than single salts and solid solutions. CaMg(CO₃)₂ has a higher density, hardness, and refractive index than simple calcite salts. However, natural dolomites commonly produced worldwide are not composed of Ca/Mg in a molar ratio of 1:1; moreover, they contain small amounts of oxides such as SiO₂, Fe₂O₃, and Al₂O₃ as impurities. Therefore, a synthetic method to prepare dolomite with high purity and enhanced functionality is strongly desired. In this study, we demonstrated a method to produce dolomite from removed-K bitterns using ultrasonic cavitation and investigated its application as an inorganic phosphor material.

2. Experimental procedure

2.1 Manufacturing removed-K bittern

The removed-K bittern used as a raw material in this study was provided by a salt manufacturing corporation in Japan. In the Japanese salt manufacturing process, brine is obtained by concentrating seawater using an electrodialysis membrane. Thereafter, NaCl is extracted from brine by evaporative crystallization. The NaCl-extracted brine then undergoes cooling crystallization to separate KCl; this KCl-extracted brine is known as removed-K bittern. The concentrations of the main components in the removed-K bittern (Table 1) are 2100, 1100, and 670 mmol·dm⁻³ for Mg²⁺, Na⁺, and Ca²⁺, respectively.

2.2 Sonochemical synthesis of CaMg(CO₃)₂ using removed-K bittern

Aqueous solutions of 1.3 mol·dm⁻³ sodium carbonate (99.8 %, Kanto Chemical Co., Inc., Japan) and 0.8 mol·dm⁻³ sodium hydrogen carbonate (99.5 ~ 100.3 %, Kanto Chemical Co., Inc., Japan) were added to 100 cm⁻³ of removed-K bittern. Subsequently, direct ultrasonic irradiation was applied to the solution using a homogenizer with a 3 mm horn tip, maintaining the reaction temperature in the range of 25 °C to 65 °C using a water bath (Fig. 2). Ultrasound irradiation was accomplished with a high-intensity ultrasonic probe (Microtec Co., Ltd., MR-50, 3 mm diameter; Ti-horn, 20 kHz, 50 W·cm⁻²) immersed directly in the reaction solution. The tip of the horn was immersed in the reaction solution for about 1 cm and irradiated. The sonication was conducted without cooling, so the temperature of the solution did not change much at the end of the reaction. The reaction was carried out for 20 min under irradiation at 20 kHz and 40 W. The sample was then filtered, washed, and dried at 40 °C. In addition, based on the optimal conditions for the sonochemical synthesis of dolomite using reagents (CaCl₂·2H₂O, MgCl₂·6H₂O, Na₂CO₃, and NaHCO₃), the Ca/Mg mole ratio in the removed-K bittern was adjusted to 0.5 using calcium chloride.

2.3 Synthesis of dolomite phosphor by immersion method

The synthesis of phosphors using seawater-originated dolomite has been reported [1]. The synthesized dolomite was converted into green- and red-emitting phosphors using the immersion method. For the synthesis of green-emitting phosphor (CaMg(CO₃)₂·Ce³⁺·Tb³⁺), 1 mass% of the dolomite was immersed in a 0.1 mol·dm⁻³ solution of terbium chloride hexahydrate and cerium chloride heptahydrate for 2 h at room temperature while stirring. The sample was filtered, washed, and dried at 40 °C. For the synthesis of red-emitting phosphor (CaMg(CO₃)₂·Eu³⁺), 1 mass% of the synthesized dolomite was added to either a 0.1 or 0.2 mol·dm⁻³ solution of europium chloride hexahydrate, and the same procedure was followed.

2.4 Characterization

The samples were characterized using X-ray diffraction (XRD, MiniFlexII, Rigaku) at 30 kV and 15 mA of CuKα radiation, and Fourier-transform infrared (FTIR) spectroscopy (Spectrum 65, PerkinElmer). The fluorescence properties of the samples were measured using a fluorescence

![Fig. 2 Schematic diagram of formation of dolomites with ultrasonic irradiation.](image)
spectrophotometer with a Xe lamp light source (RF-5300PC, Shimadzu). All the measurements were performed at room temperature.

3. Results and Discussion
3.1 Sonochemical synthesis of CaMg\((\text{CO}_3)_2\) using removed-K bittern

The XRD patterns of the samples (Fig. 3) synthesized using ultrasonic cavitation of removed-K bittern at different reaction temperatures are presented along with the reference pattern of CaMg\((\text{CO}_3)_2\) (ICSD 152202). For the untreated removed-K bittern sample, the position of the strongest diffraction peak near \(2\theta = 30^\circ\) compared with the strongest diffraction peak \(2\theta = 30.96^\circ\) of the target dolomite, which was slightly off. In addition, by-product or degradation phases, which are not associated with dolomite, were confirmed near \(2\theta = 13^\circ\) and \(27^\circ\). These were hydro magnesite \((\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2\cdot4\text{H}_2\text{O}))\). Most of the samples were magnesian calcite. It is considered that this is because the amount of Ca\(^{2+}\) in the removed-K bittern is low. It was not possible to synthesize dolomite directly using removed-K bittern; therefore, the Ca/Mg molar ratio was changed to 0.5 based on the sonochemical synthesis results of reagents used. The removed-K bittern sample synthesized with adjusted Ca concentration was in good agreement with most of the diffraction peaks of dolomite (Fig. 4). The crystallite diameter of the synthesized dolomite estimated using Scherrer’s equation was 17 nm. Using the calculation method \(^{14}\) of the Ca/Mg ratio from the observed diffraction peak, the Ca/Mg ratio was calculated to be 1.68 for the removed-K bittern sample and 1.12 for the adjusted Ca concentration sample, respectively. Regarding the yield of dolomite, almost all of Ca concentration in solution was formed as dolomite.

The composition and structure of dolomite synthesized using the Ca concentration-adjusted removed-K bittern was further investigated by FTIR spectroscopy (Fig. 5). The absorption spectrum of dolomite is similar to that of CaCO\(_3\). The absorption band around 729 cm\(^{-1}\) is due to \(\text{v}_4\) (stretching mode) of the incorporated CO\(_3\) group of dolomite \(^{15,16}\). The absorption band at 1815 cm\(^{-1}\) arises from combination bands \(^{17,18}\).

It is believed that the solubility product is closely related to the formation mechanism of dolomite using ultrasonic cavitation. The solubility products \(K_{sp}\) of typical calcium and magnesium compounds in seawater at 18 to 25 \(^\circ\)C are CaCO\(_3\) (aragonite) \(6.9 \times 10^{-9}\), CaCO\(_3\) (calcite) \(4.8 \times 10^{-9}\), CaCO\(_3\) (vaterite) 2.4 mg/100 ml, CaSO\(_4\).2H\(_2\)O \(2.26 \times 10^{-9}\), MgCO\(_3\) \(3.5 \times 10^{-8}\), and dolomite 16.90. Calcium carbonate is rapidly formed after the addition of the carbonic acid source (CO\(_3^{2-}\)) to the removed-K bittern. At the same time, calcium carbon-
ate is presumed to incorporate various cations into the crystal structure and is rapidly crystallized by the application of ultrasonic cavitation. In the direct use of the removed-K bittern, the Ca/Mg molar ratio was approximately 0.32. In the presence of many dissolved cationic species, aragonite is likely to be formed in large quantities; dolomite will not be produced. When the Ca/Mg molar ratio was adjusted to 0.5 by adding calcium chloride, the amount of Ca$^{2+}$ ions in the reaction solution increased, and the formation of calcite was mainly promoted. In addition, dolomite nanoparticles were easily synthesized with a reaction time of 20 min by the ultrasonic cavitation of removed-K bittern.

### 3.2 Synthesis of dolomite phosphor by immersion method

Subsequently, we examined the conversion of the synthesized dolomites into inorganic phosphor materials. Fig. 6(a) shows the emission spectrum of the Ce$^{3+}$ and Tb$^{3+}$ co-doped dolomite obtained by the immersion treatment. Generally, when Ce$^{3+}$ and Tb$^{3+}$ ions are co-doped in the host crystal, the emission and absorption bands of Ce$^{3+}$ and Tb$^{3+}$ ions overlap, respectively, resulting in energy transfer. Therefore, the fluorescence characteristics, such as emission intensity, are improved in the Ce$^{3+}$ and Tb$^{3+}$ co-doped phosphor material, compared to the solid solution of Tb$^{3+}$ ions alone. Four emission bands were observed at 490, 543, 585, and 622 nm corresponding to $D_{4h} \rightarrow F_{6g}$, $F_{5g}$, $F_{4g}$, and $F_{3g}$ transitions of Tb$^{3+}$ ions, respectively. The dolomite phosphor that emits green light with high luminous efficiency under ultraviolet light ($254 \text{ nm}$) can be easily synthesized. The XRD patterns after immersion treatment are shown in Fig. 6(b). The crystallinity of the green-emitting dolomite phosphor decreased significantly because the concentration of the prepared immersion solution was high. However, no new by-products or degradation phases were observed. When the concentration of the immersion solution is high, double salt compounds also gradually dissolve. It is probable that concentration of the immersion solution was high and the particle surface of the synthesized dolomite was dissolved. Therefore, the crystallinity was greatly reduced. Using dolomite synthesized with reagents and pure water, the same immersion treatment was carried out, and the emission intensities of each phosphor were compared. Almost the same emission intensities were observed for all the phosphors. That is, the same fluorescence properties presented as that of the dolomite phosphor synthesized using pure water and reagents (CaCl$_2$ and MgCl$_2$). These results suggest that high-purity dolomite can be synthesized from removed-K bittern. Similarly, when the excitation emission spectra of the Eu$^{3+}$ doped dolomite phosphor obtained by the immersion treatment were measured, an emission band corresponding to Eu$^{3+}$ ions was also observed (Fig. 7(a)). The emission transitions of Eu$^{3+}$ ions were observed at $D_{4h}$

![Fig. 6 Emission spectrum (a) and X-ray diffraction patterns (b) of Ce$^{3+}$, Tb$^{3+}$ co-doped dolomite.](image)

![Fig. 7 Emission spectra (a) and X-ray diffraction patterns (b) of Eu$^{3+}$ doped dolomite.](image)
The emission photographs under 254 nm irradiation phosphors can be used as guide lights and interior lights. such as green, yellow-green, yellow, orange, and red. These green- and red-emitting dolomite phosphors, it is possible to spectrally. By changing the mixing ratio of the synthesized phosphors: green, yellow-green, yellow, orange, and red, respectively. The different emission colors for the as-synthesized dolomite radation phases were observed. Reduced crystallinity of the red-emitting dolomite synthesized from removed-K bitterns in a luminescent ion solution, it was possible to synthesize green- and red-emitting dolomite similarly. The crystallinity of the red-emitting dolomite synthesized from CaCl₂ and adjustment of the Ca/Mg molar ratio in the solution to 0.5. By immersing the dolomite synthesized from reduced-K bittern alone. However, synthesis of dolomite could not be performed using ultrasonic cavitation of the removed-K bittern. Single-phase conversion of low-temperature dolomites, Mineral. Mag., 40, 579-587 (1976)

4. Conclusions

Dolomite was synthesized for the first time from removed-K bitterns using ultrasonic cavitation and then converted to phosphor by immersion treatment. Single-phase synthesis of dolomite could not be performed using ultrasonic cavitation of the removed-K bittern alone. However, most can be synthesized as dolomite by the addition of CaCl₂ and adjustment of the Ca/Mg molar ratio in the solution to 0.5. By immersing the dolomite synthesized from removed-K bitterns in a luminescent ion solution, it was possible to synthesize green- and red-emitting dolomite phosphors with luminescence intensity equivalent to that of dolomite synthesized from reagents. Various emission colors can be controlled by changing the mixing ratio of the synthesized green- and red-emitting dolomite phosphors.

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References


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