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Aging in strontium–calcium titanate crystals

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Abstract. The complex dielectric constant $\varepsilon'(\omega, t)$ of the orientational glass $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ (SCT) with $x = 0.0055$ was measured as a function of time at 4.2 K, for frequencies ranging from 1 kHz to 1 MHz, after different thermal histories. Both the in-phase component ε' and the out-of-phase component ε'' clearly exhibit aging as shown by the cooling rate dependence of their evolution. Moreover, a weak dependence has been seen for the asymptotic values of both components at very long time. Hence, evidence exists for ergodicity breaking. This is in contrast to what was seen for spin glasses, and similar to what was observed for the series $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$ (KLT) of orientational glasses studied previously. However, when temperature jumps are imposed on the SCT sample, the response differs both from that of spin glasses and from that of the KLT series.

1. Introduction

Aging is a phenomenon that has known of for a long time. For instance, the relaxation of the strain, after a mechanical stress is applied, and then switched off, has been studied at length for a large number of glasses, polymers, and various other materials [1]. In particular, it has been shown that the residual strain depends not only on the time t elapsed since the stress was switched off, but also on the waiting time t_w during which the sample was submitted to the stress. From these experiments, scaling laws were deduced, showing that the ratio t/t_w is the relevant parameter of the relaxation. However, for the materials studied, the characteristic times are so long that the asymptotic limits for physically infinite times could not be evaluated. Therefore the question of the dependence of the equilibrium state on the initial conditions of the relaxation was not answered.

Aging has also been observed in systems with charge-density waves [2, 3]. However, the most extensive studies on aging were done on spin glasses [4–8]. Here a magnetic field is applied over the period of time t_w , and the relaxation of the magnetization is measured as a function of time t . In this case too, the important parameter is the reduced time t/t_w . Measurements of the out-of-phase component $\chi''(\omega, t)$ of the magnetic susceptibility were also achieved. Here too a scaling was found: the variable ωt allows one to put all of the data on a unique master curve [9]. Temperature cycle experiments give additional information on the structure of the phase space [8–10]. However, it seems that no dependence of the

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equilibrium state on the (thermal or magnetic) history of the samples could be inferred from any of these experiments.

In order to put the question of the uniqueness (or lack of it) of the equilibrium state in an unambiguous framework, we have adopted the following definition: a system which tends towards the same equilibrium state, independently of the initial conditions, is said to be ergodic; a system for which this is not the case is said to be non-ergodic. We adopt this definition of ergodicity breaking throughout this paper. Accordingly, there is no evidence of such ergodicity breaking in spin glasses.

Recently, the kinetics of the complex elastic and dielectric constants $c(\omega, t)$ and $\varepsilon(\omega, t)$ were studied for the family $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$ (KLT) of orientational glasses [11, 12]. In these disordered and frustrated compounds, evidence was provided for the important role of the thermal history of the samples: the form of the relaxation and the equilibrium value of the in-phase components $c'(\omega, t)$ and $\varepsilon'(\omega, t)$ clearly depend on the cooling rate or the quenching temperature. These features are, following our definition, the signatures of aging and ergodicity breaking. Here too, temperature cycle experiments give complementary insight into the structure of the phase space [11, 12]. Unfortunately, the elastic and dielectric losses are weak in these compounds; as a consequence, if aging was qualitatively observed for the out-of-phase components $c''(\omega, t)$ and $\varepsilon''(\omega, t)$, its smallness prevented any quantitative measurements. All of these experiments were done on the same family of tantalate crystals. Therefore, it is of interest to speculate on whether these properties are shared with other types of material.

In the present paper, we report on experiments on the kinetics of a $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ (SCT) crystal in which calcium atoms are randomly substituted for strontium atoms. The Ca^{2+} ions mainly occupy Sr^{2+} sites, but alternatively some of them may be located at Ti^{4+} sites, forming an O^{2-} vacancy [15]. The SCT crystal belongs to a titanate series known to provide orientational glasses. The pure crystal SrTiO_3 (ST) undergoes near 105 K an antiferrodistortive phase transition from a high-temperature cubic phase to a low-temperature tetragonal phase. Pure ST is a quantum paraelectric, and the occurrence of a so-called ‘quantum coherent’ state in this material below 40 K has been recently reported [13, 14]. For temperatures lower than 10 K, the zero-point fluctuations hinder the onset of a ferroelectric state, and for $T < 4$ K a saturation of the dielectric constant takes place. Above the critical concentration $x_c = 0.0018$, the temperature dependence of the real part ε' of the dielectric constant measured along the cubic [100] direction in the mixed crystals $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ presents a broad maximum for a temperature T_{max} increasing with x ; this behaviour is interpreted as the onset of a transition to a ferroelectric domain state [15]. A systematic analysis of $\varepsilon'(T)$ in SCT shows that the Barrett parameters [16] are clearly modified by the Ca content. The values obtained for the fitted parameters in the Barrett formula allow one to trace the boundary of the low-temperature quantum paraelectric regime. This boundary occurs for a value of x between 0.0058 and 0.0110 [17]. This analysis also provided evidence for the existence of polar nanoregions for temperatures lower than $T_{\text{max}} + 5$ K, in good agreement with the results obtained from the study of Raman diffusion [18]. In spite of the detailed study reported for the complex SCT system, the role played by the calcium ions in the host lattice is not yet understood—in particular the anomalous non-linear dielectric behaviour [19].

For a crystal of the SCT series we have measured the time dependence of the complex dielectric constant $\varepsilon(\omega, t)$ at several frequencies, focusing our attention on the asymptotic (equilibrium) limits, extrapolated for infinite time. For this crystal the loss is larger than for the KLT series, and we were able to get, in addition to quantitative data on the in-phase component $\varepsilon'(\omega, t)$, semi-quantitative data on the out-of-phase component $\varepsilon''(\omega, t)$.

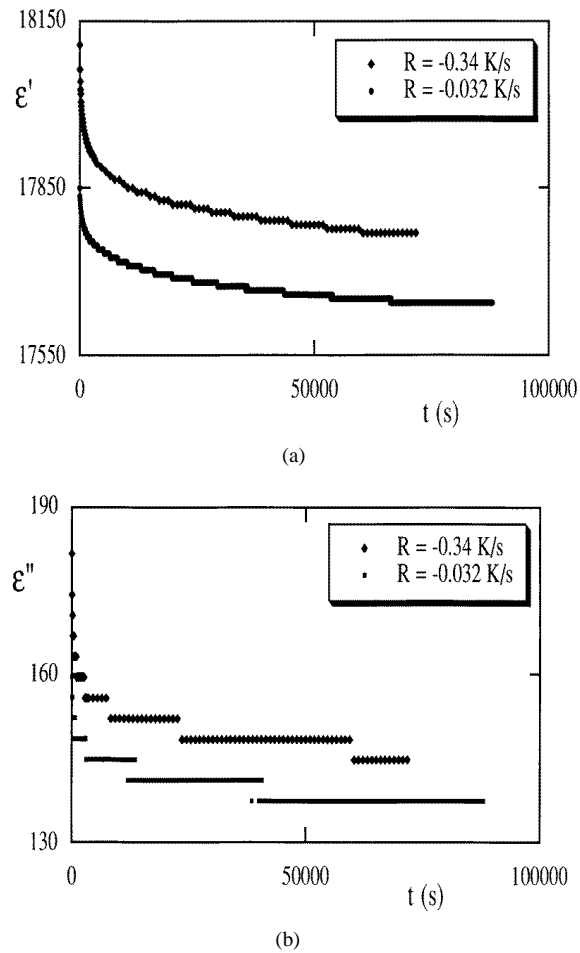
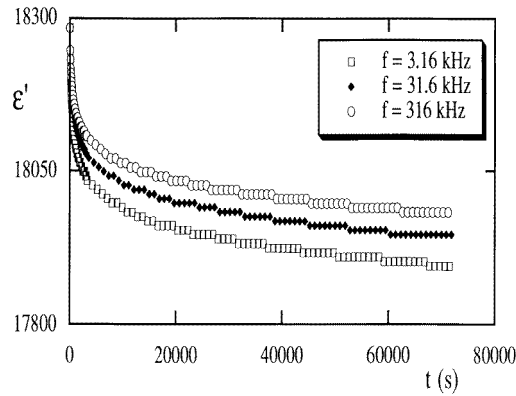


Figure 1. The variation with time of the complex dielectric constant of a $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ sample with $x = 0.0055$ after zero-field cooling at different rates, drawn without any shift. The data were recorded at $T = 4.2$ K with the a.c. field at $f = 31.6$ kHz. (a) The real part ϵ' recorded after cooling at the rates $R = -0.34$ K s $^{-1}$ (upper curve) and $R = -0.032$ K s $^{-1}$ (lower curve). (b) The imaginary part ϵ'' recorded after cooling at the same rates.

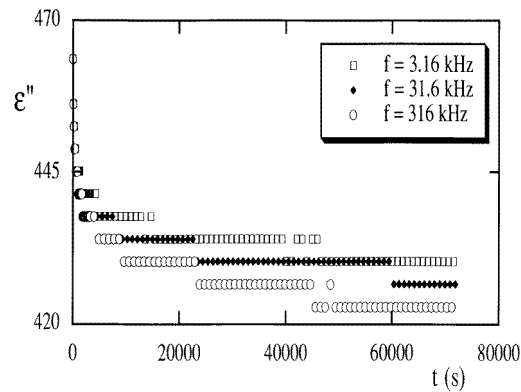
Therefore, the responses to cooling at different rates and to temperature jumps furnish a complete set of information on aging and possible ergodicity breaking for this orientational glass.

2. Experimental data

In the present study we have used a sample with $x = 0.0055$ which shows a maximum in $\epsilon'(T)$ at $T_{\text{max}} = 18.1$ K. According to the results of [15], this sample behaves like a quantum ferroelectric. The sample was cut into a parallel-plate shape perpendicular to the cubic axes, and the major faces were electroded by gold vapour deposition. No particular care was taken to avoid the onset of a multidomain state below the tetragonal phase transition temperature [20]. By the means of a Hewlett–Packard 4192A impedance



(a)



(b)

Figure 2. The time evolution of the dielectric constant measured at $T = 4.2$ K for several frequencies: $f = 3.16$ kHz (open squares), $f = 31.6$ kHz (full diamonds), and $f = 316$ kHz (open circles). (a) The real part ϵ' . (b) The imaginary part ϵ'' . The two scales for the dielectric constant are relative to the lowest frequency. The other data sets are vertically shifted in order that the initial data points of the curves coincide. The dispersive character of the relaxation is clearly evident.

analyser, we have simultaneously measured the electric capacitance and the dielectric losses at seven frequencies ranging from 1 kHz to 1 MHz. They are easily transformed into the real part (or in-phase component) ϵ' and the imaginary part (or out-of-phase component) ϵ'' of the complex dielectric constant $\epsilon = \epsilon' - i\epsilon''$. In order to prevent spurious effects, we have carefully used the same procedure for each of our experimental runs. For all of our experiments the oscillating field was equal to $E = 200$ V m $^{-1}$ at all of the measuring frequencies; no biasing electric field was applied; the duty rate of the impedance analyser was kept constant; and the sample was heated at $T = 40$ K for ten minutes before cooling. For these conditions, the data are reproducible. We were able to cool the sample at quasi-constant cooling rates $R = dT/dt$ ranging from $R = -0.01$ K s $^{-1}$ to $R = -0.34$ K s $^{-1}$. As is usual for this type of experiment, any systematic effect was ruled out by randomly choosing the order of the values of R . Every measurement lasted typically 20 hours.

Figure 1(a) shows the time dependence of ϵ' , measured at $f = 31.6$ kHz and $T = 4.2$ K, after cooling at different rates; ϵ' decreases over time. Obviously, the faster the cooling

rate, the larger the ε' -value and the larger the difference between the initial and the final values. The time dependence of ε'' at the same frequency, after cooling at the same rates, is shown in figure 1(b); ε'' too decreases over time.

From the comparison of the relaxation curves recorded for the same conditions, at different frequencies, we deduce that the evolving part is dispersive at any temperature $T \geq 4.2$ K. The two components have opposite behaviours in our frequency range: for the in-phase component, the lower the frequency, the larger the amplitude of the evolution (figure 2(a)); this is reversed for the out-of-phase component (figure 2(b)).

An important point is the description of the shape of the relaxation curves. This was easily achieved for KLT by the means of simple functions of the form $\varepsilon'(\omega, t) = A + Bf(t)$ where $f(t)$ is a decreasing function starting from 1 at $t = 0$ and tending towards 0 as t goes to infinity. In that case [11], the best overall fit, selected by the least-squares method, was given by the power law $f(t) = ((t + t_0)/t_0)^{-\alpha}$ with $0 < \alpha < 1$. Things are not so simple for SCT, since overall fits are not good with such functions: the rapid beginning of the relaxation does not comply with this scheme. Indeed, in this case a better fit is obtained using the sum of a slowly varying function and a rapidly vanishing function which goes to zero in a few thousand seconds. However, this complexity is not too serious a difficulty as regards our main aim, which is the study of the dependence of the very-long-time behaviour on the cooling rate. Therefore, we have used the following procedure: we have discarded from our data set those values recorded during the first ten thousand seconds, and then we have tried several (slowly varying) functions [12], selecting the best one by means of the Levenberg–Marquardt least-squares method [21]. The criterion used here is that of obtaining the least value of the merit factor Q defined as

$$Q = \left(\frac{1}{N} \sum_{i=1}^N (F_i - M_i)^2 / \Delta^2 \right)^{1/2}$$

with

$$\Delta^2 = \frac{1}{N} \sum_{i=1}^N \left[M_i - \left(\frac{1}{N} \sum_{i=1}^N M_i \right) \right]^2.$$

In these equations, the N numbers M_i are the measurement data and the N numbers F_i are the values of the fitting function calculated at the same time; the normalization constant Δ makes the merit factor Q dimensionless. Typical values of Q are around 5×10^{-2} .

In fact, two functions provide fits to the in-phase component with equivalently good

Table 1. Values of the asymptote ε'_∞ leading to the best fit for the power law and the stretched exponential for a $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ sample with $x = 0.0055$. The measuring frequency was $f = 10$ kHz and the temperature was $T = 4.2$ K. From left to right: cooling rate R (in K s^{-1}), and the dimensionless asymptotes ε'_∞ for the power law and the stretched exponential, respectively.

Cooling rate R (K s^{-1})	Power law ε'_∞	Stretched exponential ε'_∞
−0.34	17 800	17 780
−0.11	17 750	17 730
−0.032	17 670	17 640
−0.010	17 550	17 380

quality. They are the stretched exponential

$$\varepsilon' = A' + B' \exp(-((t + t_0)/\tau)^\gamma) / \exp(-(t_0/\tau)^\gamma)$$

and the power law

$$\varepsilon' = A' + B'((t + t_0)/t_0)^{-\alpha}.$$

The former is slightly better, but it contains five free parameters while the latter has only four. This is, in principle, an argument in favour of the power law. In any case, the asymptotes provided by the two functions coincide within a relative accuracy better than 5×10^{-3} . These data are given in table 1 together with the corresponding cooling rate.

For the out-of-phase component, owing to the lower accuracy, we have attempted an independent fit; we have just checked that the two functions

$$\varepsilon'' = A'' + B'' \exp(-((t + t_0)/\tau)^\gamma) \exp(-(t_0/\tau)^\gamma)$$

and

$$\varepsilon'' = A'' + B''((t + t_0)/t_0)^{-\alpha}$$

agree with the experimental data if we impose on the parameters t_0 , α , τ , and γ the values found for the in-phase component, and we only adjust the parameters A'' and B'' .

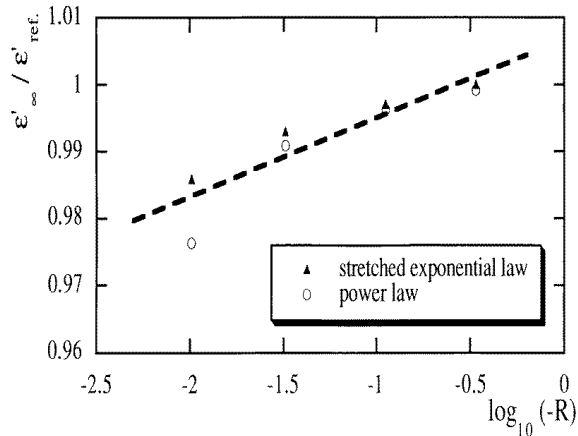


Figure 3. The reduced asymptotic value ($t \rightarrow \infty$) of the real part ε' of the dielectric constant as a function of the logarithm to the base 10 of $|R|$. The data were recorded at $T = 4.2$ K with the a.c. field at $f = 10$ kHz.

The role of the cooling rate is of fundamental importance here. Different cooling rates result in different initial conditions, and, therefore, the dependence of the limit $\varepsilon'_\infty = A'$ on the cooling rate R gives the most striking evidence of non-ergodicity. Figure 3 shows the reduced asymptotic values for the two fitting functions. The two values corresponding to the same value of R are close to each other; hence we have every confidence in them. 'Reduced values' means that the outcomes ε'_∞ of the fits are divided by the largest one. They are plotted as a function of $\log_{10}(|R|)$. Ergodicity breaking manifests itself by a representative line with a slope not equal to zero. It is seen that there is a weak effect. The effect has the same sign as it has for KLT [12]: the asymptote ε'_∞ increases when the cooling rate becomes faster. Its magnitude is close to that obtained for a KLT sample with a lithium concentration $x = 0.011$: a relative variation of ε'_∞ of about 10^{-2} over one decade of cooling rate.

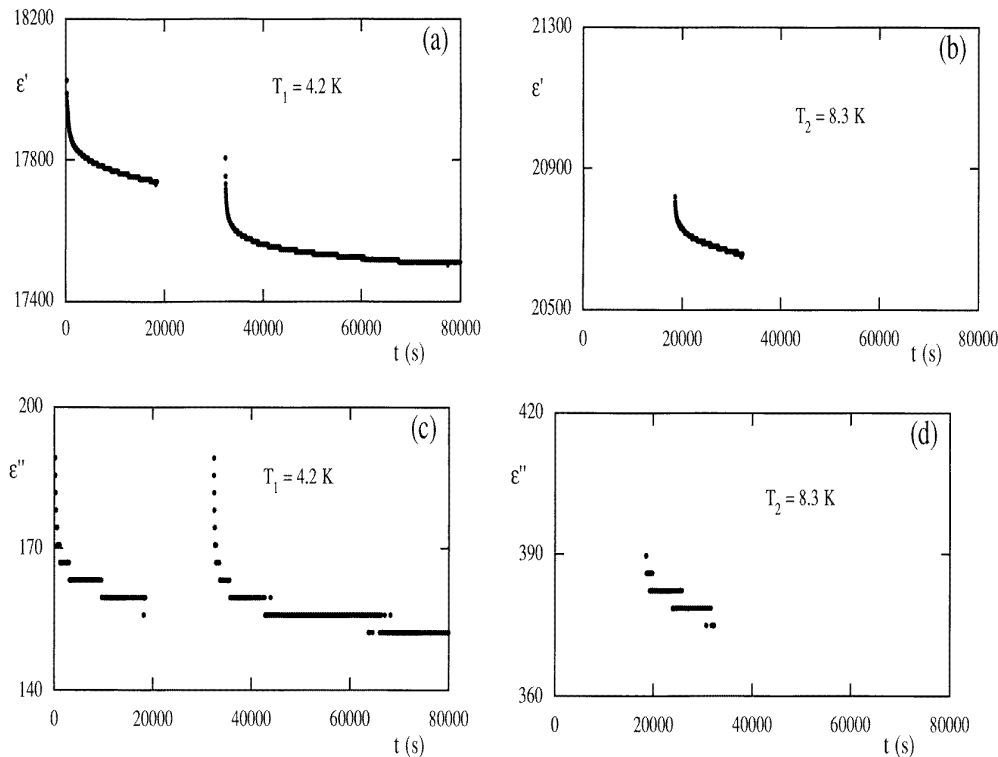


Figure 4. The time evolution of the complex dielectric constant for a positive temperature cycle ($T_1 \Rightarrow T_2 \Rightarrow T_1$) where $T_1 = 4.2$ K and $T_2 = 8.3$ K, measured with the a.c. field at $f = 31.6$ kHz. (a) ϵ' at T_1 ; (b) ϵ' at T_2 ; (c) ϵ'' at T_1 ; (d) ϵ'' at T_2 .

In order to get supplementary information, we have performed temperature cycles: the evolution at temperature T_1 is first recorded; then the temperature is suddenly changed to T_2 and the evolution is recorded; finally the temperature is suddenly brought back to T_1 and the ultimate evolution is recorded. Such a procedure had already been used for spin glasses [10] and KLT [11, 12]. Figures 4(a), 4(b), 4(c), and 4(d) show the values of ϵ' and ϵ'' for experiments with $T_1 < T_2$ (the positive cycle), while figures 5(a), 5(b), 5(c), and 5(d) show the values of ϵ' and ϵ'' for experiments with $T_1 > T_2$ (the negative cycle). During the first period (at temperature T_1), the behaviours are similar in the two cases: ϵ' and ϵ'' tend towards their equilibrium values which depend on the temperature T_1 and thermal history. The second period (at temperature T_2) begins with jumps and ends with opposite jumps, flanking relaxational evolutions. The two types of cycle differ in their further evolutions.

(i) If $T_1 < T_2$, the evolution strongly restarts in the third period (at temperature T_1), and leads to an asymptotic value of ϵ' (and possibly for ϵ'' too) lower than that of the first period (see figures 4(a) to 4(d)); this feature favours ergodicity breaking.

(ii) If $T_1 > T_2$, during the third period (at temperature T_1), ϵ' and ϵ'' obviously tend towards asymptotic values different to those predicted when fitting the first-period relaxation (see figures 5(a) to 5(d)). As a consequence, the third part cannot be put, by means of a backward translation parallel to the time axis, onto the curve extrapolated from the first part. This is in contrast with the remarkable property observed both for spin glasses [8–10] and KLT [11, 12].

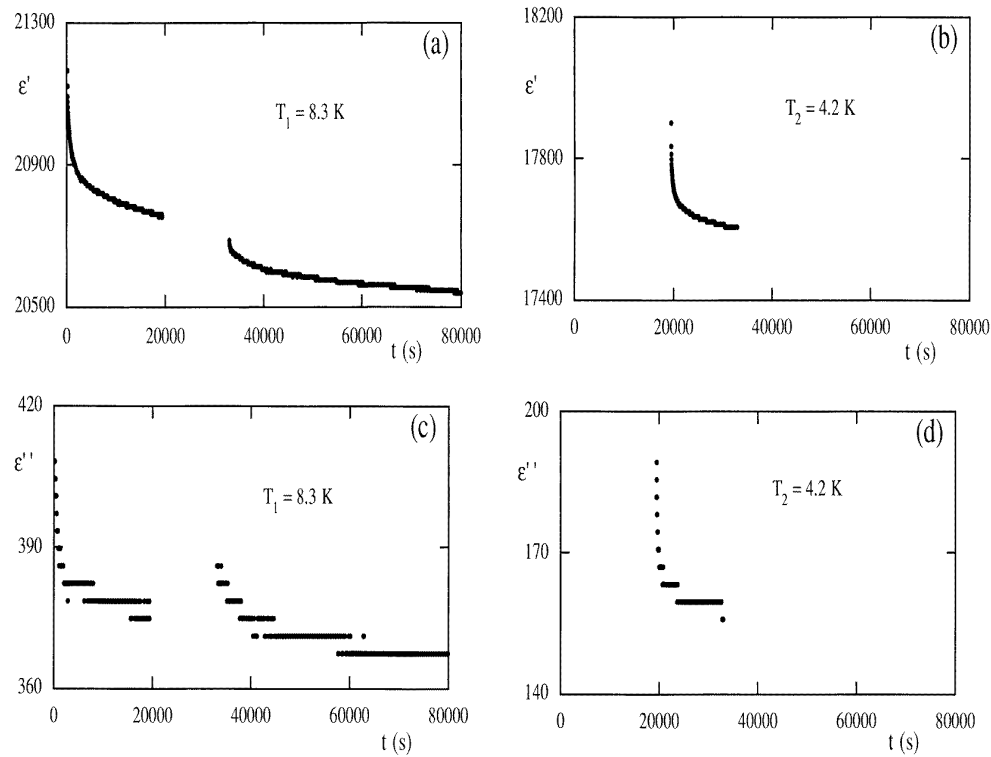


Figure 5. The time evolution of the complex dielectric constant for a negative temperature cycle ($T_1 \Rightarrow T_2 \Rightarrow T_1$) where $T_1 = 8.3$ K and $T_2 = 4.2$ K, measured with the a.c. field at $f = 31.6$ kHz. (a) ϵ' at T_1 ; (b) ϵ' at T_2 ; (c) ϵ'' at T_1 ; (d) ϵ'' at T_2 .

3. Analysis

In order to discuss the present data in a general context, we first recall some results obtained for spin glasses and orientational glasses.

Aging is a phenomenon currently observed in spin glasses. It is also observed in other disordered and frustrated systems such as $K_{1-x}Li_xTaO_3$ (KLT). However, there are differences between these two kinds of material. The most important difference is the ergodicity breaking for KLT, evident from the dependence of the equilibrium state on the thermal history, while there is no such measurable effect for spin glasses. On the other hand, the time-dependent part of aging in KLT depends on frequency in a way that is not simple: there is no dispersion at all at 4.2 K, but it becomes strong on approaching the transition temperature. Nevertheless, no scaling was found, while for spin glasses a master curve is obtained with the variable ωt .

Concerning the temperature cycles, we first recall the results for the magnetic susceptibility χ of spin glasses [10] and those obtained for KLT [11, 12]. It is sufficient to consider just the third period.

(i) If $T_1 < T_2$, for spin glasses, the susceptibility χ'' tends towards the same asymptote as in the first period, while for KLT, ϵ' tends towards a new and lower asymptote. These two results explain why ergodicity breaking is observed for KLT, while it is not seen for spin glasses. In the latter case, the sojourn at T_2 has annealed the sample and changed its

thermal history.

(ii) If $T_1 > T_2$, χ'' and ϵ' tend respectively towards the same asymptotic values predicted when fitting the first-period relaxation. More precisely, for both spin glasses and KLT, it is possible to put the two parts of the curves recorded at T_1 onto the same relaxation curve, after a translation along the time axis.

This may be explained in the framework of the phase space [10–12], if it is assumed that it is hierarchically organized. This means that the organization in valleys separated by free-energy barriers at a given temperature T_a is transformed upon cooling to T_b in such a way that new and smaller valleys (daughter valleys) and barriers appear in every ancient valley (mother valley) present at T_a . In this scheme, the behaviour during negative cycles (then $T_1 = T_a$ and $T_2 = T_b$) is easily described. The evolution during the first and the third parts occurs in the landscape of large valleys, while the evolution during the second part is among the small valleys. Upon heating back to T_a , the daughter valleys merge into their common mother valley, and the relaxation at T_b is nearly cancelled. In other words, the sojourn at $T_2 = T_b$ has not fundamentally changed the thermal history of the sample. In particular, if the second period (at T_2) does not change the asymptote (at T_1), this means that the energy barriers between the mother valleys are high enough to prevent relaxing jumps at T_2 . In an analogous manner, the behaviour during positive cycles (then $T_1 = T_b$ and $T_2 = T_a$) may be explained. However, a supplementary hypothesis has to be made in order to explain the difference between spin glasses and KLT. In the first case this may be due to some similarity between the mother valleys. This similarity seems absent in the second case; for that reason the asymptote is changed by the sojourn at $T_2 = T_a$.

What can be said for SCT? The positive ($T_1 < T_2$) temperature cycle gives information (small ergodicity breaking [22]) compatible with that from the experiments after cooling at various rates. For the negative ($T_1 > T_2$) temperature cycle, the influence of the second period is specific (i.e. different for spin glasses and KLT). It may possibly be accounted for, in the scheme of the hierarchically organized phase space, by the smallness of the energy barriers. This is coherent with the dispersion observed in SCT at any temperature $T \geq 4.2$ K, which means that relaxation times $\tau \approx 1/\omega$ exist.

4. Conclusion

Our dielectric measurements done on a $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ crystal with $x = 0.0055$ have provided two main results.

Firstly, clear evidence for aging is provided by the dependence of the relaxation on different thermal histories realized by cooling at different rates. This aging is observed both for the real part and for the imaginary part of the complex dielectric constant. Moreover, it appears that this aging results in a small degree of ergodicity breaking. Therefore, our initial aim is reached: ergodicity breaking (as defined in classical mechanics) is not just a property of the singular and unique KLT series; a compound belonging to another series shares this property. From this result, it may be thought that disorder and frustration are necessary conditions for non-ergodicity.

Secondly, the response of SCT to temperature cycles is very complex.

(i) For positive cycles, it corresponds to an annealing, a behaviour coherent with ergodicity breaking.

(ii) For negative cycles, it is different for the spin glasses and the orientational glass KLT. This may be explained by differences between the energy barriers which split the phase space into more or less separated valleys.

In any case, a microscopic theory has still to be provided. One idea which deserves attention was already invoked for KLT [12]; indeed, it was suggested that the kinetics observed at low temperatures for KLT could be associated with polar domains. These domains are forerunners of the ferroelectric transition actually aborted by the quantum thermal motion, the growth of which is hindered by the static random fields generated by frozen Li^+ ions. A similar assumption could possibly be adapted to SCT.

Acknowledgments

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