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Significance of considering pellet molding pressure and dielectric experimental conditions in the [dielectric constant—temperature] response of switchable dielectric molecular materials: illustration on dabcoHBF₄ polycrystals

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ABSTRACT

In this study, we investigate the temperature-dependent dielectric response of dabcoHBF₄ molecular switchable dielectric materials. This compound made of polycrystals has been shaped into pellets under different controlled applied pressures [0.2–1 GPa]. The dielectric analysis carried out on these samples showed that the mechanical stresses induced by this shaping pressure had a significant effect on the value of the dielectric constant in both the ferroelectric and the paraelectric phase. However, the impact of this pressure remains secondary in the AC electrical conductivity, determined for the first time in these compounds. Thus, conductivity values around 2×10^{-7} S/cm in the ferroelectric phase and 2×10^{-6} S/cm in the paraelectric phase were found. The behavior of these compounds over wide frequency ranges [1–1 MHz] and temperature ramps [0.5–10 K/min] revealed that the frequency had no effect on the transition temperature at the difference of temperature rate as expected in most ferroelectric materials. When decreasing the frequency, the dielectric constant gains in value and can reach values higher than 50 in the ferroelectric phase and 1000 in the paraelectric phase with a frequency solicitation at 10 Hz. At lower frequencies, the Curie–Weiss law is lost in the paraelectric regime and an enhanced rise of the dielectric constant with increasing temperature probably reflects an interfacial polarization mechanism. Finally, this dielectric analysis in frequency, temperature (323–403 K) and along temperature ramps allowed to extract analytical laws of behavior associating some of these parameters. For example, one of these equations will be useful in the choice of the temperature ramp to be applied to optimize the switching time between a ferroelectric and a paraelectric state according to a condition on the value of the desired dielectric constant at the low and high states in the implementation of memories.

Introduction

Recently, molecular switchable dielectric compounds have received considerable attention as functional electric materials potentially envisioned for application in the field of molecular electronics (memories), energy harvesting, phase shifters, data communications, and so on [1–6]. These systems, mostly made of cationic/anionic pair of molecules, exhibit a solid–solid structural phase transition: at the molecular scale, the switching between low and high dielectric states originates from motional change of the polar counterpart occurring at the vicinity of the transition temperature T_c : below T_c , the ionic building blocks are fully ordered within the crystal network, resulting in a poorly polarizable material while above T_c , the degrees of freedom gained by the disordered molecules allows an easy orientation of the local dipoles when an electric field is applied, resulting thus in a large variation of the permittivity. Researchers worldwide have made great efforts to synthesize and investigate switchable dielectrics, and many interesting materials have been described, ranging from the (serendipity-found)

isolated molecules to the more sophisticated (host–guest) systems [7–9]. Even if a lot of progress have been achieved, much remains to be done for a deeper understanding on the intrinsic mechanism driving the dielectric switch and to make it suitable for applicative purpose, in order to integrate such materials as active element in commercial devices. 1,4-diazabicyclo[2.2.2]octane (dabco) reacted in various acid solutions is a candidate of interest for memories and high- ϵ dielectrics due to its ease of processing, non-toxicity and switchable dielectric properties [10–12]. Dabco has long been used as a compound in various applications. Recent interests are for instance like a pillar ligand in metal–organic framework for supercapacitors [13], a catalyst and surfactant in biomass castor oil-based rigid polyurethane foams [14], a structure-directing agent for the synthesis of new indium selenides by solvothermal synthesis [15], it is one of the components of an ion exchange membrane for lithium-ion batteries [16] and a new catalyst combined with nanoparticles [17, 18]. The ability of [dabcoH] $^+$ A $^-$ (with A $^-$ standing for tetrahedral anions) to be a ferroelectric switchable dielectric molecular material has recently opened a new focus on applications related to information storage (memory) due to its bistability in terms of dielectric constant value. The ferroelectric character of dabcoH $^+$ -related materials, the capability of mixing it with polymer matrices and the ability to develop large-scale crystals have accentuated a research dynamic in its use for smart devices and especially in its potential for non-volatile memories [1, 19–23]. The understanding of the polarization mechanisms in [dabcoH] $^+$ A $^-$ inherent to these simple molecular structures has been the subject of intense research over the last twenty years to better appreciate the phenomena at the origin of the identified phase transitions. Within this series of molecular dielectric switch materials, dabcoHBF $_4$ (A $^-$ is in this case corresponding to BF $_4^-$) published by Katrusiak and Szafranski twenty years ago [24], stands as the most widely studied and continues to be of interest [25–29], as depicted recently as potential candidate for non-volatile memories [19], eventually mixed in a polymer matrix for such application [20]. While most of published studies focus on single crystal (through an accurate crystal-oriented analysis of dielectric analysis), few works describe the studies of molecular dabcoHBF $_4$ processed as pressed pellets. Especially, none examined the pellets molding pressure effect on the [dielectric constant–temperature] response in the ferroelectric–paraelectric regions. This molding pressure can cause mechanical stresses affecting the dielectric response of the compounds. In this way, we present here a complete dielectric re-investigation of dabcoHBF $_4$ with a special emphasis devoted to the effect of pellet molding with pressure ranging from 0.2 to 1 GPa. This study is supplemented by a dielectric analysis of the behaviour of dabcoHBF $_4$ according to the external parameters (excitation frequency, temperature ramp) applied to it in order to evaluate their importance in the [dielectric constant–temperature] response.

Materials and methods

The title compound dabcoHBF $_4$ was synthesized according to adapted previously published procedure by the molar to molar reaction of (1,4-diazabicyclo[2.2.2]octane) (dabco, purchased from Acros) and tetrafluoroboric acid (48 wt. %, Acros) in a 1:1 molar ratio at room temperature. After 10 min stirring and complete dissolution of dabco in water diluted acidic solution, white single crystals were easily grown by slow evaporation of the mixture after few days. The pellets were fabricated using a ca. 100 mg amount of crystalline powder placed into a 1.1 cm diameter anvil, then pressed during 2 min with a manual hydraulic press affording up to 12 tons constraint and sample thickness of ca. 0.5 mm. The pellets were pressed at 0.2, 0.4, 0.6, 0.8 and 1 GPa. Finally, the pellets were sputtered using a Quorum Techno QT150 TES sputter coating affording a 200 nm gold thick deposit on both side. The bottom electrode diameter is 0.9 cm while the upper electrode (0.5 cm) was surrounded by a guard ring (diameter

0.8 cm, width 0.2 cm) in order to ensure the uniformity of the electric field and limit bypass currents (although the e/D ratio (thickness/electrode diameter) is here already small, thus providing reliable measurement). Dielectric measurements were acquired with a Novocontrol high performance frequency analyser under $1V_{\text{rms}}$ alternative voltage ranging from 1 Hz to 1 MHz. This voltage amplitude enables to preserve a sound signal-to-noise ratio for measurements at the lowest frequencies and we made sure that the applied electric field (around 20 V/cm) was low enough not to disturb the response of the material in the ferroelectric—paraelectric transition. For this purpose, point measurements were conducted at voltages of 0.05 V (1 V/cm electric field) that confirmed, as expected, the absence of effect of the applied AC voltage in our experimental conditions. Temperature scans ranged from 0.5 to 10 K/min. Contact with sample electrodes was achieved through micro-positioner metallic tips. The heating plate connected with a Linkam temperature controller was electrically isolated from the sample by a 0.2 cm thick AlN substrate covered with a thin layer of copper on both side. In order to check the sample purity and confirm the temperature transitions following the scanning temperature solicitation, dynamic scanning calorimetry (DSC) was carried out on a Metler Toledo DSC1/500/2412 under a nitrogen atmosphere.

Results and discussion

The behavior of the dielectric constant versus temperature at a frequency of 1 MHz and with a positive temperature slope of 10 K/min is reported in the Fig. 1 for pellets processed at pressures from 0.2 to 1 GPa.

At a given pressure, an expected temperature-dependent dielectric response is observed. A Curie temperature T_c of 380 ± 1 K is identified. Values of T_c around 378 K were obtained in crystal dabcoHBF_4 [24, 30]. Our slight shift on the T_c value is related to the temperature slope adopted to scrutinize the dielectric constant as will be seen later in the paper. For $T < T_c$, the material is ferroelectric (orthorhombic phase) and for $T > T_c$, it is paraelectric (tetragonal phase) [24]. As a consequence of a displacement of BF_4^- anions and dabcoH^+ cations, a spontaneous polarization is established as well investigated by Katrusiak, Szafranski and co-workers [24, 27]. At increasing temperature, when approaching T_c , the twisting of dabcoH^+ cations and the moving of BF_4^- anions are breaking the crystalline symmetry and are thus at the origin of the clearly observed ferroelectric—paraelectric transition. It was demonstrated that fluctuations of the BF_4^- anions occur as early as $T_c - 60$ K, thus inducing a change in the polarization mechanism around 320 K [24], explaining the slight increase of the dielectric constant from the ferroelectric phase with the rising temperature, as clearly observed in Fig. 1. These ionic movements from their equilibrium position will lead to instability of the material when increasing more the temperature and will cause it to tilt into a disordered state as soon as T_c is reached. The temperature-dependent dielectric behavior in the paraelectric phase follows the expected Curie–Weiss law.

The amazing result observed in Fig. 1 relates to the significant effect of the pressure applied in the pellet making process on the dielectric-temperature response of the material. The general shape of the dielectric response as a function of temperature is maintained, but the value of the dielectric constant is all the more important as the pellets have been more strongly pressed. We can therefore claim that mechanical stress induced on the dabcoHBF_4 powders by this molding pressure has an appreciable impact on the [dielectric constant—temperature] response. A slight decrease in T_c is also observed when increasing pressure (381 K@0.2GPa vs 379 K@1GPa). This increase in the dielectric constant with pressure behaves quasi-linearly in both the ferroelectric and the paraelectric phase (see inset of Fig. 1: a linear-dependence of the dielectric constant ϵ' vs pressure P : $\epsilon' = aP + b$ is observed with $a_{@353\text{ K}} = 6.61$, $b_{@353\text{ K}} = 5.96$, $a_{@403\text{ K}} = 20.9$, $b_{@403\text{ K}} = 12.6$). The steeper linear slope in the paraelectric phase is a

way to express that more strongly mechanically pressed pellets will induce a higher ‘order–disorder degree’ within the material if one defines this ‘order–disorder degree’ as the dielectric constant difference $\Delta\epsilon'$ between the well-established paraelectric and ferroelectric phases. This finding seems consistent with the shift of T_c depending on the pressure as a ferroelectric material with more oriented dipoles will have a higher electrostatic energy and at the same time the system will be potentially more unstable [31]: a transition to a lower T_c is thus expected.

To explain the increase in the dielectric constant with the pressure required to manufacture the pellets, several hypotheses can be stated and the most evident hypothesis is to consider that air cavities are present between the pressed grains. The increase in pressure will lead evidently to a decrease of these air cavities and the global tendency of the dielectric constant will be to an increase of its value with the pressure. This is indeed the trend that we observe, but can we consider that the presence of air has a significant impact on this dielectric constant? To do this, let’s have a look at the value of the dielectric constant obtained at 0.2 GPa, which corresponds to a moderate pressure to manufacture pellets. The obtained dielectric constant in the ferroelectric phase is $\epsilon'_{@353\text{ K}} = 6.8$. This value is fully within the range of those obtained on a dabcoHBF₄ crystal (so no air voids) [24], thus excluding the influence of air cavities in the dielectric values obtained in our study. To definitively rule out this hypothesis, as shown in the inset of Fig. 1, obtaining values of dielectric constants increasing linearly beyond the values observed in a crystal cannot be explained by a simple effect of reduction of the air pores between the crystals constituting the pellet.

In the study of the dielectric properties of ceramics, and more generally of powders to be shaped into pellets, the interface effects between the grains can constitute an essential part of the dielectric response [32]. Interfacial polarizations, more or less accentuated by specific surface area in contact are of importance. In Fig. 1, our results are presented at 1 MHz and typically interfacial polarization affects the dielectric constant at lower frequencies. Besides, an increase in pressure reduces both interfaces and the potential interfacial polarization at the grain boundaries. A decrease in the contribution of the dielectric constant value induced by the interfacial polarization is therefore expected with increasing pressure. This is indeed what is observed for example in work of Meng-Meng and co-workers relating to pressure pellet influence on the dielectric properties of titanium compound/polymer composite nanofibers [33]. Similarly, a significant effect of pellet pressure on the dielectric response occurred at lower frequencies below kHz on sol–gel prepared Bismuth titanate ceramics [34]. The opposite trend observed in our work therefore excludes this possibility. Strong local mechanical interactions at the grain boundaries during pellet production could possibly favor local preferential crystal orientations but these orientations will relax once the mechanical stress is removed. It thus seems unlikely that the grain boundaries are at the origin of the changes observed on the dielectric constant according to the mechanical stress induced by the manufacturing pressure of the pellets.

Having ruled out the most probable hypotheses external to the bulk of the crystals, other hypotheses are to be sought. It is well-known that dielectric properties of materials are strongly dependent of internal mechanical stress inside the material. Particularly, phonon mean free path and especially soft mode phonon will be conditioned by tensile or compression strains, thus changing the high-frequency polarization and consequently the dielectric constant at optical frequencies. Undoubtedly, the pressure applied to manufacture pellets will induce such local mechanical strains inducing changes in the high-frequency dielectric response. As our experiments are made not higher than 1 MHz, the measured dielectric constant value integrates already such possible high-frequency dielectric values

changes. However, it appears difficult to investigate this hypothesis within the scope of our study. Even if the shift in T_c is consistent with this suggestion, it is difficult to answer here whether, once the mechanical constraint is relaxed, the influence of the soft mode is also relaxed.

The AC conductivity σ' extracted from dielectric measurements can provide information on dynamics of charges inside dabcoHBF_4 (Fig. 2a). Values around $2.9 \cdot 10^{-7}$ S/cm are thus noted in the ferroelectric orthorhombic phase. In paraelectric tetragonal phase, this conductivity increases by a tenfold. Increased mobility of BF_4^- anions induced by thermal excitation in the paraelectric phase and the moving of H^+ protons through thermally assisted hopping conduction could explain this increase in AC electrical conductivity. It is observed that when increasing pellet pressure, conductivity increases but this trend is no longer true at higher pressures and the change from 0.8 to 1 GPa shows a decrease in σ' . This finding is particularly clear in the paraelectric phase. However, as reported in Fig. 2b, one can approximate with a good accuracy the global shape of σ' as a function of pressure by a power law in both the ferroelectric and paraelectric phase. This one-decade increase in conductivity between the orthorhombic and tetragonal phases is valid for each pellet processing pressure, thus indicating a negligible effect of the processing mechanical stress on the crystal structure of the material. It is, however, complex at this stage to evaluate the effect of local mechanical stresses induced in the compound on the electrical conductivity. The loss factor σ'' against pressure (Fig. 2c) is in tune with the changes in ac conductivity σ' . Loss factor is representative of dipolar relaxation added with a conduction mechanism if exists. The electrical conductivity values measured are in the range of those obtained in the conjugated polymers. Consequently, at the difference of strongly insulating materials where the loss factor reflects mainly the relaxation mechanisms induced by polarization mechanisms, here the AC conductivity will take a significant part in the loss factor response and explains the good correspondence between the loss factor and AC conductivity trends. The dissipation factor $\tan\delta$ versus pressure (Fig. 2d) is corresponding to the ratio of ϵ'' over σ' , and represents dissipative energy induced by polar relaxations in the material. As previously discussed, this dissipation factor is well representative of the dielectric relaxation phenomenon when the electrical conductivity has only a minor role, which is not the case here. A lowering of the conductivity σ' (Fig. 2a, b) and a reduction of dielectric losses (Fig. 2c) at highest pressure for the manufacture of pellets is benefit for applications where it is intended to develop both high dielectric constant (Fig. 1) and weak dissipation factor (Fig. 2d) insulating materials for high-k capacitors for example.

The results presented in Figs. 1 and 2 show that the 1 GPa pellet has the highest dielectric constant and the lowest dielectric losses: it is therefore interesting for applications and this is the reason why it was chosen for the continuation of this study. Figure 3a illustrates the dielectric constant ϵ' change as a function of temperature for different solicitation frequencies at $1V_{\text{rms}}$ applied. The temperature ramp is 10 K/min. The solid/dashed lines correspond to the measurement during the temperature rise/drop. At a given frequency, a hysteresis is clearly observed in the temperature switching between rising and falling temperatures. This behavior is expected for this material and it is representative of a first order phase transition [26, 35]. Then, it can be noticed that the temperature switching (up and down) is not affected by the excitation frequency. This result is explained by the fact that the physical mechanism at the origin of the ferroelectric—paraelectric switching has no reason to be modified by the frequency: whatever the frequency,

same polar species are involved with the change in temperature and according to the same kinetics. In contrast, the excitation frequency has an importance in the value of the dielectric constant at a given temperature: with the lowering of the frequency, a strong increase of the dielectric constant is consistently observed in both ordered and

disordered phase. The decrease in frequency allows more time for the dipoles to orient themselves in the direction of the electric field before the frequency alternating changes sign. It may therefore be advantageous to introduce dabcoHBF₄ in host polymer matrices for energy storage or recovery applications working in low frequencies such as those encountered in the harvesting of ambient mechanical energy to produce electricity [36, 37]. At the lowest frequencies (10 Hz but especially 1 Hz), one observes that the Curie–Weiss behavior trend is lost in the paraelectric phase. In this phase, at 1 Hz we even notice a significant increase in the dielectric constant with increasing temperature. The explanation is to be sought in an interfacial (space charge) polarization mechanism. Even if it is difficult to assert the interfaces involved in this mechanism, we can assume that the anions have time to migrate to the limits of the polar nanoregions introduced in [27], inducing this interfacial polarization. However, this hypothesis remains difficult to confirm and localized defects could also be susceptible to such space-charging mechanisms. The last observation we can make relates to the dielectric constant strength jump (dielectric strength $\Delta\epsilon'$) between paraelectric and ferroelectric step which differs according to the excitation frequency: the lower the frequency, the greater the $\Delta\epsilon'$ value, as clearly observed in Fig. 3b. Except for lowest frequencies (where space-charge polarization takes place, as just discussed), the $\Delta\epsilon'$ —frequency trend obeys to a power law (see Fig. 3b for equation). This power law is first of all of interest to estimate the gain in the value of the dielectric constant during the ferroelectric—paraelectric transition for excitation frequencies not experimentally tested. In addition, the power exponent of this law can be used, for example, as a standard value to evaluate ‘the degree of order–disorder’ in the transition temperature response: a higher coefficient will reflect a higher sensitivity of the material to a change in frequency, which in turn will result in a more significant effect on the polar dynamics of species involved in the phase change. Inset in Fig. 3b presents such effect of the power exponent simulated in the range -0.36 ± 0.1 .

While frequency is a usual input parameter used in memory control applications or for tuning electronic devices, the applied temperature rate also could constitute an input parameter of importance for this control for temperature sensible materials. In this context, we have considered the dielectric response of the dabcoHBF₄ to temperature gradients of $\pm 0.5 \text{ Kmin}^{-1}$ to $\pm 10 \text{ Kmin}^{-1}$ (Fig. 4a). It is clearly observed that the temperature sweep rate has a very significant influence on the dielectric response of the material, not in the well-established ferroelectric and paraelectric phases but during the initiation of the phase change in both directions (ferro\–[para): the higher the scan speed S , the larger the temperature hysteresis window ΔT , as reported in Fig. 4b. A linear fit approximates this trend well overall (see equation in Fig. 4b): with a rate of 0.5 K/min, it will take 5 min to go through the 2.5 K allowing to go from one state to the other. With a ramp of 10 K/min, this switching time will be reduced to about 40 s, time necessary to execute a temperature variation of about 7 K. We can thus find an optimum ramp in the temperature of the material to optimize the switching time between the ferroelectric and the paraelectric state. These results are consistent with the thermal activation importance of the mechanisms at the origin of the phase transition as confirmed by the DSC spectra obtained for different scanning speeds (inset of Fig. 4b).

Conclusion

This dielectric spectroscopic analysis of polycrystals of dabcoHBF₄ shaped in pellets revealed several results. The mechanical stresses induced by the pellet molding pressure have a well-identified impact on the dielectric response of the compound. This parameter must therefore be clearly specified in any study requiring the shaping of powders for a dielectric study. The physical mechanisms involved after applying this mechanical stress remain

difficult to identify in the context of our study. The standard hypotheses of reduction of the inter-grain cavities have been excluded to explain this dependence. We speculate a possible soft mode effect but this suggestion is only one lead to be explored among others.

A possible modulation of the dielectric constant value in the ferroelectric and paraelectric well-established phases according to the pellet processing pressure provides an additional interest to properly control and use this pressure regarding an application that can incorporate a pellet made of a switchable dielectric compound.

The transition temperature remains little impacted by the pellet processing pressure and a slight shift toward lower temperatures is observed with molding pressure increase. For a more detailed analysis of this trend; however, it would be necessary to also conduct these studies with lower temperature rates in order to have a material in a more established steady state.

The AC conductivity obeys in a power law as a function of the molding pressure both in the ferroelectric and in the paraelectric phases. However, this processing pressure does not seem to play any role in a possible change of the conductivity during the phase transition (whatever the chosen processing pressure, the increase of the conductivity between the ferroelectric and the paraelectric phase remains equal to a tenfold). From our work, we extracted an AC conductivity value of the order of 2×10^{-7} S/cm in the orthorhombic ferroelectric phase. This conductivity is of the order of 2×10^{-6} S/cm in the tetragonal paraelectric phase.

The frequency of the applied signal has a large effect on the dielectric constant value in both the ferroelectric and paraelectric phase. High dielectric constant values are reached at the lowest frequencies investigated (between 50 and 100 in ferroelectric phase and over 1000 in paraelectric phase). The transition temperature is not affected by the frequency of solicitation of the compound. This information is interesting as generally the studies on this type of material are carried out at frequencies higher than a few kHz and rarely the choice of the frequency of measurement is justified. By focusing only on the physical phenomena associated with this phase transition, the choice to remain on high frequencies will be the right one to gain both measurement time and signal-to-noise ratio. Finally, and as expected, the temperature ramp will affect the dielectric response at the phase transition since the mechanisms involved in this phase transition are thermally assisted. Thus, the temperature spread on the value of the hysteresis of the [dielectric constant—temperature] characteristic in the transition phase goes up with a higher temperature slope. A linear relationship between this temperature range and the applied temperature ramp is identified.

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Figure 1 Dielectric constant as a function of temperature (+ 10 Kmin⁻¹) for pellets pressed at 0.2, 0.4, 0.6, 0.8 and 1 GPa. Dielectric measurements performed at 1 MHz. Inset: Dielectric constant as a function of pressure at isothermal 353 and 403 K (dashed line: linear fitting of curves).

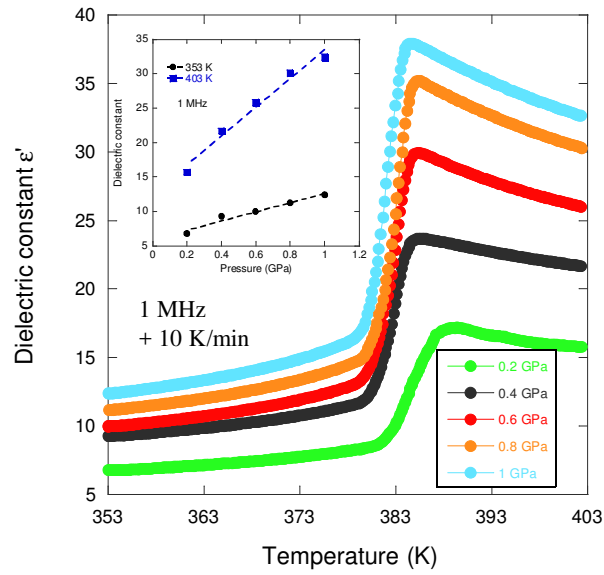


Figure 2 a, b Alternative (ac) conductivity σ' vs temperature T and pressure P. c Loss factor ϵ'' vs T and P. d Loss tangent $\tan\delta = \epsilon''/\epsilon'$ vs T and P. Frequency 1 MHz. Temperature slope: 10 K/min.

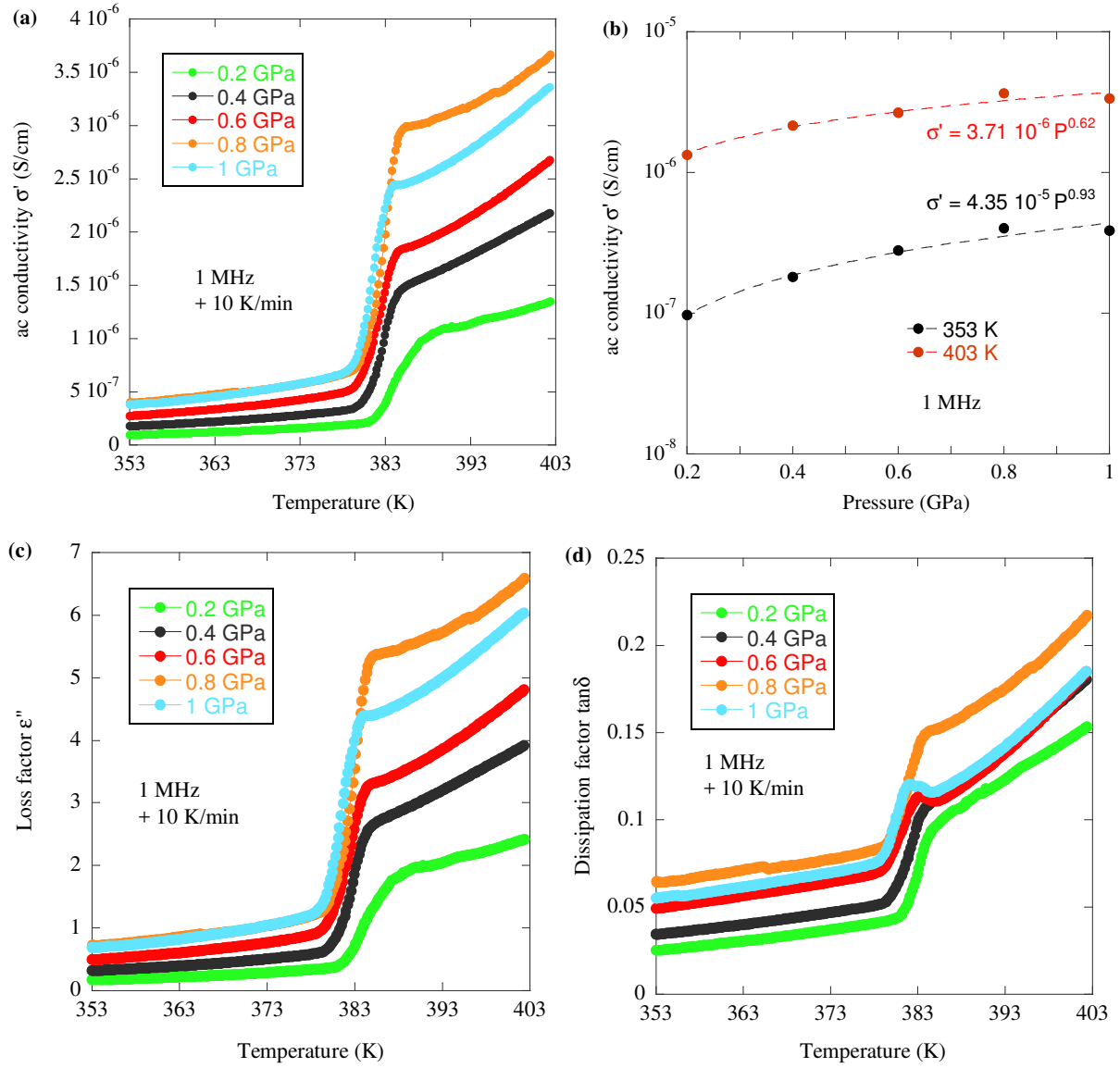


Figure 3 a Dielectric constant ϵ' vs temperature: influence of the frequency excitation of the signal. b dielectric strength $\Delta\epsilon'$ of the phase transition. b Inset Simulation of the influence of the power exponent on the dielectric strength. Pressure: 1 GPa. Scan speed: 10Kmin⁻¹.

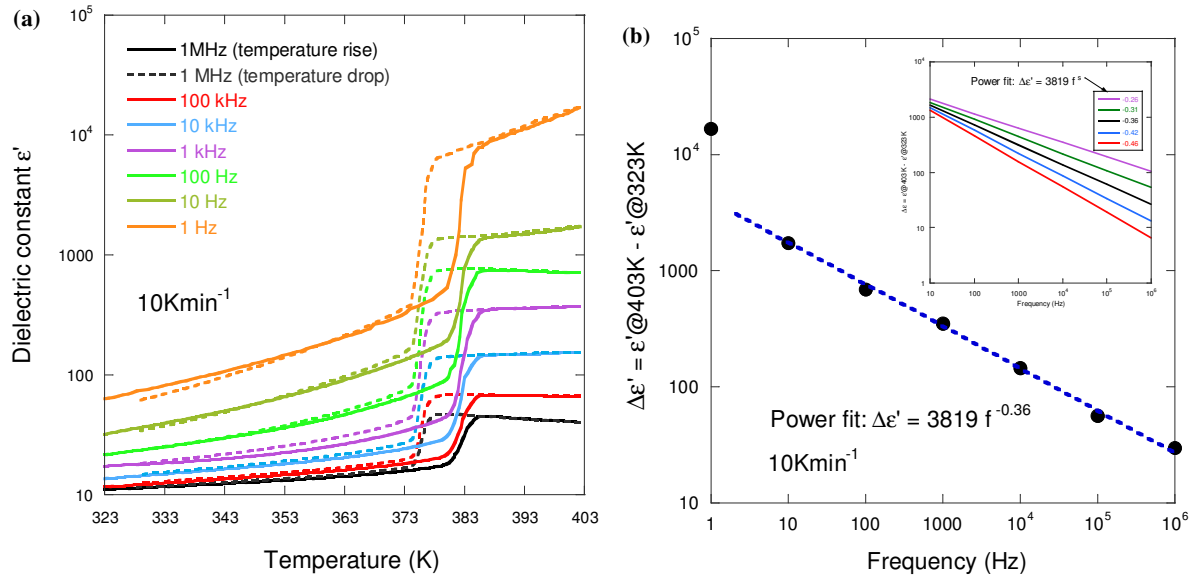


Figure 4 a Dielectric constant ϵ' vs temperature: influence of the scan speed S . b Temperature hysteresis window ΔT (extract from a for $\epsilon' = 25$) vs the scan speed. b inset DSC spectra vs the scan speed S .

