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2007 J. Phys.: Condens. Matter 19 102201

(http://iopscience.iop.org/0953-8984/19/10/102201)

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J. Phys.: Condens. Matter **19** (2007) 102201 (6pp) doi:10.1088/0953-8984/19/10/102201

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Extremely slow time evolution of the order parameter under an electric field in relaxor $K_{0.97}Li_{0.03}TaO_3$

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Received 27 November 2006
Published 15 February 2007
Online at stacks.iop.org/JPhysCM/19/102201

Abstract

The time evolution of the order parameter (OP) of the relaxor $KTaO_3$ doped with 3% molar ratio of Li is measured under an electric field using a second harmonic generation microscope. The OP develops with quite long relaxation times which are of the order of minutes or sub-hour. The time evolution changes drastically at a critical temperature T^* of 40 K, which is below the transition point of 50 K. Above T^*, the OP develops steeply at first and then gradually towards the saturated value. Below T^*, it develops after a long incubation time. On further cooling, the OP does not develop even under an electric field and it shows non-ergodic behaviour. We examine the applicability of some domain growth theories to the present experimental results and find that the Avrami theory with different exponents can explain the results both above and below T^*.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Nucleation and growth processes in various kinds of the first-order phase transition have been extensively investigated as a fundamental subject of non-equilibrium thermodynamics and statistical physics [1, 2]. Domain reversal phenomena in ferroelectrics belong to the same category of physics when a domain state is presumed to be a thermodynamic phase. There exists a lot of research on this standpoint since the phenomenon is also important in practical applications [3, 4]. The domain switching time of usual ferroelectrics is known to be the order of microseconds. However, in relaxor ferroelectrics, the time to approach the equilibrium state under an electric field is several tens of minutes [5–7]. The origin of the slow kinetics in relaxors is still open at present [8].

The present paper reports that the order parameter (OP) of a relaxor $K_{0.97}Li_{0.03}TaO_3$ (KLT-3) with nearly critical concentration of Li also shows extremely slow time evolution under an

electric field E. This phenomenon resembles the time evolution observed in a prototype relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) [5–7]. The time dependences of some physical quantities have been already investigated in KLT, i.e., P_s determined by the piezoelectric effect [9], neutron Bragg intensities [10], strain-induced and stress-induced birefringences [11, 12], and dielectric constants [13]. However, measurements with a more sensitive method in a wider temperature range are needed to elucidate the origin of the complicated behaviour of nuclear and growth processes of domains in KLT. For this purpose, it is necessary to specify the phase on which the measurement is performed. We have recently investigated the temperature dependence of the OP of KLT-3 on different paths of the (E, T) space [14]. Based upon these experimental results, we measure the time evolution of the OP of KLT-3 at several temperatures precisely, using an optical second harmonic generation (SHG) microscope, because the SHG is a quite sensitive tool for detecting P_s. The results are analysed by the Avrami theory by fitting the experimental data by numerical calculations.

2. Experimental conditions

The sample used in the present experiment was cut from a single crystal of KLT-3 which was grown by the self-flux method with Ta_2O_5, Li_2CO_3 and an excess of K_2CO_3 as a flux [15]. The concentration of Li ions was estimated from the empirical relation between x and the transition temperature [16] where the SH intensity vanishes in zero-field heating (ZFH) after a field-cooling (FC) process.

The sample was a (100) rectangular plate with edges parallel to ⟨100⟩, an area of $9.4 \times 5.0\ mm^2$ and a thickness of 0.85 mm. Both surfaces were polished for optical measurements. A pair of narrow gold electrodes separated by 3 mm were evaporated onto the top surface to apply an electric field along the [001] direction. The distribution of SH intensities ($\lambda = 532$ nm) in the sample generated by the fundamental wave from a Q-switched Nd^{3+}:YAG laser ($\lambda = 1064$ nm) was detected by the SHG microscope. See the details in [14].

The sample was set in a liquid He cryostat for microscopy (CF2101, Oxford instruments). All measurements were performed in the following thermal cycles. First the sample was cooled down to 24 K without an electric field E, and heated without E to a certain temperature at which a time evolution measurement was performed. When the temperature became stable, the electric field of 80 V mm^{-1} was applied and the field-induced SH intensity was observed as a function of time. After finishing a measurement, the sample was heated to room temperature without E and kept for several hours to erase the memory effect. We selected the field magnitude of 80 V mm^{-1} owing to the fact that previous measurements of the history dependence of the SH intensity were performed under the same field [14], which enables us to examine the relation between the saturated SH intensity in time revolution experiments and the field-cooling (FC) SH intensities. Another reason is that stronger fields produce free charges in a sample to cause remarkable photo-currents.

Seven temperatures below T_p of 50 K were chosen to observe the temporal evolution: $T = 30$, 31.1, 33.4, 35.3, 39.7, 42 and 43 K.

3. Experimental results

Figure 1 shows the time evolution of the SH intensity at each temperature. Below 35 K, the SH intensity is almost null and it does not increase within the experimental time of 2 h in spite of applying the electric field E. At 35.3 K, the SH intensity is found to increase slightly with time. At 39.7 K, it begins to increase dramatically after a long incubation time of 40 min. This interesting phenomenon seems to be overlooked in the previous research. At 42 and 43 K,

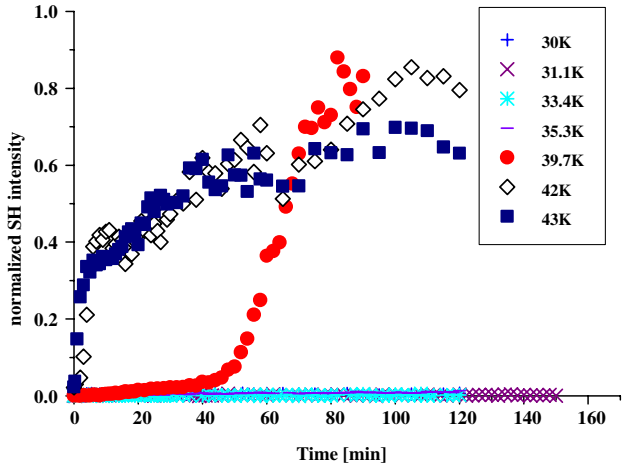

Figure 1. Time evolutions of SH intensities under an electric field of 80 V mm^{-1}. The SH intensity at each temperature is normalized to the saturated value.

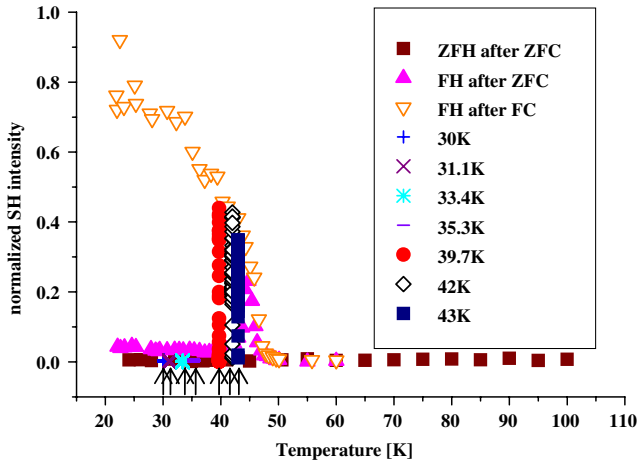

Figure 2. The relation between the time evolutions and the history dependences of SH intensities. The arrows show the temperatures where the time evolutions are measured.

the SH intensity seems to increase in two steps: it increases rapidly for a first few minutes immediately after applying E, and then slowly towards the saturated value.

It is interesting to compare the present results with our previous measurements of SH intensities in different cooling and heating processes with or without E (figure 2) [14]. In the figure, the results of the time evolution are also indicated with arrows. It is seen that the SH intensities finally reach the FH values after FC processes above 35 K. These results show that FH after the FC process is an equilibrium state under the applied field, but FH after ZFC is a transitional process depending on the heating speed. However, below 35 K, the FH after ZFC path cannot attain the corresponding point in the FH after FC process. This means that the temperature region below 35 K is a non-ergodic region in KLT-3 with an applied field of 80 V mm^{-1}.

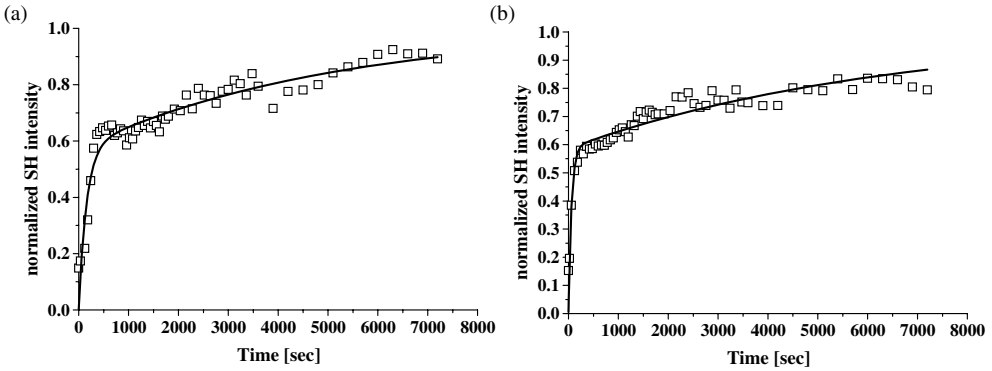

Figure 3. Results of the fitting of time evolutions of SH intensities using the bi-exponential model at 42 K (a) and 43 K (b). Solid lines indicate the calculated values.

It should be pointed out that the time evolution of the OP in KLT-3 resembles to that of PMN. This fact also supports KLT being a relaxor [17].

4. Analyses of the time evolution and discussions

The present results reveal that the time evolution of the SH intensity strongly depends on the temperature at which an electric field is applied. In particular, the behaviour of SH intensity, i.e., the square of OP, varies drastically within a few kelvins around 40 K. In this sense, 40 K is a critical temperature. Below 40 K, the SH intensity develops abruptly after a long incubation time. Above 40 K, the SH intensity apparently grows in two steps, as shown in figure 1: the fast evolution is followed by a slow one. Therefore, the temporal behaviour above 40 K is first analysed by the bi-exponential model. This model is simply phenomenological and is used to determine two relaxation times. The time evolution of the OP is expressed as

$$P = 1 - \frac{\exp(-t/\tau_1) + r\exp(-t/\tau_1)}{1+r}, \tag{1}$$

with three fitting parameters, fast and slow relaxation times τ_1 and τ_2, respectively, and the portion of weight r. $I^{(2\omega)}$ is fitted using the square of the OP. The experimental results at 42 and 43 K can be well described by equation (1), as shown in figure 3. From these fittings, three fitting parameters are obtained: $\tau_1 = 155$ s, $\tau_2 = 5030$ s and $r = 0.744$ at 42 K, and $\tau_1 = 58.8$ s, $\tau_2 = 6367$ s and $r = 0.705$ at 43 K. τ_1 at 43 K is found to be one third of τ_1 at 42 K. This means that the OP response to the electric field becomes faster at higher temperature above 40 K.

Since all measurements were performed below the transition temperature of 50 K, the temporal development of SH intensities is strongly coupled with the growth of domains with the same polarity of applied electric field. In order to explain the slow kinetics of the OP of KLT-3, we examined three theories concerning the domain growth, i.e., the Avrami theory [1], the thermally activated domain growth theory [13] and the Chandra theory [3], and found that the Avrami theory can explain quantitatively the whole present results as follows.

In the Avrami theory, the total volume v of nuclei is described with fitting parameters k and n as

$$v = 1 - \exp(-kt^n). \tag{2}$$

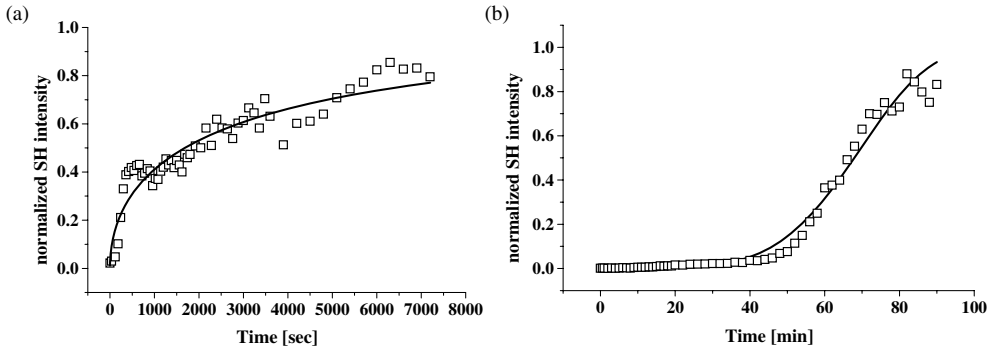

Figure 4. Results of the fitting of time evolutions of SH intensities using the Avrami theory at 42 K (a) and 39.7 K (b). Solid lines indicate the calculated values.

Table 1. Fitting parameters determined by the Avrami theory.

Temperature (K)	n	k
42	0.5	1.5×10^{-2}
43	0.4	4.3×10^{-2}
39.7	4.8	9.7×10^{-10}

Assuming that the SH intensity is proportional to v, we fitted the time evolution of the SH intensity $I^{(2\omega)}$ using equation (2), where $I^{(2\omega)}$ is normalized to the FC value at the corresponding temperature. The results at 42 and 39.7 K are shown in figure 4, from which fitting parameters k and n are determined. The same fitting procedure was also performed with the data obtained at 43 K, and the results are summarized in table 1. The determined exponent n is about 0.5 above 40 K and between 4 and 5 at 39.7 K.

According to Avrami, n changes depending on the nucleation and growth velocities. If we presume that the nucleation and growth velocities are constant with respect to time, n takes the value 2, 3 or 4 depending on the domain shape:, linear, plate-like and polyhedron, respectively. When the number of nuclei is constant and domains grow with diffusion-controlled velocity, n takes the value 0.5. The present analysis shows that the exponent n changes from 0.5 to about 4 at T^*. This indicates that the temporal behaviour above 40 K is governed by the diffusion-controlled process with a constant nuclei number, while domains grow in all directions with the nucleation number proportional to t below 40 K. A question could arise concerning the origins of quite slow temporal behaviour and incubation time observed in KLT-3 in comparison with usual ferroelectrics, since the Avrami theory is a general theory of nucleation and growth. This could be explained by introducing a long-range strain field $\tilde{\Sigma}$ proposed by Chandra, who explained the long switching time observed in $BaTiO_3$ near the transition temperature [3]. Here $\tilde{\Sigma}$ is introduced into k in equation (2), as k is a function of the nucleation rate I and growth velocity v, both of which depend on $\tilde{\Sigma}$. A long incubation time is explained by $\tilde{\Sigma}$ dependence of k. The larger the growth velocity v and/or I, the shorter is the incubation time with a fixed value of $n(=4)$. In KLT, off-centred Li ions could produce the strain field. It should be noted that the stretched exponential approach [12] is a particular case of the Avrami theory.

Lastly, we compare the present results with time evolutions in PMN. Although both behaviours of long time evolution of the OPs are quite similar, the phenomena observed in KLT-3 are much more complicated, as described above. In the case of PMN, no critical temperature exists and all time evolutions at various temperatures can be scaled using a normalized time [8],

while such a treatment cannot be applied to KLT-3. New microscopic approaches are awaited to explain the whole phenomena in KLT, which would also shed light to the origins of the relaxor, in particular the concrete origin of the random force [18].

In summary, the present experiments reveal that the OP of KLT-3 develops with quite long relaxation times under an electric field. This process depends sensitively on temperature, and within a narrow temperature range around 40 K (T^*) the behaviour drastically changes. Above T^*, the OP develops soon after the application of the field and then increases gradually to the equilibrium FC value. In the range 35 K $< T <$ T^*, the OP develops rapidly with a long incubation time of several tens of minutes. Below 35 K, the OP does not exhibit an increase under an electric filed and the region is non-ergodic in the sense that no path exists from the ZFC to the FC path in the (E, T) diagram. The time evolution of the OP can be explained by the Avrami theory with different exponents above and below T^*. The long-range strain field produced by substituted Li ions plays an important role in the extremely slow time evolution observed in the present experiments.

This work is supported by the grants-in-aid of scientific research (A) of MEXT, 'Academic Frontier' Project of MEXT, and the 21st century COE program 'Physics of systems with self-organization composed of multi-elements' of MEXT, Japan.

We are grateful to M Maglione in the Institute of Condensed Matter Chemistry of Bordeaux and W Kleemann in Duisburg University, for their valuable discussions and comments.

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