Stress relaxation in ferroelectric materials

V C S PRASAD

Materials Development Laboratory, Bharat Electronics Limited, Bangalore 560 013, India

MS received 25 March 1982; revised 24 July 1982

Abstract. Stress relaxation takes place in BaTiO₃ type ferroelectric materials due to the motion of non 180° domain boundaries, which are the twin boundaries. The nature of stress relaxation taking place due to plastic deformation in crystalline solids and that due to twin boundaries in ferroelectric materials is discussed. The usefulness of the stress relaxation data for the study of domain wall motions in this type of ferroelectrics is pointed out.

Keywords. Stress relaxation; ferroelectric domains; thermally activated deformation; ageing.

1. Introduction

Stress relaxation is a method to study the time-dependent deformation in solids. It has been widely used to study dislocation motions in plastically-deformed solids (Guiu and Pratt 1964; MacEwen *et al* 1969, Lloyd and Embury 1971; Lee and Hart 1971). Time-dependent deformation under constant load (creep) takes place in ferroelectric materials such as BaTiO₃, due to the motion of the domain boundaries (Subbarao *et al* 1957; Syrkin and El'gard 1965). This time-dependent deformation also results in stress relaxation (Prasad and Subbarao 1973, 1977; Esaklul *et al* 1980). The present paper attempts to distinguish the type of information that can be obtained by stress relaxation studies in plastically-deformed solids and in ferroelectric materials, and examine the usefulness of this information to study the domain wall motions (twin boundaries) in ferroelectric materials.

2. Stress relaxation in plastically deformed solids

When a solid is plastically deformed in a testing machine and the motion of the cross-head arrested, stress relaxation takes place due to the motion of free dislocations. The decrease in load with time in such a case generally follows a logarithmic dependence. This test can be used to derive information on different aspects of the deformation process such as the activation energy and activation volume associated with the plastic deformation (Guiu and Pratt 1964), stress-strain rate dependence (Lee and Hart 1971), estimation of the thermal and athermal components of the flow stress (MacEwen *et al* 1969, Lloyd and Embury 1971) and information regarding the parameters controlling the dynamics of dislocation motion (Guiu and Pratt 1964).

In a stress-relaxation test, when the motion of the cross-head is arrested, the specimen continues to deform plastically at a decreasing rate under the action of a decreasing applied stress. In such a case, the plastic strain rate ($\dot{\epsilon}^*$) is related (Guiu and Pratt 1964)

to the stress relaxation rate ($\dot{\sigma}^*$) as

$$\dot{\epsilon}_p^* = - (\dot{\sigma}^* / M_U) \quad (1)$$

where M_U is the unrelaxed modulus. The plastic strain rate in terms of thermally activated plastic flow may also be given as

$$\dot{\epsilon}_p^* = A \exp - \left[Q - V\tau^* / RT \right] \quad (2)$$

where $\dot{\epsilon}_p^*$ is the plastic strain rate; A is a constant which contains the entropy term; Q is the activation energy of the deformation process[‡]; V the activation volume of the deformation process; τ^* is the shear stress or the flow stress; R , the gas constant; and T , the temperature in °K.

Using eq. (1), eq. (2) can be integrated after converting the shear stress to the applied stress to obtain a relation between σ^* and t which is of the general form

$$\sigma^* = K_1 - K_2 \log(t + c) \quad (3)$$

where K_1 and K_2 are terms related to the activation volume, and C is a constant. Hence a plot of σ^* vs $\log t$ obtained from the stress relaxation data gives a straight line from which the activation volume of the deformation process can be estimated (Guiu and Pratt 1964).

3. Stress relaxation in ferroelectric materials

Stress relaxation in these materials takes place almost at negligible stresses, e.g. at approximately 0.1 kg/mm² in the single crystal BaTiO₃ (Prasad and Subbarao 1973, 1977). The relaxation is due to the movement of twin boundaries which are the 90° domain walls in BaTiO₃. In single crystals, the relaxation takes place only in the region of deformation associated with twin boundary motions. In this region, the relaxation rate passes through a maximum (figure 1) with increasing stress (Prasad and Subbarao 1977). This relaxation depends on the stress, strain rate and temperature and hence can be treated as a thermally-activated process similar to dislocation motions in plastically-deformed solids (Esaklul *et al* 1980). However, unlike in plastic deformation, the material exhibits strong recovery effects (figure 2). Also, at low values of initial stress, the plot of the stress vs $\log$ time (figure 3) is convex towards the time axis whereas it tends to be concave with increase in stress (Prasad 1973). Similar relaxation behaviour was also observed in orthorhombic KNbO₃ single crystals due to the motion of 60° domain walls (Prasad and Subbarao 1972; Prasad 1973). Thus, it appears, that the above described relaxation behaviour is typical of polysynthetically-twinned crystals, the twinning taking place due to a single-twin system. Therefore qualitatively a similar relaxation behaviour might be expected in other systems such as In-Tl, Au-Cd, etc, which deform by twin boundary motions. Table 1 shows different twin systems and their associated Burgers vectors for twin dislocations in some ferroelectric materials known to show stress relaxation.

indicates the thermal component of the particular parameter. For eg. σ^ is the thermal component of the stress (or the effective stress) which is different from the long range internal stress.

‡Activation enthalpy H is more often used by metallurgists in this expression although activation energy Q was used by Esaklul *et al* (1980) who were the first to apply thermally-activated deformation analysis to ferroelectric materials.

Figure 1. The stress relaxation behaviour of BaTiO₃ single crystal with increasing stress (due to increasing deformation) 4. 0.11 kg mm⁻² 5. 0.16 kg mm⁻² 6. 0.3 kg mm⁻² 7. 0.41 kg mm⁻² 8. 0.53 kg mm⁻² 9. 0.65 kg mm⁻². (after Prasad and Subbarao 1977).

Table 1. Twin systems and Burgers vectors in some ferroelectric materials known to show stress relaxation.

	BaTiO ₃	KNbO ₃	PZT
Crystal system	Tetragonal	Monoclinic* (with respect to pseudo cubic edges)	Tetragonal ⁺
Twin plane	{110}	{110}	{110}
Twin direction	$\langle 110 \rangle$	$\langle 110 \rangle$	$\langle 110 \rangle$
Twinning shear <i>S</i>	0.022	0.03	0.0533
Burgers vector of the twin dislocation (Å units)	0.063	0.086	0.154
Type of domain wall causing relaxation	90° domain wall	60° domain wall	90° domain wall
Reference for lattice constant data	(Rhodes 1951)	(Wood 1951)	(Esakul <i>et al</i> 1980)

*The monoclinic angle between a_m and c_m axis (the pseudocubic edges of the unit cell) is 90° 21'. This angle is assumed to be 90° in estimating the Burgers vector.

⁺ This material may also exist in rhombohedral form at room temperature (Jaffe *et al* 1971).

Figure 2. Relaxation and recovery behaviour of a BaTiO₃ single crystal.

The above described features of relaxation are obviously due to anelastic deformation associated with twin boundary movements (ferro-electric domain walls) and is different from the plastic deformation due to dislocation motions that was discussed earlier. Such a relaxation behaviour was recently analyzed by Esaklul *et al* (1980) using Reed Hill and Dahlberg's analysis (1966) for thermally-activated deformation in anelastic materials. The main point of difference in this analysis from that due to plastic deformation arising due to dislocation motions is the introduction of a term which contributes to reverse activation also, in (2) for thermally-activated deformation. In such a case, the relaxable strain rate as given in (2) takes the form (Reed Hill and Dahlberg 1966)

$$\dot{\epsilon}_p^* = A \exp \left(\frac{Q - V\tau^*}{RT} \right) - \exp \left(\frac{Q + V\tau^*}{RT} \right) \quad (4)$$

Substituting for $\dot{\epsilon}^*$ from (1) after converting the shear stress to the applied stress and the above equation can be integrated with respect to time gives the following equation (Esaklul *et al* 1980).

$$\log \tanh \left(\frac{\beta \sigma^*}{2 RT} \right) = (t/\tau_e) + C \quad (5)$$

where C is a constant of integration t the time and τ_e the relaxation time, defined by

$$1/\tau_e = (2M_U\beta/RT) A \exp \left(\frac{Q}{RT} \right) \quad (6)$$

where β is directly proportional to the activation volume V , and M_U is the unrelaxed modulus.

From these equations, the activation energy and the activation volume associated with the relaxation process can be estimated as shown by Esaklul *et al* (1980). From

Figure 3. Time dependence of stress relaxation for different initial stresses for a BaTiO₃ single crystal.

such an analysis, an activation energy of 25 kcal/mol was obtained for the motion of boundaries in ceramic Lead Zirconate titanate (PZT). This activation energy was interpreted as the energy necessary to homogeneously nucleate a twinning dislocation loop adjacent to an existing twin boundary. Cottrell's expression (1953) for the activation energy (U_c) necessary to homogeneously nucleate a twinning dislocation loop with a radius of r_c is given by

$$U_c = \frac{G B^2 r_c}{4} \left[\ln \frac{r_c}{r_0} - 1 \right] \quad (7)$$

where G is the shear modulus, b the magnitude of the Burgers vector and $r_0 = b/4$. In tetragonal systems, the twin dislocation Burgers vector b may be related to the lattice constants (a and c) by the relation

$$b = (c^2 - a^2)/(c^2 + a^2)^{1/2}. \quad (8)$$

Since, the ageing behaviour (the degradation of properties with time) is known to depend upon the c/a ratio of the material (McQuarrie and Bussem 1955) the magnitude of the dislocation Burgers vector might have an influence on the ageing behaviour of the material. Ageing is an important property of the ceramics for consideration when they are to be used in practical application. Although it is not seriously considered for commercial capacitor and transducer applications, it becomes quite important for high reliability applications such as high drive sonar ceramics and high quality PTC materials. It is known that ageing in these ceramics takes place due to the stress induced motion of non 180° domains. The motion of these domains is influenced by various additives and hence by the composition of the body. The stress relaxation test gives scope to predict the ageing characteristics of different compositions.

Further, in the dislocation theory, the plastic strain rate is expressed as a power function of the shear stress as (Orowan 1940°, Johnston and Gilman 1959)

$$\dot{\epsilon}_p^* = \phi b N (\sigma^*)^m \quad (9)$$

where ϕ is a geometrical factor, b the dislocation Burgers vector, N the mobile dislocation density and m the velocity stress exponent. Equations (1) and (9) permit estimating the velocity stress exponent m , a parameter which gives an index of the twin dislocation velocity in these materials. Thus, the stress relaxation technique offers the possibility of studying the kinetics of non 180° domain walls in ferroelectric materials. In single crystals domain-wall kinetics were earlier studied (Bogdnov 1962) by optical observations using photographic techniques. Obviously such studies are cumbersome and time-consuming. The stress relaxation method offers a more convenient method of study in such cases.

4. Conclusion

Stress relaxation studies on ferroelectric materials offer two important possibilities for study. (i) In polycrystalline ceramics, particularly in ceramics for use in professional and military applications, the stress relaxation test gives scope to predict the degradation characteristics or the ageing behaviour of the material. (ii) In small single crystals, it offers a convenient method of studying the kinetics of non 180° domain walls under mechanical stress.

Acknowledgement

The author wishes to thank the management of Bharat Electronics for their encouragement to present this paper in the first conference on ferroelectrics, held at Delhi, December 1980 and also Prof Y V R K Prasad of the Indian Institute of Science, Bangalore, for helpful discussions.

References

- Bogdnov S V 1962 *Sov. Phys. Cryst.* **7** 611
- Cottrell A H 1963 *Dislocations and plastic flow in crystals* (Oxford: Clarendon Press) p 53
- Esaklul K A, Gerberich W W and Koepke B G 1980 *J. Am. Ceram. Soc.* **63** 25
- Guiu F and Pratt P L 1964 *Phys. Status Solidi* **6** 111

- Jaffe G, Cook W R and Jaffe H 1971 *Piezoelectric ceramics* (London, New York, Academic Press), 135
- Johnston W G and Gilman J J 1959 *J. Appl. Phys.* **30** 129
- Lee D and Hart E W 1971 *Mater. Trans* **2** 1245
- Llyod D J and Embury J D 1971 *Phys. Status Solidi* **43** 393
- MacEwen S R, Kupcis O A and Ramaswami B 1969 *Scr. Metall.* **3** 441
- McQuarrie M C and Bussem W R 1955 *Am. Ceram. Soc. Bull.* **34** 402
- Orowon E 1940 *Proc. Phys. Soc.* **52** 8
- Prasad V C S and Subbarao E C 1977 *Ferroelectrics* **15** 143
- Prasad V C S and Subbarao E C 1973 *Appl. Phys. Lett.* **22** 424
- Prasad V C S 1973 *Stress induced motion of twin boundaries in BaTiO₃ and KNbO₃ single crystals* Ph.D Thesis Indian Institute of Technology, Kanpur
- Prasad V C S and Subbarao E C 1972 *Mater. Sci. Eng.* **10** 297
- Reed-Hill R E and Dahlberg E P 1966 *Trans. AIME* **236** 679
- Rhodes R C 1951 *Acta Crystallogr.* **4** 105
- Subbarao E C, McQuarrie M C and Bussem W R 1957 *J. Appl. Phys.* **28** 1194
- Syrkin L N and El'gard A M 1965 *Sov. Phys. Solid State* **7** 967
- Wood E A 1951 *Acta Crystallogr.* **4** 353