

MINERALOGICAL NOTES

Hydrothermal Growth of Magnesite Single Crystals

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Abstract

Magnesite single crystals up to 250 μm were synthesized from an equi-molal solution of MgCl_2 and Na_2CO_3 in an autoclave at 180-190°C. Results of X-ray and of DTA, TGA, IRA, and EPMA studies indicate that synthesized magnesite has properties similar to those of natural magnesite.

Introduction

Several investigators have reported on the synthesis of magnesite. Roy, Roy, and Osborn (1953) and Harker and Tuttle (1955) synthesized magnesite with CO_2 as the fluid phase. Magnesite was also produced at low temperatures ($21 \pm 2^\circ\text{C}$) by Halla and Van Tassel (1964). The stability of carbonates in the system $\text{MgO-CO}_2\text{-H}_2\text{O}$ was reported by Langmuir (1965). During investigations in our laboratory of hydrothermal reactions of artinite (Iwai *et al.*, 1971b) and nesquehonite (Iwai *et al.*, 1971a), magnesite crystals of 10-30 μm were formed. We then undertook to hydrothermally synthesize single crystals of magnesite large enough to determine its structure.

Experimental

Equi-molal solutions of 0.1-3.0 mol/l MgCl_2 and Na_2CO_3 of reagent grade were poured into glass tubes within an autoclave and set in a silicon oil bath. They were then heated from one to 240 hours at 140-230°C at resultant water vapor pressures of from 3.5 to 27.6 atm. The pH values of the residual solutions after precipitation of magnesite were in the range of 7.2-8.4. Optimum conditions for growing large single crystals were a 180-190°C heating temperature and a 0.5 mol/l concentration of starting solution.

At lower temperatures ($<140^\circ\text{C}$) basic magnesium carbonates are formed in less than 12 hours. At higher temperatures ($>190^\circ\text{C}$) the formation of magnesite is favored but foreign material is increased.

The products were examined with an optical

microscope, a scanning electron microscope, and an X-ray diffractometer. When the heating time ranged from 1 to 12 hours, hydromagnesite and magnesite of 10 μm size were obtained. Material which was heated for 20 hours produced magnesite 20 μm in size; heating for 140 hours produced large rhombohedral single crystals of magnesite 250 μm in maximum size. Magnesite up to 150 μm in size was transparent, whereas above 150 μm it changed from translucent to opaque. A micro-photograph of these crystals is reproduced in Figure 1.

A least squares analysis based on the UNICS program (Sakurai, 1967) was applied to 28 reflections to obtain the lattice constants for synthetic magnesite [$a = 4.6369(7)$, $c = 15.0230(25)$ Å] and for natural magnesite [$a = 4.6355(10)$, $c = 15.0300(37)$ Å]. The values in parentheses represent the estimated standard deviations (*esd*) in terms of the last decimal place cited. Thus 15.0230(25) indicates an *esd* of .0025 Å. Results agree well with the lattice constants [$a = 4.6330$, $c = 15.016$ Å] reported for synthetic magnesite by Deer *et al.* (1963).

Thermal analyses were performed with a heating rate of 5°C/min. DTA curves are characterized by the endothermic peak at about 615°C for synthetic magnesite and at about 635°C for natural magnesite. The weight loss of 51.7 percent for synthetic magnesite and of 50.1 percent for natural magnesite is near the theoretical value of 52.2 percent for magnesite.

An infrared analysis showed prominent absorption bands of carbonate at 1440, 880, and 745, and

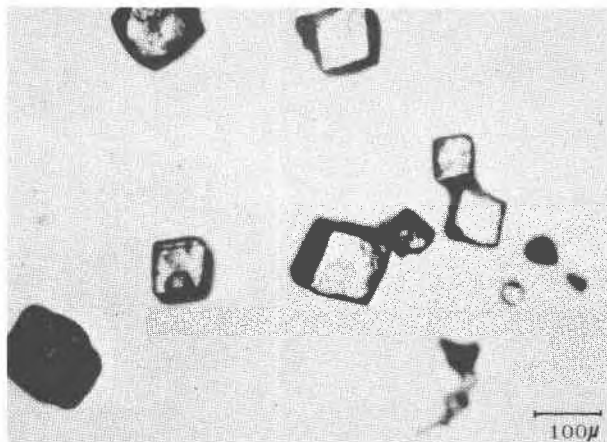


FIG. 1. A microphotograph of magnesite single crystals in plane polarized light (180°C, 144 hours).

weak ones at 2510 and 1820 cm^{-1} . These are in good agreement with absorption bands of natural magnesite and those of magnesite reported by Hung (1960).

The impurities of Ca, Na, and Si components in the magnesite crystals were checked by a 3 channel electron probe microanalyzer using line scanning methods. No significant amounts of Ca and Si were detected; the very small amount of Na detected is

considered to be precipitated on the surface of the magnesite crystal in a later stage of reaction.

Acknowledgment

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