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1990 J. Phys.: Condens. Matter 2 4579

(http://iopscience.iop.org/0953-8984/2/20/004)

J. Phys.: Condens. Matter 2 (1990) 4579–4585. Printed in the UK

Low-frequency mechanical relaxation in lithium tantalate

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Received 9 March 1989, in final form 8 August 1989

Abstract. The anelastic relaxation of lithium tantalate crystal is studied by using a multi-function inverted torsion pendulum. A relaxation internal friction (IF) peak is observed in the temperature range 100 °C to 350 °C and the orientation, domain and oxygen-deficiency effects on the IF peak are studied. The activation energy of this process is determined to be 1.26 ± 0.02 eV and the IF peak is shown to be associated with the stress-induced anelastic motion of the electric domain boundaries.

1. Introduction

The study of properties of ferroelectric materials such as $LiNbO_3$ and $LiTaO_3$ is of interest because of their applications in electro-optic devices. Stress within a ferroelectric crystal may be produced by vibration, luminescence etc and can affect its electro-optic properties. Hence, it is important to study the response of ferroelectric crystals to low-frequency oscillating stress.

For $LiNbO_3$ crystal, the temperature dependence of low-frequency damping has been studied (Postnikov 1978). Three internal friction peaks have been observed from measurements at frequencies of 1 Hz and 3 Hz. Two of these peaks (at temperatures of −30 °C and 250 °C respectively) are associated with point defects; the other (at 310 °C) is a phase transition-like peak.

Many mechanical, thermal, electrical and optical investigations have been carried out on $LiTaO_3$ crystal, e.g. studies have been made of the elastic and dielectric properties (Yamada *et al* 1969, Smith *et al* 1971, Prieto *et al* 1985, 1986, Kappers *et al* 1985), the thermal properties (Kim and Smith 1969) and birefringence (Fridkin 1979). However, there is no reported study of the effect of stress on the properties of $LiTaO_3$. This paper describes a study of the relaxation process in a $LiTaO_3$ crystal, using a low-frequency internal friction (IF) probe, and aims to determine whether the relaxation peak is due to point defects or ferroelectric domain boundaries (domain walls, DW). We show, for the first time, that DW play an important role in the relaxation phenomena of $LiTaO_3$.

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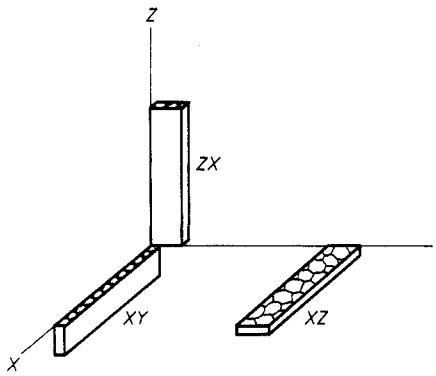

Figure 1. The orientation and specimen designations.

2. Experimentation

$LiTaO_3$ crystal, like $LiNbO_3$ crystal, has a perovskite-like structure (space group R3c below T_c, and $R\bar{3}c$ above T_c). In orientation, the Z axis is taken along the fundamental translation vector c, which is the direction of spontaneous polarisation. Ferroelectric domains most probably orient themselves along the Z axis. The lithium tantalate crystal used in our present investigation is grown by using the Czochralski technique. It is acoustic grade with a Curie temperature $T_c = 610 \pm 5$ °C. Rectangular-plate specimens of size $55 \times 6 \times 1$ mm^3 ($l \times w \times t$) are cut and polished for IF measurements. The orientation of the specimen is defined by its maximum dimension (the length) and its plane of maximum area. Gold films are deposited on the specimen XY planes (see figure 1) to facilitate heat treatment together with an electric field applied between the planes.

Table 1 lists all the samples' conditions. The first and second letters in the designation refer to the orientations of the maximum dimension and the maximum area plane respectively, according to the coordinates defined in figure 1. The following numbers specify the treatments applied to the samples: 1: as-grown state; 2: held at 680 °C for 10–15 min, with an applied 50 Hz AC field; 3: held at 680 °C for 10 min, with DC field applied (field gradient $\geqslant 5$ V cm^{-1}). Following treatments 2 and 3, the samples are cooled down to room temperature at a rate of 2 °C min^{-1}. The last letter, R, signifies a further reducing treatment, in which the sample is held in an argon atmosphere at 860 °C for 4 h.

Different orientations and treatments result in the samples having different characteristics. The different orientations ZX, XY and XZ result in different mobilities of the DW related to the oscillating stress. For the ZX and XY samples, the Z direction lengths are 55 mm and 6 mm respectively but for the XZ sample the Z direction length is only 1 mm. This implies that the predominantly Z-aligned domains of the XZ sample may be pinned down by the 90° domains near the surface.

Different treatments result in the samples having different domain numbers: heat treatment with an AC electric field gives a 'multi-domain' sample, heat treatment with a DC field gives a sample with a decreased domain number. Direct SEM analysis shows the domain size in the sample with the decreased number of domains is about two orders of magnitude larger than that of the multi-domain specimens (table 1). In addition, the reducing treatment gives a sample with increased oxygen deficiency.

A multi-function IF inverted torsion pendulum system (MFIFA-1, made by the Institute of Solid State Physics, Academia Sinica) is used for investigating the relaxation processes. Internal friction Q^{-1} and relative shear modulus G are measured as function

Table 1. The treatments and corresponding data of specimens†

Specimen designation	Treatment	Field gradient at the *c* direction (V/cm)	Average domain size on the *c* face (μm)	Domain distribution on the *c* face	Peak temperature T_p (K)§	IF peak Q^{-1}_{max} ($\times 10^3$)§
*ZX*1	nil	—	0.9	uniform	458, 482, 507, 536	20.3, 20.0, 19.2, 18.5
*ZX*2	AC field	5	0.9	uniform	446, 470, 494, 524	19.4, 18.7, 18.0, 18.2
*ZX*3	DC field	4	>100	no wall‡	431, 451, 477, 504	4.4, 4.4, 3.5, 3.6
*XY*1	nil	—	0.9	uniform	460, 484, 510, 538	27.9, 26.8, 25.0, 24.0
*XY*2	AC field	5.5	0.9	uniform	462, 488, 513, 543	27.8, 26.9, 26.0, 25.9
*XZ*1	nil	—	0.9	uniform	451, 479, 499, 528	11.9, 10.7, 9.2, 7.9
*XZ*2	AC field	5.5	0.9	uniform	456, 480, 503, 534	8.4, 7.9, 7.6, 7.3
*XZ*3	DC field	5.5	>100	no wall‡	451, 481, 505, 531	5.3, 4.5, 4.1, 4.2
*XZ*2R	AC field + reducing	5.5	0.9	uniform	454, 474, 502, 532	8.4, 7.7, 6.6, 6.4

† The sample *XY*3 (DC annealing) was broken during the IF measurement (the preliminary IF measurement showed drastic peak reduction).

‡ No wall can be seen on the screen of the SEM due to the indistinguishability (figure 6).

§ Frequencies 0.0473, 0.224, 1.057 and 5.00 Hz correspond to the peak temperature T_p and Q^{-1}_{max} values respectively.

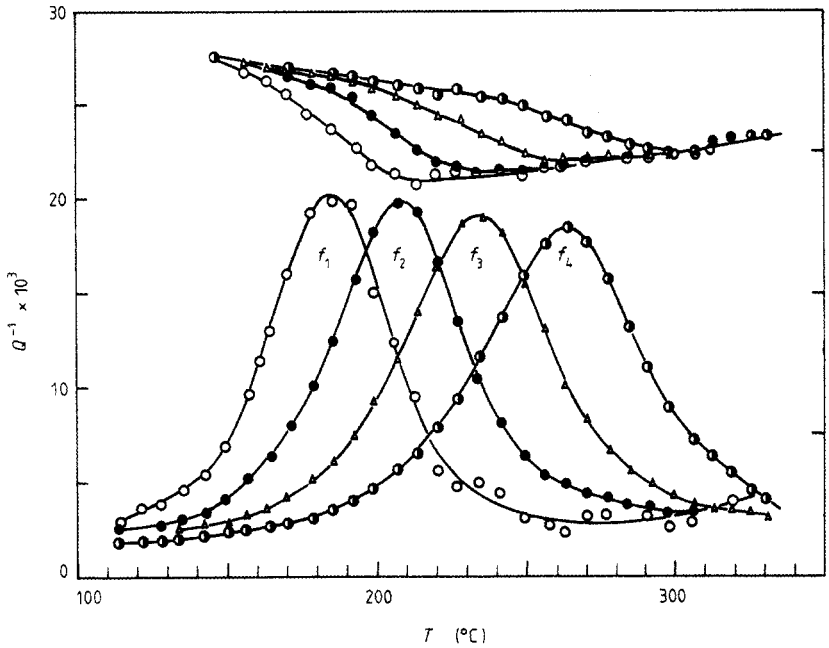

Figure 2. The temperature dependence of Q^{-1} and G for specimen $ZX1$.

of temperature at four selected frequencies in the range of 5×10^{-2} to 5 Hz. The strain amplitude is 5×10^{-6}. IF peaks appear at $\omega\tau = 1$ where ω and τ are the oscillation frequency and the relaxation time, respectively. Once the peak is located for a frequency ω, then τ and the activation energy H can be determined according to $\tau_p = \tau_0 \exp(H/kT_p)$, where p pertains to a peak and k is the Boltzmann constant. The whole experiment is carried out under a low pressure of 60 Torr and the temperature is increased, in steps of about 5 K, from room temperature to 350 °C. The forced-oscillation mode is over a wide frequency range in order to obtain precise values for the activation energy in a single temperature-increasing process. The accuracy of Q^{-1} is about 1% and the temperature fluctuation over a period of one point measurement does not exceed 0.2 K.

Separate x-ray diffraction measurements show that there is no detectable structure phase transition in the range from room temperature to 350 °C.

3. Results and discussion

Figures 2–5 show the experimental results—curves of IF Q^{-1} versus T for the ZX and $XZ2R$ specimens; the Arrhenius graphs of specimens $ZX1$, 2, 3 and $XZ1$, 2, 2R. In each IF figure, there are four curves corresponding to the four frequencies used: $f_1 = 0.0473$ Hz, $f_2 = 0.224$ Hz, $f_3 = 1.057$ Hz and $f_4 = 5.00$ Hz. Each Q^{-1}–T curve shows a relaxation peak in the temperature range 100 °C to 350 °C and each G–T curve shows a modulus defect (MD) in the same range. The IF peak temperature T_p and the MD temperature T_d, shift to higher values with increasing frequency. These features are common to the relaxation process. The results in the range from room temperature to 100 °C are more complicated and will not be discussed here.

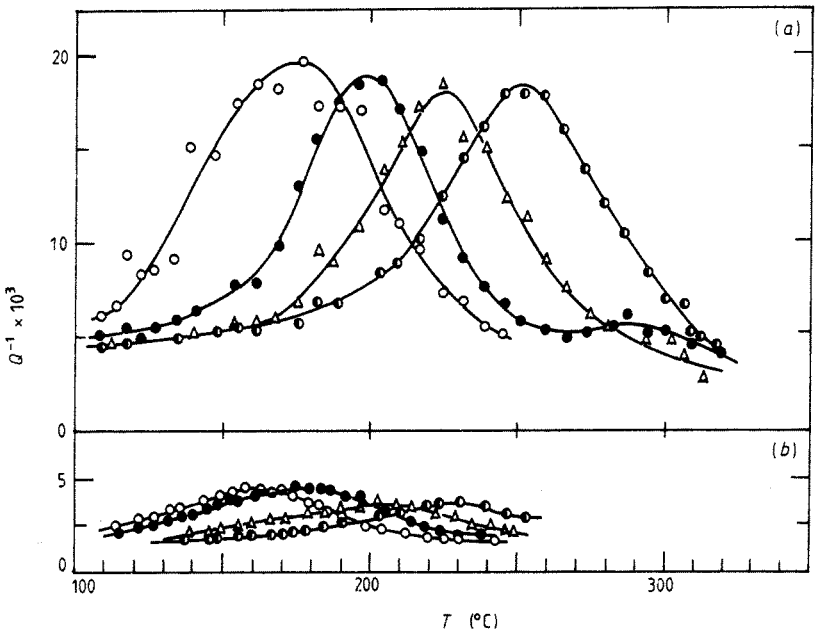

Figure 3. The temperature dependence of Q^{-1} for (*a*) specimen *ZX*2, (*b*) specimen *ZX*3.

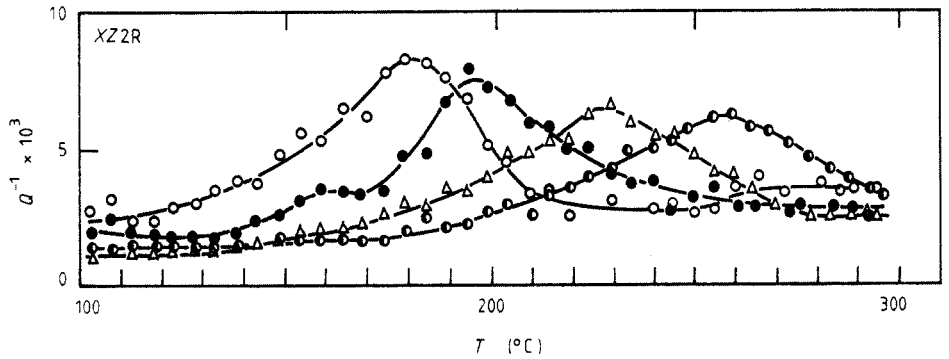

Figure 4. The temperature dependence of Q^{-1} for specimen *XZ*2R.

The oscillation effect on the relaxation process is shown by comparing the results for the samples *ZX*1, *XY*1 and *XZ*1 (figure 2 and table 1). The peak height ($Q^{-1}_{max} = \frac{1}{2}\Delta$, where Δ is the relaxation strength) of *XY*1 (see table 1) is the largest and that of *XZ*1 is the smallest. The domain effect on the relaxation can be considered by comparing the curves for *ZX*1, 2 and 3 (figures 2 and 3) or *XY*1 and 2 or *XZ*1, 2 and 3 (see table 1), respectively. The peak height of IF Q^{-1} for *ZX*1 and 2 (or *XY*1 and 2, or *XZ*1 and 2 (see table 1) does not exhibit any notable change; however the Q^{-1}–T curve is almost flattened for *ZX*3 and *XZ*3. Only the Q^{-1}–T curves of the *ZX* specimens are shown in figures 2 and 3. Those for the *XY* and *XZ* specimens are similar to these and have similar variations. The oxygen-deficiency effect may be shown by comparing *XZ*2 and *XZ*2R

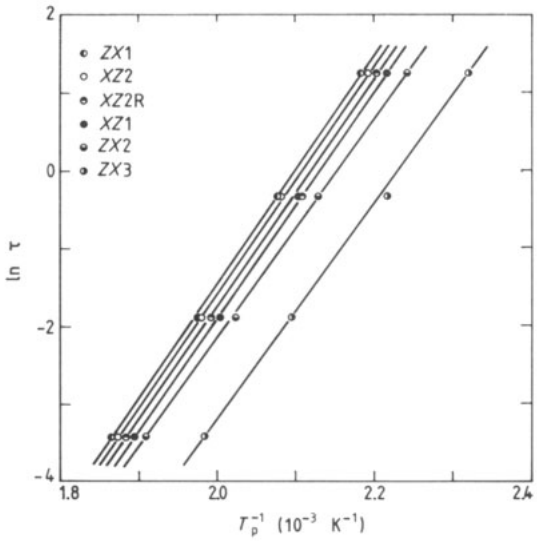

Figure 5. ln τ versus $1/T_p$ for specimens $ZX1$, $ZX2$, $ZX3$, $XZ1$, $XZ2$ and $XZ2R$.

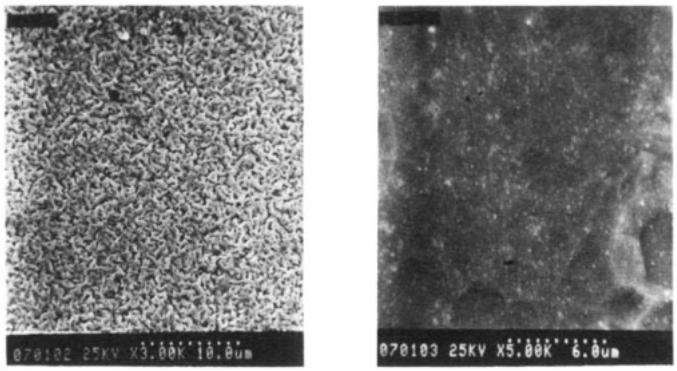

Figure 6. SEM pictures of $ZX2$ and $ZX3$.

(table 1). Allowing for some minor scattering in the data points, the height of the Q^{-1} peak and the temperature value T_p are preserved. The activation energy H of the relaxation process is determined from the slope of the Arrhenius graph of ln τ versus T_p^{-1} (figure 5). This is found to be 1.26 ± 0.02 eV for all samples.

Our results show that:

(i) The relaxation strength ($\Delta = 2Q_{max}^{-1}$) is related to the relative orientation of the samples. Torsional stress is much more efficient for the XY and ZX specimens than for the XZ specimen, and the relaxation strength in the XY and ZX specimens is much higher than in the XZ specimen. This indicates that the orientation of the maximum plane affects the relaxation strength remarkably.

(ii) The relaxation strength of the multi-domain specimen (including the as-grown samples) is much higher than that of the specimens with much fewer domains.

(iii) The $LiTaO_3$ relaxation process is independent of the concentration of oxygen vacancies (based on the fact that no perceivable oxygen-deficiency effect is shown).

The relaxation process that originates from point-defects has to follow the thermodynamic selection rule for anelasticity—relaxation may occur for those point defects whose symmetry is lower than that of the crystal when the crystal is subjected to a type II strain or stress (Nowick and Berry 1972). Thus, for $LiTaO_3$, with trigonal symmetry, monoclinic and triclinic point defects may be relevant under a torsion stress. These 'point defects' originated relaxation processes will depend only on the orientation of the longest dimension (i.e. the axis of stress) and will be independent of the orientation of the maximum plane. This is contrary to our experimental result (i). Also, the usual τ_0 for point defects should be about 10^{-13}–10^{-14} s. Experimental results give 10^{-14}–10^{-15} s. In addition, result (iii) dismisses the effect of oxygen deficiency. Clearly the relaxation process studied in our experiment does not originate from point defects.

The IF peak associated with the DW motion will depend on the domain orientation and the length of Z axis. If the edge length along the Z direction is comparable to the average domain size, a pinning effect should be noticable, so that the Q^{-1} peak height is drastically reduced. This is consistent with what has been reported here (i). Our result (ii) shows directly that the relaxation is associated with the DW. The DW motion concerns the diffusion of point defects on the DW, so that the effects of on DW point defects and their interaction with the DW are included. Only one anelastic process is involved, so that the activation energy of the relaxation process is the same for all specimens.

4. Conclusions

In summary, the observed anelastic relaxation in $LiTaO_3$ originates from stress-induced motions of the domain boundaries and is associated with the low-frequency response of $LiTaO_3$ to stress. It is independent of point defects within the domain. Further studies will be carried out for the relaxation in the lower and higher temperature ranges.

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