

Rapid Research Note

Pressure Variation of the Conductivity in Single Crystal Calcite

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The calcite group, which consists of calcite (CaCO_3), magnesite (MgCO_3) and their mixed crystal dolomite ($\text{CaMg}(\text{CO}_3)_2$), is the most representative among the trigonal carbonate salts [1]. A potential difference between these crystals and typical ionic crystals like NaCl is that the structural units of a simple ionic material are single cations and anions, which are ionically bonded; while the carbonate matrix consists of cations and a trioxycarbon radical. Experiments of charge transport under pressure provide information on the nature of the conduction mechanism and provide volume defect parameters, like the activation volume [2]. The collection of the values of the activation volume for the mixed crystal and its compounds is desirable, for understanding the influence of the lattice constant variation (long range effect) and the modification of the environment (the structural units), which surrounds the transferring charge carrier, on the value of the activation volume. The activation volumes for the electric charge transport in dolomite and magnesite were presented previously [3, 4]. In the present work, the pressure variation of the conductivity of calcite was studied and the activation volume was estimated. A correlation between the activation volume and the unit cell volume of the matrix is discussed.

The samples of CaCO_3 were prepared from a high quality and known impurity content single crystal of calcite from Iceland, by cutting them along their cleavage planes. Detailed information is given in [5]. The conductivity measurements were performed at room temperature in a piston-type apparatus, which operated from the atmospheric pressure to 3 kbar. Details about the experimental setup and the measuring procedure can be found in [3, 4].

In Fig. 1 the logarithm of the conductance G reduced to the ambient-pressure conductance G_0 is depicted as a function of pressure. A heat bath maintained a constant temperature value $T = 298$ K. The reduction of the conductance indicates that the conduction mechanism proceeds through ionic transport. The value of the activation volume v^{act} , which is defined as the pressure derivative of the Gibbs free energy g^{act} of the activation process at constant temperature [6] is obtained from conductivity measurements [6]:

$$v^{\text{act}} = -kT \left[\left(\frac{\partial \ln G}{\partial P} \right)_T - \gamma\chi \right], \quad (1)$$

where k denotes the Boltzmann constant, G is the sample conductance, γ is the Grüneisen constant for the mode related to ionic conduction and χ is the isothermal compressibility of the material. The $\ln(G/G_0)$ values fall linearly with pressure up to about 2 kbar. A departure from linearity appears in the high-pressure limit. The curvature may be attributed to the activation of additional migration paths with the increased pressure. By fitting a line to the low-pressure data points, we get $(\partial \ln G / \partial P)_T = -(0.54 \pm 0.04) \text{ kbar}^{-1}$. The Grüneisen constant was set equal to 1.7, which is a value typical for the majority of ionic materials [7]. The isothermal compressibility is $\chi = 1.37 \text{ kbar}^{-1}$ [8]. By replacing the aforementioned data in Eq. (1) we get $v^{\text{act}} = (13.1 \pm 0.9) \text{ cm}^3/\text{mol}$.

The activation volume values for the calcite group members against the volume of the unit cell are shown in Fig. 2. We observe that the activation volume decreases linearly with increasing unit volume V at a rate of $dv^{\text{act}}/dV = -1.7 \pm 0.1$. This systematic trend can be understood as follows: The activation volume can be viewed as the difference of the volume of the sample when the transferring ion is located at the saddle point (separating two neighboring equilibrium sites) and at

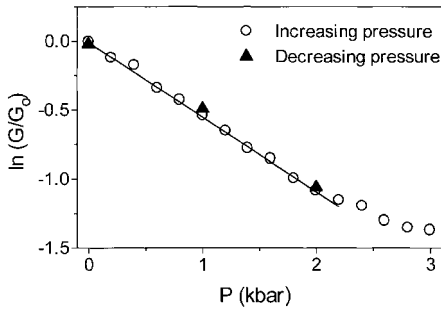


Fig. 1

Fig. 1. The logarithm of the conductance G reduced to the ambient conductance G_0 as a function of pressure. The circles correspond to the pressurization stage and the triangles to the stage of pressure release. The line was fitted to the low-pressure data points. The temperature was kept constant at $T = 298$ K

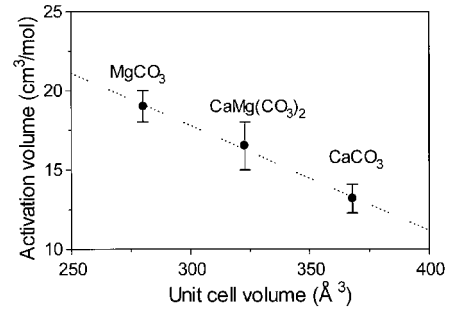


Fig. 2

Fig. 2. The room temperature activation volume values for the calcite family members: magnesite (MgCO_3) [5], dolomite ($\text{CaMg}(\text{CO}_3)_2$) [4] and calcite (CaCO_3) (present work). The dashed line was fitted to the data points

its equilibrium site (ground state) [7]. In this sense, a large activation volume value is indicative for a significant lattice distortion as the transferring ion passes over the saddle point. A small unit cell (as that of magnesite) provides a restricted 'free' volume to the ion migration and, therefore, the activation volume value is large. On the contrast, in calcite, where the unit cell volume is large, the lattice distortion is small and the activation volume value is reduced.

References

- [1] J.R. REEDER, in: *Reviews in Mineralogy*, Vol. 11: Carbonates: Mineralogy and Chemistry, Ed. J.R. REEDER, Mineralogical Society of America, Washington 1983.
- [2] G.A. SAMARA, *J. Phys. Chem. Solids* **40**, 509 (1979).
- [3] A.N. PAPATHANASSIOU and J. GRAMMATIKAKIS, *Phys. Rev. B* **53**, 16247 (1996).
- [4] A.N. PAPATHANASSIOU, *Phys. Rev. B* **58**, 4432 (1998).
- [5] N. BOGRIS, J. GRAMMATIKAKIS, and A.N. PAPATHANASSIOU, *Phys. Rev. B* **58**, 10319 (1998).
- [6] D.R. FIGUEROA, J.J. FONTANELLA, M.C. WINTERSGILL, and C.G. ANDEEN, *Phys. Rev. B* **29**, 5909 (1984).
- [7] P.A. VAROTSOS and K.D. ALEXOPOULOS, *Thermodynamics of Point Defects and Their Relation with Bulk Properties*, Eds. S. AMELINCKX, R.GEVERS, and J. NIHOUL, North-Holland, Amsterdam 1985.
- [8] W.C. CADY, *Piezoelectricity*, McGraw-Hill, New York 1964 (p. 414).

