American Mineralogist, Volume 106, pages 581–598, 2021

High-pressure and high-temperature vibrational properties and anharmonicity of carbonate minerals up to 6 GPa and 500 °C by Raman spectroscopy

STEFAN FARSANG[1,*], REMO N. WIDMER[2], AND SIMON A.T. REDFERN[3,†]

[1]Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, U.K.
[2]EMPA, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Mechanics of Materials and Nanostructures, Feuerwerkerstrasse 39, Thun, 3602, Switzerland
[3]Asian School of the Environment, Nanyang Technological University, 50 Nanyang Avenue, Singapore, 639798, Singapore

ABSTRACT

Carbonate minerals play a dominant role in the deep carbon cycle. Determining the high-pressure and high-temperature vibrational properties of carbonates is essential to understand their anharmonicity and their thermodynamic properties under crustal and upper mantle conditions. Building on our previous study on aragonite, calcite (both $CaCO_3$ polymorphs), dolomite [$CaMg(CO_3)_2$], magnesite ($MgCO_3$), rhodochrosite ($MnCO_3$), and siderite ($FeCO_3$) (Farsang et al. 2018), we have measured the pressure- and temperature-induced frequency shifts of Raman-active vibrational modes up to 6 GPa and 500 °C for all naturally occurring aragonite- and calcite-group carbonate minerals, including cerussite ($PbCO_3$), strontianite ($SrCO_3$), witherite ($BaCO_3$), gaspeite ($NiCO_3$), otavite ($CdCO_3$), smithsonite ($ZnCO_3$), and spherocobaltite ($CoCO_3$). Our Raman and XRD measurements show that cerussite decomposes to a mixture of Pb_2O_3 and tetragonal PbO between 225 and 250 °C, smithsonite breaks down to hexagonal ZnO between 325 and 400 °C, and gaspeite to NiO between 375 and 400 °C. Spherocobaltite breaks down between 425 and 450 °C and otavite between 375 and 400 °C. Due to their thermal stability, carbonates may serve as potential reservoirs for several metals (e.g., Co, Ni, Zn, Cd) in a range of crustal and upper mantle environments (e.g., subduction zones). We have determined the isobaric and isothermal equivalents of the mode Grüneisen parameter and the anharmonic parameter for each Raman mode and compare trends in vibrational properties as a function of pressure, temperature, and chemical composition with concomitant changes in structural properties. Finally, we use the anharmonic parameter to calculate the thermal contribution to the internal energy and entropy, as well as the isochoric and isobaric heat capacity of certain carbonates.

Keywords: Anharmonicity, cerussite, diamond-anvil cell, gaspeite, high pressure, high temperature, otavite, pressure sensor, Raman spectroscopy, smithsonite, spherocobaltite, strontianite, witherite