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Dielectric relaxation in calcite by piezostimulated depolarization-current spectroscopy

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The dielectric relaxation of calcite ($CaCO_3$) is investigated in the present work by using the piezostimulated depolarization current (PSDC) technique. The migration volume corresponding to the dipole rotation was evaluated following different methods of analysis of the PSDC signal. A full curve fitting procedure yielded the migration enthalpy h^m, the pre-exponential factor τ_0 and the migration volume v^m. These results permit the correlation of the PSDC signal with a relaxation mechanism detected alternatively in the thermally stimulated depolarization current (TSDC) spectrum of calcite. The value of v^m provides information about the relaxation of point defect agglomerates, with Sr^{2+} being the dominant participant to the dipoles' configuration. Our results are discussed in relation with those reported for calcite by employing the TSDC scheme.

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I. INTRODUCTION

Thermally stimulated depolarization current (TSDC) spectroscopy was employed during the last decade to investigate the dipole relaxation in single crystal calcite ($CaCO_3$)[1] and calcite compounds.[2,3] The calcite matrix favors a dielectric relaxation mechanism, which is attributed to the presence of defect dipole agglomerates.[1] It is probable that strontium cation impurities are participants of these dipoles.[3] The migration enthalpy h^m and the pre-exponential factor τ_0 of the dipole rotation were reported in these works. However, the migration volume v^m, which provides evidence about the size of the rotating entities, is lacking up to date.

In the present work, the single crystal calcite is studied by employing the piezostimulated depolarization currents (PSDC) spectroscopy.[4] This type of dielectric spectroscopy is isothermal and is based on monitoring the relaxation time upon the change of the thermodynamic parameter of pressure. In contrast to the TSDC method,[5] the PSDC is isobaric. We have shown very recently[6] that The PSDC is an advantageous technique due to its capability of yielding the evaluation of the migration enthalpy h^m, the pre-exponential factor τ_0 and the migration volume v^m that govern the dipole rotation through a full curve fitting analysis. The value of the migration volume provides information about the nature of the migrating species: In the case of LiF:Be^{2+}, a dielectric relaxation mechanism that was characterized by an unreasonably large value of τ_0, was attributed to the relaxation of extended defects (dislocations) by performing PSDC experiments.[6]

II. THEORY

The relaxation time of rotating dipoles is[7]

$$\tau = \tau_0 \exp\left(\frac{Pv^m + E}{kT}\right), \tag{1}$$

where τ^0 denotes the pre-exponential factor, v^m is the migration volume, E is the activation energy, and k is the Boltzmann's constant. The term $Pv^m + E$ corresponds to the migration enthalpy h^m. In the low pressure limit (i.e., close to the ambient pressure), $Pv^m \ll E$. Subsequently, E is approximately equal to h^m.[7]

The PSDC experiments are performed at constant temperature.[4,6] The dielectric is polarized at constant pressure P_p by an external electric field for a time interval t_p, which is much longer than the relaxation time of dipoles $\tau(P_p)$. By keeping the polarizing field on, the material is subjected to a high pressure P_f, where $\tau(P_f)$ is so long that the dipoles remain oriented even if the external polarizing field is removed. Afterwards, in the absence of an external field, the pressure is reduced at a constant pressure rate $b = dP/dt$, while the temperature remains constant.

The density of the depolarization current emitted is[4,8]

$$j = \frac{d\Pi}{dt} = \frac{d\Pi}{dP}\frac{dP}{dt} = \frac{d\Pi}{dP} b. \tag{2}$$

We assume that the decay of the polarization is described by the following first-order kinetics equation:

$$\frac{d\Pi(t)}{dt} + \frac{\Pi(t)}{\tau(t)} = 0. \tag{3}$$

From Eqs. (2) and (3), we get

$$\frac{d\Pi(P)}{\Pi(P)} = -\frac{1}{b}\frac{dP}{\tau(P)}. \tag{4}$$

The solution of Eq. (4) is

$$\Pi(P) = \Pi_0 \exp\int_{P_f}^{P} -\frac{dP'}{b\,\tau(P')}, \tag{5}$$

where Π_0 is the initial polarization achieved by applying the external electric field.

Considering v^m and τ^0 independent of pressure, Eqs. (5) and (1) provide the piezostimulated current density:

$$j(P)=\frac{\Pi_0}{\tau_0}\exp\left(-\frac{Pv^m+E}{kT}\right)\left(\exp\left\{\frac{kT}{bv^m\tau_0}\left[\exp\left(-\frac{E}{kT}\right)\right]\right.\right.$$
$$\left.\left.\times\left[\exp\left(-\frac{Pv^m}{kT}\right)-\exp\left(-\frac{P_f v^m}{kT}\right)\right]\right\}\right). \tag{6}$$

The evaluation of the migration volume is achieved by the following methods.[6,8,9]

(a) Area method: The relaxation time can be obtained by graphical integration

$$\tau(P)=\frac{1}{[b]j(P)}\int_{P_f}^{P} j(P)dP. \tag{7}$$

By using Eq. (1), we get $v^m = d \ln \tau/d(P/kT)$.

(b) Initial rise method: For $P \approx P_f$, the current density reduces to

$$j(P)\cong\frac{\Pi_0}{\tau_0}\exp\left(-\frac{Pv^m++E}{kT}\right). \tag{8}$$

Therefore, $v^m = -d \ln j(P)/dP$.

(c) Maximum current method: The migration volume is given by

$$v^m=-2.718kTj_M/b\Pi_0, \tag{9}$$

where j_M is the amplitude of the signal and the polarization Π_0 is obtained from the area enclosed between the curve of $j(P)$ and the axis of pressure.

(d) Inflexion points method: Labeling j_1 and j_2 the current density values at the inflection points of the PSDC curve, we get

$$\begin{aligned} v^m&=-j_1kT/0.181\Pi_0 b,\\ v^m&=-j_1kT/0.260\Pi_0 b. \end{aligned} \tag{10}$$

(e) Peak-maximum coordinates method: The migration volume v^m is obtained by solving the maximum current density j_M relation:

$$j_M=\frac{\Pi_0 bv^m}{kT}\exp\left\{\exp\left[-\frac{(P_f-P_M)v^m}{kT}\right]-1\right\}, \tag{11}$$

where P_M is the pressure where the (absolute) value of the depolarization current reaches its maximum.

The different methods of analysis mentioned above provide a reliable range of values of the migration volume. A three-parameter (E, τ_0, and v^m) full curve fitting of Eq. (6) to the experimental $j(P)$ data points is enabled by constraining v^m within the range obtained by conventional analyses [methods (a)–(e)]. It should be mentioned that the exploitation of the full curve fitting is advantageous in providing the values of h^m and τ_0, which actually identify the relaxation mechanism.[6] The knowledge of h^m and τ_0 for a relaxation mechanism appearing in the PSDC spectrum permits its interconnection with those mechanisms that are detected by the TSDC and/or dielectric relaxation experiments.

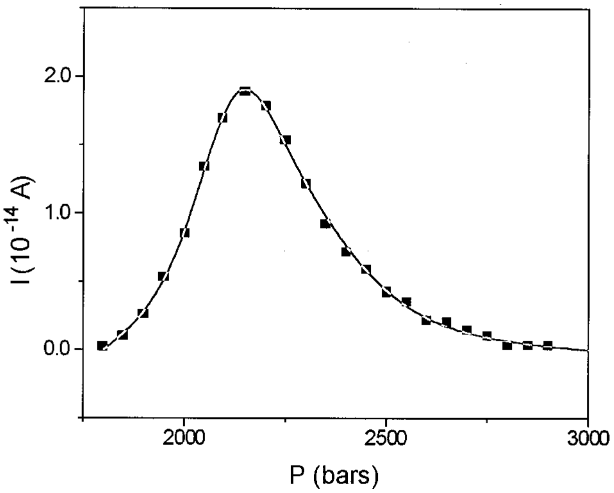

FIG. 1. The piezostimulated depolarization current $I(P)$ of calcite (squares) together with the theoretical curve (line) that best matches the experimental data points. The pressure rate was $b = -1$ bar/s.

III. EXPERIMENTAL DETAILS

The experiments were performed at room temperature (RT) in a piston-type pressure anvil operating from the ambient pressure to 3.5 kbars. Details are given in Ref. 6. Specimens of high-quality single crystals of calcite of known impurity content were used. Details were given in Ref. 1.

IV. RESULTS AND DISCUSSION

The piezostimulated depolarization spectrum of calcite consists of a dominant relaxation mechanism, which reaches its maximum at $P_M = 2136$ bars (Fig. 1). The room temperature was $T = 298$ K and the pressure was reduced at constant rate $b = -1$ bar/s. The logarithm of the relaxation time τ, which was obtained through Eq. (3), is plotted against pressure in Fig. 2. A linear fit to the ln $\tau(P)$ data points provides

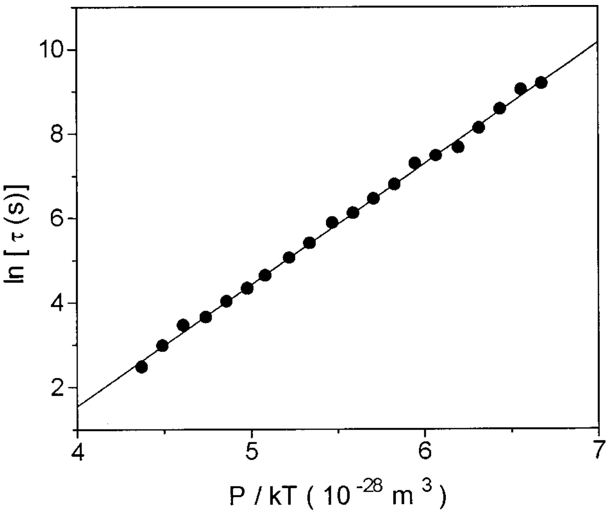

FIG. 2. The logarithm of the relaxation time τ vs P/kT (circles). The relaxation time was evaluated by employing Eq. (6). The line was fitted to the data points.

TABLE I. The values of the migration volume v^m obtained by employing different methods of analysis.

Method of analysis	$v^m (10^{-28}\,\mathrm{m}^3)$
Area method	2.726
Initial rise	2.552
Maximum current	2.858
Inflection points: Left	2.446
Right	2.724
Peak-maximum coordinates method	2.857
Full-curve fitting	2.726

the value of v^m [see method of analysis (a)]. The value of the migration volume that was estimated by applying the methods mentioned in the theory is presented in Table I.

The PSDC equation [Eq. (6)] was exploited to find a theoretical curve that best matches the experimental data points. In the three-parameter (E, τ_0, and v^m) nonlinear least squares fitting, the values of v^m were constrained between 2.000×10^{-28} and $3.000\times10^{-28}\,\mathrm{m}^3$. The values of the activation volume that were obtained with the conventional analyses (Table I) lie within the above-mentioned range. The result of the computer fitting was

$$h^m = 0.66\ \mathrm{eV},$$

$$\tau_0 = 6.70\times10^{-16}\ \mathrm{s},$$

$$v^m = 2.726\times10^{-28}\ \mathrm{m}^3.$$

The error estimates on these parameters were about 1%. We observe that the value of v^m is compatible with those presented in Table I.

A relaxation mechanism, which exhibits its maximum at 188 K in the thermogram of calcite recorded via the thermally stimulated depolarization current (TSDC) is governed by the following relaxation parameters:[1]

$$h^m = (0.66\pm0.02)\ \mathrm{eV},$$

$$\tau_0 = 1.33\times10^{-16}\ \mathrm{s}.$$

Comparing the latter values with those resulting from the full-curve fitting to the piezostimulated signal, we notice that the migration enthalpies are identical and the values of τ_0 are of the same order of magnitude. It is evident that the PSDC relaxation mechanism coincides with the relaxation mechanism, which was previously detected by employing the thermally stimulated current technique.[1] The discrepancy between the τ_0 values can be explained by the unavoidable large experimental error in determining τ_0.

The ratio of the migration volume over the mean molar volume Ω of calcite is $v^m/\Omega = 1.84$. It was postulated that the relaxation mechanism corresponds to the rotation of defect dipoles with strontium impurities as the major participants of those agglomerates.[2,3] It was proposed previously that the calcite matrix favors the incorporation of Sr^{2+} at interstitial sites.[2] Local charge compensation is attained by the creation of Ca^{2+} vacancies. Although the ionic radius of Sr^{2+} is about 10% larger than that of the host cations, the fact that v^m exceeds the mean molar volume of calcite indicates that the rotating dipoles are large agglomerates with more than one strontium cation. The latter aspect is in accordance with the results for the defect dipole aggregation under thermal anneal by means of thermally stimulated depolarization current (TSDC) experiments.[1–3]

V. CONCLUSION

A relaxation mechanism, which was studied previously via thermally stimulated depolarization currents (TSDC), is identified in the present work by employing the piezostimulated depolarization current (PSDC) scheme. The correlation between the results of these techniques is achieved by mutually comparing the values of h^m and τ_0 resulting from the full-curve fitting of the PSDC signal with those obtained from the TSDC results. The migration volume corresponding to the dipole rotation was evaluated through different analyses. These values suggest that the relaxation is produced by the rotation of large agglomerates of point defects with Sr^{2+} as a dominant participant.

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