

# Identification of dipole relaxation in LiF:Be<sup>2+</sup> crystals through piezostimulated depolarization currents

J Grammatikakis, M Manolopoulos and A N Papathanassiou

University of Athens, Department of Physics, Section of Solid State Physics, Panepistimiopolis, GR 157 84 Zografos, Greece

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## Abstract

The piezostimulated depolarization currents technique was applied to the study of the relaxation mechanisms in LiF crystals doped with Be<sup>2+</sup> impurities. By using different methods for the analysis of the experimental data, the migration volume  $v^m$  of a properly cleaned peak was determined. The resulting  $v^m$  value significantly exceeds the mean molecular volume.

## 1. Introduction

Twenty-five years ago, a method for the study of dielectric relaxation phenomena in solid insulators, analogous to that of thermally stimulated current, was proposed by Bui Ai *et al* [1]. This is the piezostimulated depolarization current (PSDC) method. Since then, only two publications (one exponential and another theoretical) have appeared concerning this method [2, 3]. To the best of our knowledge, the only experiment which was carried out, was on 6-polyamide [1].

In a series of papers [4–8], the thermally stimulated depolarization current (TSDC) technique was used to study LiF doped with different divalent cation impurities. This experimental technique, as well as that of the dielectric losses, is unable to unambiguously identify each relaxation peak. For LiF:Be<sup>2+</sup>, after a proper thermal pretreatment, a dominant relaxation mechanism, with activation enthalpy  $h^m = 0.31$  eV and pre-exponential factor  $\tau_0 = 8.9410^{-7}$  s, was found [4]. This was assigned to the nn→nn jumps of the cation vacancy, which is bound to the divalent impurity. However, the unreasonably large value of the pre-exponential factor remained an open question. In the present paper, the PSDC scheme was applied to LiF:Be<sup>2+</sup> and was aimed at providing additional information on the mechanisms involved, in comparison to the standard TSDC and dielectric losses method [9]. PSDC enables the experimental evaluation of the migration volume  $v^m$ , the activation energy  $E$  and the pre-exponential factor  $\tau_0$  of the Arrhenius-type relaxation time:  $\tau = \tau_0 \exp[(Pv^m + E)/kT]$ . In the latter expression, the quantity  $Pv^m + E$  corresponds to the activation enthalpy [9], i.e.  $h^m = Pv^m + E$ . Thus, under ambient conditions (i.e. ambient pressure) only  $h^m$  is approximately equal with  $E$ , because  $Pv^m \ll E$ .

In order to obtain additional information about the type of the aforementioned dispersion, we constructed a fully automated press transmitting the force to a high-pressure vessel

appropriate for electrical measurements in insulators and we performed PSDC experiments. The signals were analysed by computer, yielding the evaluation of  $E$ ,  $\tau_0$  and  $v^m$ . The quantities  $E$  and  $\tau_0$  may be used to identify the PSDC mechanisms corresponding to those that are present in the TSDC thermograms. At the same time,  $v^m$  gives evidence for the size of the rotating entities. We note that PSDC spectroscopy is advantageous with respect to the usual impedance spectroscopy measurements under pressure, due to its sensitivity, resolution and its capability of obtaining the abovementioned set of relaxation parameters from a single signal. We note that PSDC method is a promising technique which uses pressure as the thermodynamic variable.

## 2. Theory

The PSDC method [1, 2], is analogous to the TSDC method introduced by Bucci *et al* [10] where pressure or temperature are the independent variables, respectively; i.e., the PSDC method is an isothermal technique, while the TSDC method is an isobaric one. The experimental procedure in the PSDC method consists of the following steps [3, 9].

- (a) At pressure  $P$  and temperature  $T$ , an electric field is applied to the dielectric for a time  $t$  that is sufficiently long, relative to the relaxation time  $\tau(T, P)$ , to allow complete polarization.
- (b) The sample is subjected to a high hydrostatic pressure  $P_f$ , in order to reduce the mobility of the defects. Then the electric field is switched off.
- (c) The pressure is then reduced at a constant rate,  $b = dP/dt$ , while the temperature remains constant. The reorientation of the polarizable units on pressure reduction results in the depolarization current (the PSDC).

We assume that the polarization decays with first-order kinetics, according to

$$\frac{d\Pi}{dt} + \frac{\Pi(t)}{\tau(t)} = 0 \quad (1)$$

where  $\Pi$  is the polarization of the sample. Then the expression for the current density is ( $T = \text{constant}$ ):

$$j(t) = \frac{d\Pi(t)}{dt} = \frac{d\Pi(t)}{dP} \frac{dP}{dt} \quad (2)$$

or

$$j(P) = b \frac{d\Pi(P)}{dP} \quad (3)$$

where  $b = dP/dt$  is the constant value for the rate of the decrease of the pressure.

From the above relation, we have the following equation:

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

where the temperature  $T$  remains constant. As a consequence we have the polarization of the sample at any pressure  $P$  [3]:

$$\Pi(P) = \Pi_0 \exp \int_{P_f}^P -\frac{dP'}{b\tau(P')} \quad (4)$$

where  $\Pi_0$  is the value of  $\Pi$  corresponding to  $P = P_f$ .

Assuming an Arrhenius-type relaxation time,

$$\tau(P, T) = \tau_0 \exp \left( \frac{Pv^m + E}{kT} \right) \quad (5)$$

with  $v^m$  and  $\tau_0$  not depending on pressure, the current density finally becomes

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

where  $v^m$  is the migration volume for the reorientation process,  $E$  is the activation energy and  $\tau_0$  is the pre-exponential term of the Arrhenius-type relaxation time  $\tau$  [3].

The maximum ( $P_M, j_M$ ) of (6), and its inflection points ( $j_1, P_1$ ) and ( $j_2, P_2$ ), are determined whenever the following conditions hold [3]:

$$P_M = \frac{kT}{v^m} \ln\left(-\frac{kT}{v^m b \tau_0}\right) - \frac{E}{v^m} \quad (7)$$

and

$$j_M = -\Pi_0 b v^m / 2.718 kT \quad (8)$$

while

$$j_1 = -0.191 \Pi_0 b v^m / kT \quad \text{and} \quad j_2 = -0.260 \Pi_0 b v^m / kT. \quad (9)$$

Equations (7) and (8) hold, since the condition  $P_f v^m + E \gg kT$  is valid, in our experiments.

The analysis of a PSDC peak can be performed as follows.

- (a) Area method. In accordance with (1) and (3), for a constant temperature  $T$ , we have that  $[\tau(P)]_T = [\Pi(P)]_T / [j(P)]_T$ . The equation  $[\Pi(P)]_T$  can be determined by the area included between the  $j(P)$  curve, the considered pressure, and the end of the pressure decrease. Then the slope of  $[\ln \tau(P)]_T$  against  $P/kT$ , because of (5) gives the value of  $v^m$ .
- (b) Initial rise method. For  $P \approx P_f$  the current density (6) can reduce to

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

Then the slope of  $\ln j(P)$  against  $P$  determines  $v^m$ .

- (c) Maximum-current method. From equation (8) we have that  $v^m = -2.718 kT j_M / b \Pi_0$ , where  $\Pi_0$  can be obtained from the total area within the limits of the current and the pressure axis.
- (d) Inflection-points method. The calculation of  $v^m$  can be made with the help of equation (9).
- (e) Curve-fitting method. Exploiting the curve  $j(P)$  against  $P$ , by means of a three-parameter computer program, we can evaluate  $v^m$ ,  $\tau_0$  and  $E$ .
- (f) Exact solution. The condition for the maximum depolarization current in PSDC is [9]

$$\frac{bv^m}{kT} = -\frac{1}{\tau(P_M, T)}. \quad (10)$$

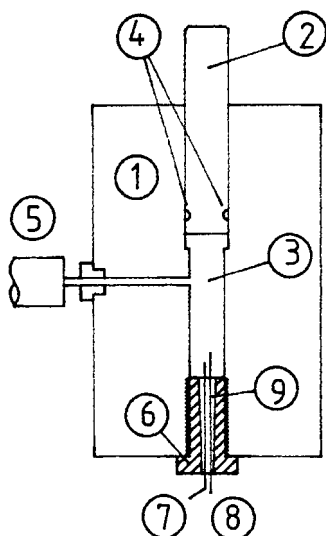
After inserting (7) into (6), and taking into account the above condition we get

$$j_M = -\frac{\Pi_0 b v^m}{kT} \exp\{\exp[-(P_f - P_M)v^m/kT] - 1\}. \quad (11)$$

The above equation can be solved with the aid of a computer program for  $v^m$  to the desired degree of accuracy.

### 3. Experimental details

The high-pressure experiments were carried out in a pressure vessel, composed of a stainless-steel cylinder and a stainless-steel piston (figure 1). Inside the cylinder there is a cylindrical concentric cavity filled with the pressure transmitting fluid (Vitrea-46 oil, Shell). A high-pressure Teflon–copper O-ring, placed on the piston, prevents leakage of the oil. A sensitive pressure sensor (sensor GM pressure transducer) was rigidly fixed in the cylinder, communicating with the pressure chamber through a narrow tunnel. Opposite the piston a steel screw served as the sample holder. The central steel electrode and the chromal–alumel thermocouple pass through a conical tunnel, filled with an araldite casting. The pressure was generated by a fully automated press, developed in our Laboratory. The desired pressure rate was monitored by a computer system. The signals from the pressure sensor and the electrometer were digitized. The system could operate in the pressure range 0–3500 bar. A system of valves maintained the stress exerted on the piston and therefore the hydrostatic pressure inside the pressure chamber constant. By manual control we succeeded in any constant rate of pressure increase or decrease, from  $0.1 \text{ bar s}^{-1}$ . The temperature variation throughout the decrease of the pressure with a constant rate  $1 \text{ bar s}^{-1}$  was no more than 2 K.

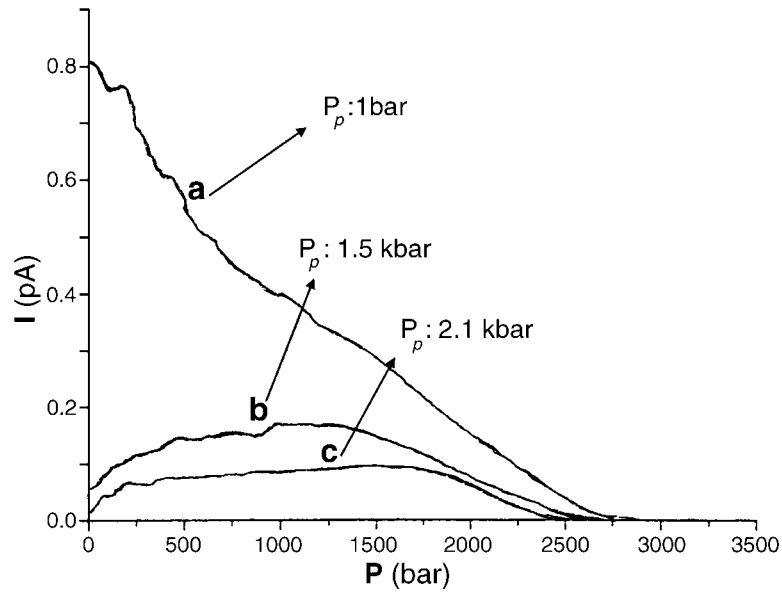


**Figure 1.** Schematic drawing of the hydrostatic pressure vessel. 1, steel pressure vessel; 2, steel piston; 3, pressure chamber; 4, high-pressure O-ring; 5, pressure sensor; 6, sample holder; 7, thermocouple; 8, central electrode; and 9, araldite seal.

The sample's dimensions were  $0.5 \times 0.7 \text{ cm}^2$  in area and it was 0.1 cm thick. The large sample faces were painted with conductive resin; two electrical leads, one for each surface of the sample, were attached to these faces. The first was then fixed to the central hot electrode and the other to the screw, which was in contact with the grounded steel bomb.

The samples were monocrystals of LiF doped with  $\text{Be}^{2+}$ , in a nominal concentration of 50 ppm. They were grown at the Crystal Growth Laboratory, University of Utah.

We note that no thermal pre-treatment [4] was followed before the measurements reported in this study.



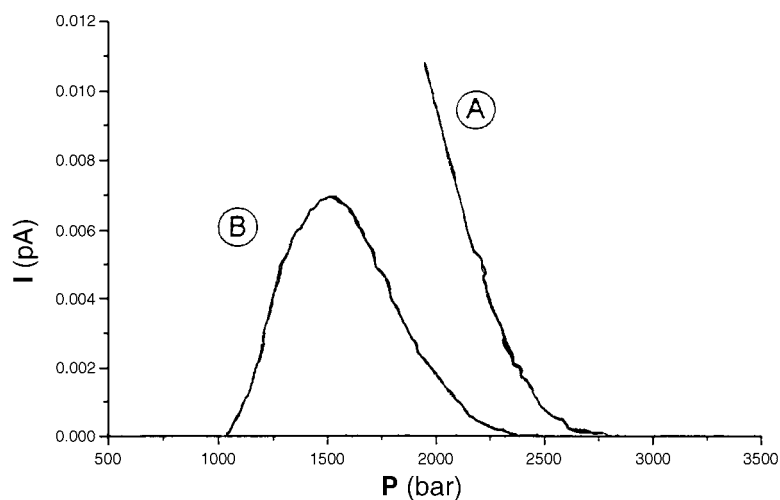
**Figure 2.** Three spectra from the same sample polarized at different pressures. The other conditions were  $T_p = 302$  K,  $E_p = 10$  kV cm<sup>-1</sup> and  $b = -1$  bar s<sup>-1</sup>.

#### 4. Results and discussion

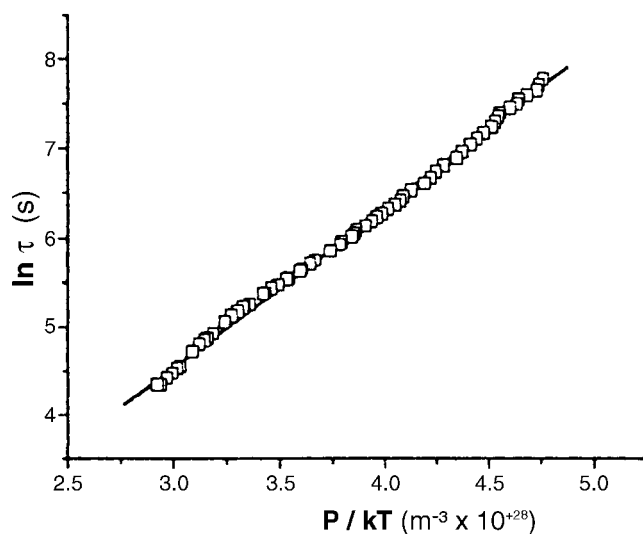
In figure 2 typical piezocurrent plots of a LiF:Be<sup>2+</sup> sample are shown. The sample (figure 2, curve a) was polarized at 302 K, for 10 min at atmospheric pressure, under the application of an external field intensity of 10 kV cm<sup>-1</sup>. Then, under the application of the field, the pressure was increased up to 3500 bar. At this pressure the field was switched off. The rate of the decreasing pressure was kept constant and equal to  $-1$  bar s<sup>-1</sup>. After that we reduced the pressure exerted on the sample. At 2750 bar, the current starts increasing and maximizes at atmospheric pressure.

By polarizing the sample at different pressures, and keeping the other parameters constant we observe a decrease of the maximum current  $I_M$ , while  $P_M$  is shifted to higher values (figure 2, curve b and c). It is obvious that the proper selection of the polarizing pressure  $P_p$ , and the intensity of the electric field  $E_p$ , combined with proper cleaning methods, can isolate one or more mechanisms. Having this in mind we polarized the sample at  $T = 303$  K for 10 min, at  $P_p = 2400$  bar. The polarization conditions were  $E_p = 10$  kV cm<sup>-1</sup> and  $b = -1$  bar s<sup>-1</sup>. In order to achieve efficient cleaning we combined the above conditions with the partial depolarization method. According to this technique, common to the TSDC method but applied for the first time to PSDC, a scan is performed up to about the maximum of the peak, which is followed by an increase of the pressure and, at last, a subsequent scan [11]. In figure 3, curve A is the first scan (i.e. the unfinished scan) and curve B is the last scan. The characteristics of the peak are  $P_M = 1496$  bar and  $I_M = 0.007$  pA.

The Arrhenius plot of the peak is drawn in figure 4. The linear relation of  $\ln \tau$  against  $P$ , attests the good cleaning of the peak, and the fact that (6) describes it. For the migration volume the result  $v^m = 1.801 \times 10^{-28}$  m<sup>3</sup> is obtained. From equation (8), since  $\Pi_0 = 1.2552 \times 10^{-7}$  C m<sup>-2</sup> (obtained from the area enclosed under the peak), we find that  $v^m = 1.800 \times 10^{-28}$  m<sup>3</sup>.

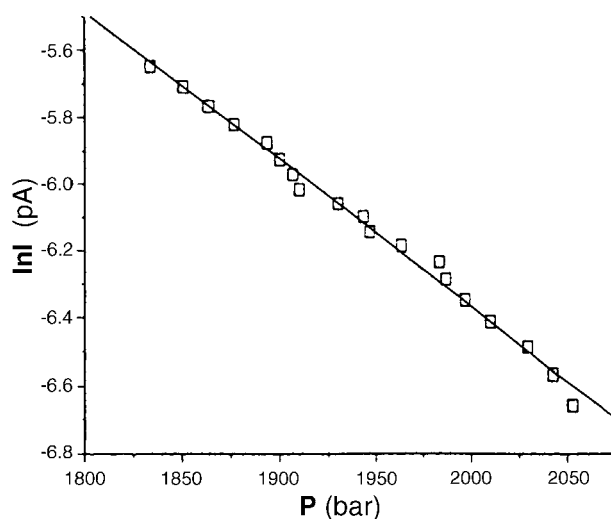


**Figure 3.** Partial depolarization method. The sample was polarized at  $T = 303$  K for 10 min at  $P_p = 2400$  bar and with  $E_p = 10$  kV cm $^{-1}$ ;  $b = -1$  bar s $^{-1}$ . Curve A is the first scan (i.e. unfinished) and the curve B is the last scan.



**Figure 4.** The Arrhenius plot of the peak with maximum at 1496 bar.

The value of  $v^m$  can be also estimated with the help of inflexion points. Since the position on the curve of the inflexion points is sometimes difficult to determine, we can use in addition the sign of the second derivative of  $j(P)$  by means of a computer program. The pressure points where the sign of  $j''(P)$  changes are the inflexion points. Keeping all these in mind, we find that  $i_1 = 0.00323$  pA and  $i_2 = 0.00536$  pA. Thus  $v^m = 1.616 \times 10^{-28}$  m $^3$  from the first inflexion point and  $v^m = 1.970 \times 10^{-28}$  m $^3$  from the second. The slope of  $\ln j(P)$  against  $P$  determines  $v^m$  (figure 5) and results in the value of  $v^m = 1.847 \times 10^{-28}$  m $^3$ . Finally the exact-solution method gives  $v^m = 1.798 \times 10^{-28}$  m $^3$ .



**Figure 5.** The initial-slope method for the peak of figure 4.

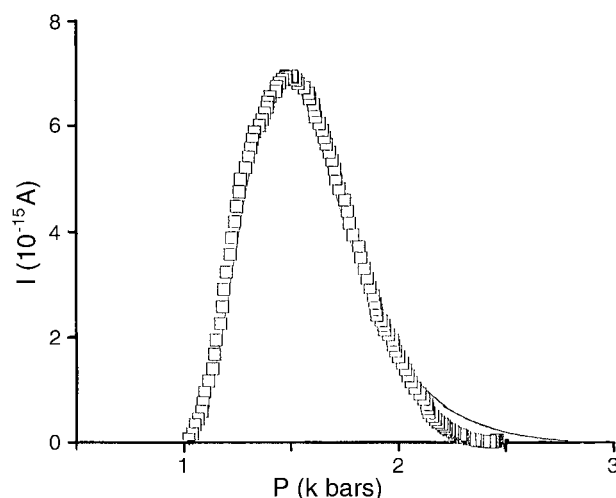
**Table 1.** Values of  $v^m$  obtained by exploiting different methods of analysis.

Method	$v^m (\times 10^{-28} \text{ m}^3)$
Area method	1.801
Maximum current	1.800
Inflexions points	
left	1.616
right	1.970
Initial rise	1.847
Exact solution	1.798
Full curve fitting	1.801

A collection of the results for  $v^m$  (table 1), indicates a small deviation of the inflexion-points method from the mean value of the rest. Notice that the position of the inflexion points on the curve is rather difficult to determine due to experimental uncertainty.

Using equation (6) and the experimental results, by means of a computer fitting, we find:  $\tau_0 = 2.8610^{-6} \text{ s}$  and  $E = 0.31 \text{ eV}$ . The good agreement between the experimental curve and the computer fitting can be seen in figure 6. The latter depicts the peak at  $P_M = 1496 \text{ bar}$  (open squares), and the theoretical PSDC peak (full curve) was obtained with the following values:  $\tau_0 = 2.86 \times 10^{-6} \text{ s}$ ,  $E = 4.966 \times 10^{-20} \text{ J}$  (0.31 eV),  $v^m = 1.801 \times 10^{-28} \text{ m}^3$ ,  $b = -1 \text{ bar s}^{-1}$ ,  $T = 303 \text{ K}$ ,  $P_f = 3.1 \times 10^8 \text{ Pa}$  (3100 bar) and  $\Pi_0 = 1.2552 \times 10^{-7} \text{ C m}^{-2}$ .

If  $\Omega$  denotes the ‘mean molecular volume’ of LiF, then we find  $v^m / \Omega = 40$ , i.e. two orders of magnitude greater than that expected, if the mechanism was attributed to reorientation of  $IV$  dipoles [4]. Such large values of  $v^m$  could be attributed to the relaxation phenomena associated with extended defects, such as dislocations. An alternative explanation could be the following. In view of the fact that  $\text{Be}^{2+}$  is only half the size of Li host cation, it will most likely occupy off-centre positions [12]. Various detailed studies [13, 14] showed that pressure can strongly change the reorientational tunnelling and the dipole moment for off-centre defects. Within such a frame, pressure-induced off-centre  $\rightarrow$  on-centre transitions of defects will surely be present, which could offer, in principle, an explanation for the large values of  $v^m$  determined



**Figure 6.** Experimental (open squares), and the theoretical PSDC peak (full curve) for the mechanism at  $P_M = 1496$  bar.

here. Such an explanation, however, faces the difficulty that the aforementioned transitions follow relationships different from a single Arrhenius type. In order to resolve this point more experiments are needed on the PSDC spectrum, which should also include the study of the influence of the thermal pre-treatment described in [4].

## 5. Conclusions

The PSDC method was applied to the  $\text{LiF}:\text{Be}^{2+}$ . The computer analysis of the signals permits the evaluation of the activation energy, the pre-exponential factor and the activation volume. A large value of the activation volume was obtained, i.e.  $v^m/\Omega = 40$ , which cannot be explained by the rotation of simple  $IV$  dipoles. It could be attributed either to relaxation phenomena associated with extended defects such as dislocations or to volume changes related to pressure-induced off-centre  $\rightarrow$  on-centre transitions, because, in view of its small ion size,  $\text{Be}^{2+}$  could occupy an off-centre position.

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