



Measurements of the dielectric properties of limestone under pressure and their importance for seismic electric signals



I. Sakellis^{a,b,*}, A.N. Papathanassiou^a, J. Grammatikakis^a

^a University of Athens, Physics Department, Section of Solid State Physics, Panepistimiopolis, GR 15684 Zografos, Athens, Greece

^b National Center for Scientific Research 'Demokritos', Institute of Materials Science, GR 15310 Agia Paraskevi Attikis, Athens, Greece

ARTICLE INFO

Article history:

Received 9 October 2013

Accepted 25 December 2013

Available online 18 January 2014

Keywords:

Dielectric relaxation

Conductivity

Activation volume

Rocks

Earthquake forecast

Pressure

ABSTRACT

The pressure and temperature evolution of an intense dielectric relaxation mechanism in as-received and wetted limestone (from Ioannina region (Greece)) are studied experimentally through complex impedance spectroscopy. The relaxation time decreases on compression, yielding a negative value for the corresponding activation volume. Furthermore, the role of water incorporated in the mineral was examined, revealing the remarkable fact that water not only enhances the absolute value of negative derivative of Gibbs energy with respect to pressure but also lowers significantly the energy barrier of the corresponding physical processes. Both findings are crucial for the explanation of the sensitivity of an electrotelluric station at Ioannina region in detecting Seismic Electric Signals emitted prior to earthquakes.

© 2013 Published by Elsevier B.V.

1. Introduction

Negative activation volume is – by definition – related with a process, the characteristic activation energy of which is reduced as pressure is increased, or in other words by increasing pressure the corresponding process (that may comprise various relaxation mechanisms) becomes energetically more favorable to occur and the corresponding relaxation time is reduced. In general, there is no restriction as far as the sign of activation volume is concerned. The experiments show that negative activation volumes are not commonly found (Fontanella et al., 1982, 1996; Papathanassiou et al., 2010, 2011, 2012; Sakellis et al., 2012). However, the negative activation volumes are of key importance for the validity of the mechanisms proposed for the generation mechanism of seismic electric signals (SES). These are low frequency electric signals that are observed (Varotsos and Alexopoulos, 1984a, 1984b; Varotsos et al., 2002, 2003a, 2003b, 2005, 2006a, 2006b) before earthquakes. Varotsos et al. (1982), (see also Varotsos and Alexopoulos, 1986) treated the earth's crust as a solid rich in 'dipoles' in a polarizing field (i.e., the mechanical stress field), and assumed that negative activation volumes

exist in rocks. They asserted that the gradually increasing stress in the focal area before an earthquake reduces the relaxation time of these 'dipoles'. Thus, at a certain critical stress (pressure), smaller than that at which rupture occurs, the relaxation time of 'dipoles' becomes short and the 'dipoles' undergo a transition from random-orientation state to an oriented one. This yields the emission of a transient polarization current before the rupture, which constitutes, an SES. SES are observed at stations situated on certain localities in the Earth's crust termed sensitive. In these localities, the electric field variations are considered to be significantly enhanced due to both large-scale and small-scale heterogeneous properties of the earth's crust (Varotsos and Lazaridou, 1991).

It is the basic scope of the present paper to investigate the existence of negative activation volume in limestone samples which were collected from Ioannina region (in Northwestern Greece) where a sensitive SES recording station is located. In addition, the critical role of water incorporated within these samples was also studied in detail for the following reasons: The time evolution of the stress field prior to an earthquake, results in the dynamic compression of water-filled rocks (Morgan and Nur, 1986; Morgan et al., 1989). Specifically in rocks, strong structural and compositional heterogeneity as well as porosity give rise to several polarization mechanisms such as, interfacial polarization, double layer polarization, space charge polarization, and defect dipole polarization (Correia, 1997; Varotsos, 2005). Furthermore, when pores are filled – partially or fully – with water, dielectric properties are enhanced on the one hand and on the other hand water induces dilatancy when rock is pressurized. The latter occurs in the hypocenter area of an earthquake which is surrounded by water saturated porous

* Corresponding author at: University of Athens, Physics Department, Section of Solid State Physics, Panepistimiopolis, GR 15684 Zografos, Athens, Greece. Tel.: +30 2107276729; fax: +30 2107661707.

E-mail address: e_sakel@phys.uoa.gr (I. Sakellis).

rock with fluid-filled pore channels and the pre-earthquake stage is assumed to be accompanied by the appearance of fresh cracks in the fracture zone (Surkov et al., 2002).

2. The methodology for the analysis of the laboratory measurements-Background

We first present some theoretical concepts which shall be used to evaluate the data and calculate the activation volume. In solids, the pressure P variation of the defects Gibbs energy g , according to the process that is related to, formation (f), migration (m) or both (act), defines a volume $v^i \equiv (\partial g^i / \partial P)_T$, where T is the temperature and the superscript i stands for f, m or act according to the corresponding process. Gibbs activation energy is defined as $g^{\text{act}} = h^{\text{act}} - Ts^{\text{act}}$ where h^{act} and s^{act} are the activation enthalpy and entropy, respectively.

According to the rate theory, the relaxation time is given by

$$\tau(P, T) = (\lambda\nu)^{-1} \exp\left(g^{\text{act}}/k_B T\right) \quad (1)$$

where ν is the vibration frequency of the relaxing charge carrier, λ is a geometrical constant, g^{act} is the Gibbs activation energy for relaxation, T denotes the absolute temperature and k_B is the Boltzmann's constant. Differentiating Eq. (1) with respect to $(k_B T)^{-1}$, at constant pressure, we get

$$\left(\partial \ln \tau / \partial (1/k_B T)\right)_P = h^{\text{act}}. \quad (2)$$

To obtain the last equation, $\ln(\lambda\nu) + (s^{\text{act}}/k_B)$ is assumed as being constant indicating that Arrhenius behavior describes the temperature dependence of the relaxation time. Differentiating with respect to pressure at constant temperature, we have

$$\left(\partial \ln \tau / \partial P\right)_T = -\frac{\gamma}{B} + \frac{v^{\text{act}}}{k_B T} \quad (3)$$

where $\gamma \equiv -(\partial \ln \nu / \partial \ln V)_T$ is the Grüneisen constant (V denotes the volume) and $B \equiv -(\partial P / \partial \ln V)_T$ is the isothermal bulk modulus. For a Debye relaxation, the tangent loss angle function $\tan \delta \equiv \text{Im}(\epsilon) / \text{Re}(\epsilon)$ (where $\text{Im}(\epsilon)$ and $\text{Re}(\epsilon)$ are the imaginary and the real part of the (relative) complex permittivity ϵ (reduced to its value of free space)), exhibits a maximum at frequency $f_{\text{max, tan}\delta} = \sqrt{\epsilon_s / \epsilon_\infty} / (2\pi\tau)$, where ϵ_s and ϵ_∞ denote the static and high-frequency (relative) permittivity, respectively. The partial derivatives of the natural logarithm of the last relation with respect to reciprocal temperature and pressure, respectively, give

$$\left(\partial \ln \tau / \partial (1/k_B T)\right)_P = \frac{1}{2} \left(\partial \ln(\epsilon_\infty / \epsilon_s) / \partial (1/k_B T)\right)_P - \left(\partial \ln f_{\text{max, tan}\delta} / \partial (1/k_B T)\right)_P \quad (4a)$$

$$\left(\partial \ln \tau / \partial P\right)_T = \frac{1}{2} \left(\partial \ln(\epsilon_\infty / \epsilon_s) / \partial P\right)_T - \left(\partial \ln f_{\text{max, tan}\delta} / \partial P\right)_T. \quad (4b)$$

Combining Eq. (2) and Eq. (4a), as well as Eq. (3) and Eq. (4b) leads to

$$h^{\text{act}} = \frac{1}{2} \left(\partial \ln(\epsilon_\infty / \epsilon_s) / \partial (1/k_B T)\right)_P - \left(\partial \ln f_{\text{max, tan}\delta} / \partial (1/k_B T)\right)_P \quad (5a)$$

$$v^{\text{act}} = k_B T \left\{ \frac{\gamma}{B} + \frac{1}{2} \left(\partial \ln(\epsilon_\infty / \epsilon_s) / \partial P\right)_T - \left(\partial \ln f_{\text{max, tan}\delta} / \partial P\right)_T \right\}. \quad (5b)$$

We stress that the relations (4b) and (5b) presume an Arrhenius temperature dependence of τ (Varotsos and Alexopoulos, 1979;

Varotsos et al., 1993). Furthermore, we note that to a first approximation, when analyzing the experimental results, the term $(\partial \ln(\epsilon_\infty / \epsilon_s) / \partial P)_T$ in the right hand side of these two relations is neglected since it is small and comparable to the experimental error, as will be further explained in Section 4.

3. Experimental setup and the samples measured

We first describe the samples measured and then summarize the experimental setup.

3.1. Samples

Samples of polycrystalline calcite (CaCO_3), of approximately 2 mm thickness and parallel surfaces with an area of about 2 cm² were immersed (and keeping) in distilled water at 363 K for one week. Continuous weighting during the water-saturation process shows that saturation was achieved in two days. Water-saturation at elevated temperature has the advantage that the expansion of the specimen and the subsequent dilation of the pore cavities assist diffusion of water molecules. Weighting the sample before and after the wetting process determines the accommodated water within the hydrated rock at about 0.5 wt.% (Papathanassiou et al., 2011, 2012).

3.2. Experimental setup

The samples are placed inside the pressure vessel, which uses silicone oil as the pressure transmitting fluid, of a Novocontrol GmbH (Germany) high pressure apparatus operating from ambient pressure to 0.33 GPa and thermostated at the desired temperature, from room temperature to 373 K. Silver paste (Granville) was placed on the parallel opposite surfaces of the specimen to achieve good contact between the metallic electrodes and the sample. A very thin insulating layer of epoxy covered the specimen to prevent contamination from the pressure transmitting fluid. Jacketing with araldite has been suggested by the manufacturer of the pressure apparatus (Novocontrol, Germany; see Reisinger et al., 1997). The manufacturer of the pressure vessel suggested independently the use of epoxy layer in order to jacket the sample. The pressure system was connected with a Solartron impedance analyzer operating from 10⁻² to 10⁶ Hz while measurements in the frequency domain were monitored by a computer.

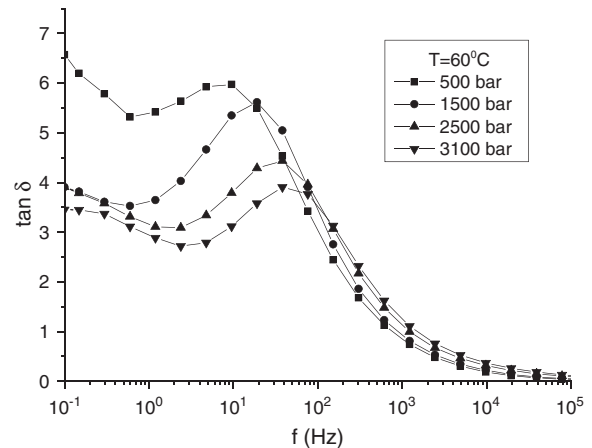


Fig. 1. Isotherms (333 K) of $\tan \delta$ vs frequency of as-received limestone at various pressures.

Download English Version:

<https://daneshyari.com/en/article/4740185>

Download Persian Version:

<https://daneshyari.com/article/4740185>

[Daneshyari.com](https://daneshyari.com)