LETTERS

Elasticity of single-crystal calcite and rhodochrosite by Brillouin spectroscopy

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ABSTRACT

The single-crystal elastic moduli of natural samples of both calcite (CaCO3) and rhodochrosite (MnCO3) have been measured by Brillouin spectroscopy under ambient condition. Based on the trigonal unit cell, the elastic constants C11, C33, C44, C12, C13, and C14 are 149.4(7), 85.2(18), 34.1(5), 57.9(11), 53.5(9), –20.0(2), and 223.9(15), 132.6(41), 44.5(9), 93.4(21), 76.0(23), –17.3(6) GPa for CaCO3 and MnCO3, respectively. Our data for calcite are in good agreement with earlier data obtained by ultrasonic experiments. The off-diagonal elastic constants (C12, C13, and C14) for rhodochrosite have systematically larger values than the trend defined by other isostructural carbonates, in all of which the divalent cations are alkaline-earth metals. This is a distinctive signature of transition–metal-bearing oxides, which is present in silicates and simple oxides as well.

INTRODUCTION

A complete set of elastic constants for materials is important to estimate physical parameters such as the Debye temperature, compressibility and acoustic anisotropy. It is also well known that elastic properties of materials depend on pressure, temperature, chemical composition and crystal orientation. An important chemical variable is the presence of transition metal ions in oxides and silicates (Sumino 1979; Weidner et al. 1982; Zhang 1998; Zhang and Reeder 1999).

There are more than ten compounds which crystallize with the calcite-type structure at ambient conditions (e.g., Wyckoff 1964). Except for calcite (CaCO3), magnesite (MgCO3) and NaN3, the elastic properties of the other calcite-type compounds are not available. Single-crystal elastic properties of calcite have been extensively studied, but exclusively by ultrasonic techniques (e.g., Dandekar 1968a, 1968b; Hearmon 1979; Vo Thanh and Lacam 1984). In the present study, we report the elastic properties of both calcite and rhodochrosite (MnCO3) as determined from Brillouin scattering measurements. The data for calcite thus obtained can be compared with those obtained by ultrasonic measurements, whereas the data for rhodochrosite are new results.

EXPERIMENTAL METHODS

The single crystals of both calcite and rhodochrosite used in the present work are natural samples. The calcite sample is Iceland spar and the pink rhodochrosite is from an unspecified locality in Mexico. The chemical composition of the latter was confirmed by electron probe analysis [(Mn0.98 Mg0.01 Ca0.01)CO3]. Both samples can be readily oriented using crystal morphology.

Calcite-type carbonates have perfect {100} cleavage in the trigonal cell (Fig. 1). A plate of calcite with parallel cleavage faces and a thickness of ~1 mm was carefully chosen for this study. The plate was optically clear and free from twins. The opposite faces of the calcite plate were not polished, and are parallel to each other within ±1°. There were many small cleavage cracks and twins inside the sample of rhodochrosite. Thus, a small optically clear plate (500 µm × 600 µm) with a thickness of ~200 µm was chosen for experiments. The opposite faces of the rhodochrosite plate were [100] cleavage faces and were finely polished to be parallel to each other within ±10°.

Samples thus prepared were then mounted on a three-circle Eulerian cradle, which was used to control the sample orientation. An argon ion laser (λ = 514.5 nm) and a six-pass tandem Fabry–Pérot interferometer were used for the Brillouin experiments. All measurements of acoustic velocities employed a symmetric scattering geometry with an external angle between the incident and scattered beams of 90°. With this geometry the refractive index can be cancelled out in the calculation of acoustic velocity, and the Brillouin frequency shift Δω is directly related to the acoustic velocity V and incident laser wavelength λ by

\[ V = \frac{\Delta \omega \lambda}{\sqrt{2}} \]  

(1)

In Brillouin scattering, the spectrum consists of an elastically scattered component with the same frequency as the excitation source and a set of inelastically scattered components. The latter display a frequency shift Δω caused by the interaction between photons and phonons in the sample. Details of the Brillouin scattering technique have been elucidated earlier (e.g., Sinogeikin and Bass 2000).

Brillouin data were also collected with the two sides of the sample plates reversed to reduce possible errors introduced by non-parallelism of the plate. A representative spectrum for MnCO3 collected at the χ angle (about an arbitrary setting mark...