PRAMANA
— journal of
physics

© Indian Academy of Sciences

Vol. 62, No. 5
May 2004
pp. 1121–1128

Nucleation of domains under the influence of temperature in $Ba_5Ti_2O_7Cl_4$

S G INGLE and N M PATIL
Kavikulguru Institute of Technology and Science, Ramtek 441 106, India
Email: naresh_patil2000@yahoo.com

MS received 16 September 2002; revised 13 October 2003; accepted 3 January 2004

Abstract. It is found that the nucleation of domains can take place in $Ba_5Ti_2O_7Cl_4$ under the influence of temperature unlike in many other ferroelectrics. The nucleated domain can also be removed from the structure under the randomizing effect of temperature. These observations have been explained on the basis of a nucleation model of Ingle and coworkers suggested for $KNbO_3$. Similarity of physical situation in $KNbO_3$ and $Ba_5Ti_2O_7Cl_4$ regarding the existence of ordered point defects inducing nucleation of domains around them has been highlighted. This surprising similarity is suggested to be due to the physical processes occurring at the phase transition rather than due to any structural resemblance. The nature of nucleation occurring under the influence of temperature is shown to be identical with the nature of nucleation occurring under the influence of externally applied stress, and/or DC electric field. A new technique of identifying point defects responsible for nucleation of domains is reported.

Keywords. Point defects; nucleation; ferroelectric domains; temperature effect.

PACS No. 77.80.Dj

1. Introduction

Domains are formed in ferroelectric crystals at the phase transition to reduce the free energy of the crystal. Aizu showed that the geometry of the nucleation must confirm to certain symmetry requirement [1,2]. The domain structures formed at the phase transition follow the process of nucleation and growth. Since the nucleation and growth, the cooling of the crystal, adjustment of electric field and stress, are all time-dependent processes, the domain structures formed at the phase transition may be unstable or metastable. Therefore, at room temperature there is considerable adjustment of domain structure. This adjustment takes place through the forward motion of the tips of the wedge-shaped domain as well as the lateral motion of the domain walls. However, there is no fresh nucleation of the domains. Generally, the nucleation of domain does not take place under the influence of temperature except under highly stressed conditions. However, in the ferroelectric $Ba_5Ti_2O_7Cl_4$ reported for the first time by the authors [3], it is found that the

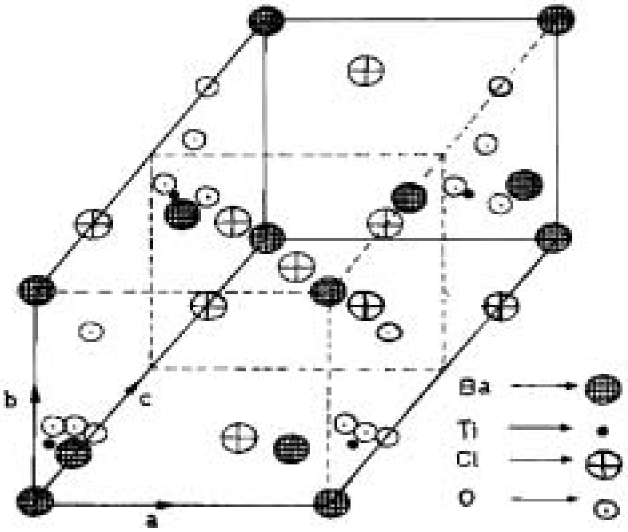


Figure 1. Unit cell of $Ba_5Ti_2O_7Cl_4$ [3].

nucleation of the domains routinely takes place under the influence of temperature. The present paper reports these observations along with the discussion of the factors responsible for such nucleation.

2. Sample preparation

The domain structure in this ferroelectric crystals has recently been studied and reported by the authors [4]. The crystal has 180°, 90° and 79° type of domains associated with twinning on respectively (0 0 1), (1 1 0) and (0 2 1) planes. For 180° and 90° domains the polar axis can lie in $\pm a$ (or $\pm b$) directions, and for 79° domains in $\pm\langle 1\,1\,0\rangle$ or $\pm\langle \bar{1}\,1\,0\rangle$ directions. The crystal has an unusual structure [3] in that a and b axes alternate continuously among themselves so that b-axis can also be the direction of polar axis. Thus, the crystal is a two-dimensional ferroelectric crystal on account of large difference between the a and c lattice parameters. The 180° and 90° domains are associated with displacement of Cl^- ions while the 79° domains are associated with displacement of Ti^{4+} ions. The crystal structure determined by the authors is reproduced in figure 1 for ready reference. Note that the environment of Ti^{4+} ions is not the same as in $BaTiO_3$.

The crystal has a rough cleavage along (0 0 1), (1 0 0) and (0 1 0) planes. When these surfaces are observed under reflected light, usually no domain structure is observed. This is because the tendency for twinning in this crystal is appreciably low. However, when the crystal surface is gently filed by a zero number file, a domain structure is seen to appear on the crystal surface. Also, a series of etch pits are seen to be associated with the domain structure. These etch pits are more or less ordered linearly on the domain regions. While the external application of stress could have nucleated the domain structure, the appearance of etch pits was surprising. It is for the first time that etch pits are observed to have been produced by the external application of stress.

It is known that etch pits of a particular type can be produced by chemical etching on a crystal surface at the defect sites, and the geometry of etch pits can be used to identify whether the defect is a point defect or a line defect. For example, if the successive etching results in growth of the size of etch pit that has a pointed optical view corresponding to the tip of the dislocation, it is obvious that the observed etch pit is at the site of dislocation. On the contrary, if the etch pit disappears on successive etching, and does not have a well-defined geometry, the etch pit is at the site of a point defect. Hence, a chemical etchant was established that produced etch pits on the crystal surfaces, the etch pits being exactly similar in nature to the etch pits produced by the applied stress. This chemical etchant was then used to etch the mechanically treated surfaces, and it was found that the attack takes place exactly at the pits already existing on the crystal surface. This procedure confirmed that the external stress does not create the point defects but only reveals the sites of point defects through some sort of etching process. Thus, a new etching technique became available to locate the point defects on the surface of the crystal. It was further confirmed that the strain sites represent the point defects and not dislocations by etching the crystal surface by an etchant that attacks the sites of dislocations. It was found that the attack did not take place at the sites of the existing etch pits. The chemical etchant used to reveal the point defects was: methanol (10 ml) + $CaCl_2$ (2 g) + KCl (1 g).

As mentioned earlier, the as-grown crystal does not show much of a domain structure. It follows that the strain sites whether in the bulk or on the surface cannot nucleate domains by themselves under the influence of the internal stresses or electric fields. However, the domain structures are found to be nucleated here under the influence of the externally applied stress of the filing process. The filing process has the added advantage that it simultaneously reveals the strain sites through the etching process. Indeed, these strains already existing in the crystal must be helping appreciably the domain nucleation process. Ingle and co-workers observed an exactly similar situation in $KNbO_3$ [5]. The point defects were found to be ordered there in the chemical etching process. In the case of $KNbO_3$, the internal stresses and electric fields were also able to nucleate domain structures around the ordered point defects, and no external stress or electric field was required for the purpose. The detailed account of the defect-dependent nucleation of domains can be obtained from the book by Ingle [6]. The revelation of the etch pits at the sites of point defects under the influence of the external stress is, however, observed for the first time as already mentioned earlier. The points of similarity as regards nucleation between $KNbO_3$ and $Ba_5Ti_2O_7Cl_4$ are:

(1) In both the cases, the nucleation of domains is strongly defect-dependent. The point defects are ordered linearly in the crystal.
(2) While the internal stress and/or electric fields are able to nucleate domain structures around these linearly ordered point defects in case of $KNbO_3$, external stress/electric field is to be applied for such nucleation in the case of $Ba_5Ti_2O_7Cl_4$.
(3) In both the cases the geometry of the nucleated domains follows the model given by Ingle *et al* [5].

3. Effect of temperature on domain structure

The defect dependence of nucleation is best illustrated by the influence of temperature. If the role of defects in nucleation is not appreciable, the domain nucleation cannot take place under the influence of temperature. Hence, if nucleation is seen to occur under the influence of temperature, the defect dependence of nucleation gets confirmed. Hence, the effect of temperature on the observed domain structure at room temperature was investigated. It may be mentioned that for simultaneous observation of defect and domain structure, optical microscopy is the best technique. The observation of nucleation is direct, and is not influenced by extraneous factors like effects of electron beam as in the case of electron microscopy. In the experimental technique used, the crystal was treated mechanically as described earlier, and mounted on the microscope stage for observation under reflection. Arrangement was made to heat the crystal slowly while on microscope stage so that simultaneous observations of crystal temperature and crystal surface could be made.

A photomicrograph of the mechanically treated crystal surface obtained at room temperature is shown in figure 2. The domain regions show arrays of etch pits as mentioned in the previous section. Some arrays have been indicated on the photomicrograph by arrows. This photograph taken at room temperature is rather typical of the view obtained on such surfaces. One normally sees many dirt-like patches like those marked by A along with domain lines that are not exactly parallel. A patient analysis of this unattractive picture however yields valuable information. In the first place, the dirt-like features are not due to dirt at all [7], and secondly, the non-parallelity of the walls is an essential feature of domain structure [4]. The two domain lines of 90°-type domains can be seen to be inclined on the (0 0 1) or (0 1 0) surface by as much as 12° or 24°. Similar dirt-like patches appear in the case of $KNbO_3$ crystal surfaces and it was shown by Ingle and Kakde [8] that they are due to non-reflection from the strain patterns on the crystal surfaces, the strain patterns being formed by point defects. The existence of similar strain patterns in the present case is in agreement with the existence of similar point defects in this crystal. It was shown by Ingle and Kakde [8] that these point defects appear to form clouds in optical view or arrange linearly in the structure. Both the situations are found in the present case also. The detailed nature of point defects in this crystal shall be studied in future work while in the case of $KNbO_3$, Ingle and coworkers showed that the point defects consist of impurity dipoles [9,10].

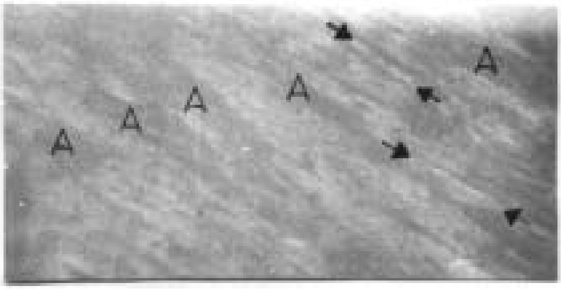
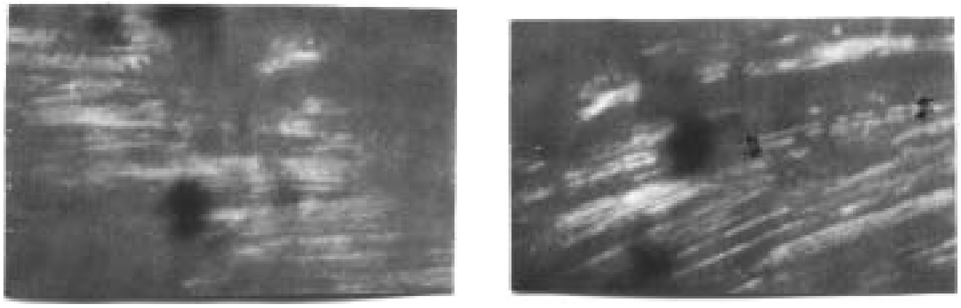


Figure 2. A photomicrograph of mechanically treated crystal surface (287×).



(a) (b)

Figure 3. (**a**) A photomicrograph of mechanically treated crystal surface before application of DC electric field (510 ×). (**b**) A photomicrograph of the crystal surface used for figure 3a after application of DC electric field 3 kV cm^{-1} for 3 min (510 ×).

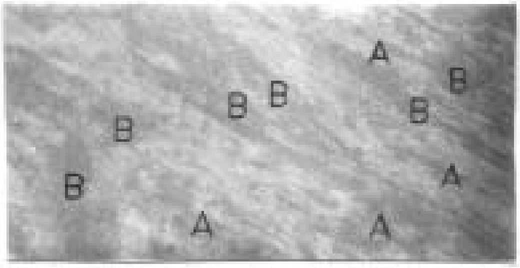


Figure 4. A photomicrograph of the crystal surface at 80°C (287 ×).

The constant association of the point defects with the domains around them is similar to that observed in $KNbO_3$ [5,8,11,12] and is suggestive of the fact that these domains are nucleated under the influence of the associated point defects. This suggestion was confirmed in $KNbO_3$ by Ingle and coworkers [5,8,11,12] and was confirmed now in $Ba_5Ti_2O_7Cl_4$ by applying a DC electric field to the crystal. Figures 3a and 3b show respectively the crystal surface before and after the application of the electric field of 3 kV cm^{-1} for 3 min. Comparing figure 3a with figure 3b, one can indeed observe the appearance of two pairs of dotted domain lines in the central right region (figure 3b). They have been indicated by arrows on the photomicrograph.

Figure 4 shows the crystal surface in figure 2 when it was heated to 80°C. It is found that some impurity patches have sufficiently thinned out while some have been thickened. Some patches of former type are shown at A while of the latter type at B. This confirms to re-distribution [13,14] of the point defects as mentioned earlier. Significantly, we observe in the above photomicrograph new domains with domain lines parallel to the domain lines in figure 2. The new domains are of smaller domain widths, and also show arrays of etch pits on their domain regions. Similar situation was observed in $KNbO_3$ when the crystal was subjected to the external electric field [8]. It was shown there, and is obvious here, that redistribution of the

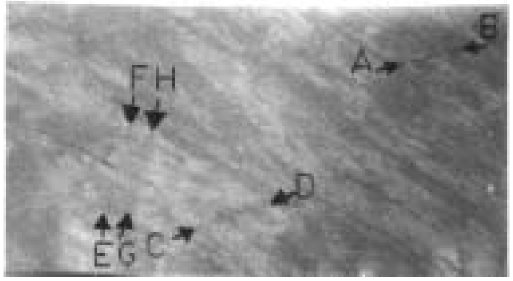


Figure 5. A photomicrograph of the crystal surface at 95°C (287 ×).

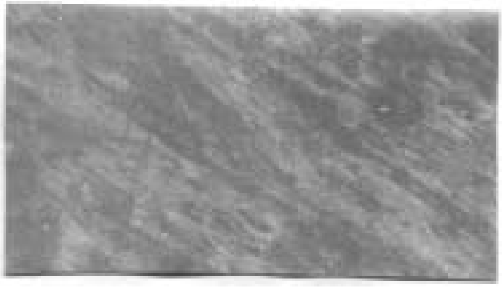


Figure 6. A photomicrograph of the crystal surface at 125°C (287 ×).

point defects occurs leading to the newly formed arrays of point defects, and these new arrays induce nucleation of domains around them, and hence the nucleation of the new domains.

If one closely observes the orientations of the etch pits in the domain region, it is seen that the etch pits are oriented at nearly 45° with the domain lines. If we correlate the orientation of etch pits with the domain structure [4], it is found that the orientation of the etch pits represents the orientation of the polar axis. Correspondingly, we get that the nucleated domain structure is that of 79° domains.

Figure 5 shows the situation at 95°C. We find here some interesting changes as compared to the situation at 80°C. In the first place we find that the point defects have produced linear impurity structures at AB and CD. They can be identified as structures formed by closely spaced point defects. As mentioned earlier, similar structures are observed in $KNbO_3$ and have been shown to be due to such point defects [9,10]. Ingle and Patil [7] have recently shown that such structures in this crystal are formed through an identical process as observed in $KNbO_3$. These lines can be distinguished from the domain lines by the fact that while the domain lines appear in pairs, the impurity lines need not be in pairs. It is worth noting that these lines are formed in polar axis directions.

In figure 5 one can observe quite clearly the nucleation of domain regions EF and GH. It can be seen that these domain regions are sandwiched between a pair of domain walls. Also the domain regions show an array of etch pits. The array of etch pits and the domain region terminate simultaneously showing that the presence of etch pits is necessary for a domain. We can therefore see that some of the point

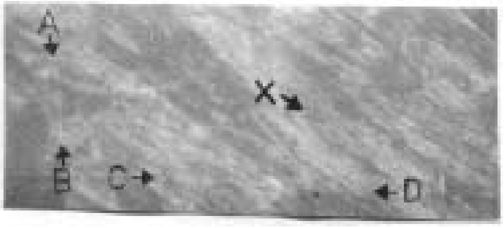


Figure 7. A photomicrograph of the crystal surface at 195°C (287 ×).

defects have rearranged themselves forming arrays and these arrays were able to nucleate domains around them under the influence of temperature. If one observes the orientation of the domain lines it is clear that the nucleated domains are 180° domains [4]. Also, the nucleation is physically exactly similar to the nucleation under the influence of the electric field. It is also similar to the nucleation occurring under the mechanical treatment.

Since the influence of the temperature is to randomize, the nucleated domain may get destabilized and removed from the structure. One finds this situation in the photomicrograph obtained at 125°C (figure 6). The domain regions EF and GH seen in figure 5 are now removed from the structure. As the temperature was gradually increased one could randomly obtain nucleation of the domain as well as the removal of the existing domains. At 195°C (figure 7) the surface showed two perpendicular domain regions AB and CD besides nucleation of some domains and removal of the others. Before the nucleation of a domain with regular walls, stages of irregular positions for the walls could also be observed. Indeed this must be so, since the point defects responsible for nucleation get linearly arranged only gradually. See, for example, the walls at X.

The geometry of the nucleated domain suggests that each point defect nucleates a microdomain and the microdomains join each other end to end to produce a macrodomain [15]. Therefore, though the photograph shows the nucleation of a macrodomain, it is essentially the case of a nucleation of microdomains. In this respect also the situation is similar to that observed by Ingle and coworkers in $KNbO_3$ [11].

After $KNbO_3$, $Ba_5Ti_2O_7Cl_4$ is the only ferroelectric crystal having this particular defect dependence of nucleation, and model of nucleation. It is of interest to know what factors create this similarity. Interestingly, there is no structural similarity between the two crystals. Possibly, the nature of phase transition has much to do with this similarity since the nucleation process basically requires the rotation of polar axes [16] where the walls of the nucleated domains terminate. The kinetics of nucleation on the lines similar to the one followed for $KNbO_3$ has been successfully worked out for this crystal also [17,18].

4. Conclusion

It is thus found that the peculiar nature of the domain nucleation makes it possible to observe the domain nucleation under the influence of temperature. The trapped point defects become free under the randomizing effect of temperature and these point defects can arrange linearly on account of the stresses associated with them. Once they are able to arrange linearly they are able to induce nucleation of domains around them. The observed nucleation of domains under the influence of temperature thus confirms the anticipated defect dependence of nucleation in this ferroelectric crystal. The nucleation follows the model of nucleation given by Ingle *et al* [5] for $KNbO_3$ with similar point defect behaviour. This is only the second ferroelectric crystal where the model of nucleation given by Ingle *et al* [5] is followed. With the finding of more ferroelectrics behaving similarly the generality of the model of nucleation shall be established. The exact conditions leading to such nucleation shall then be possible to be worked out leading to a significant contribution to the field of defect-dependent nucleation.

References

[1] K Aizu, *J. Phys. Soc. Jpn.* **28**, 717 (1970)
[2] K Aizu, *J. Phys. Soc. Jpn.* **32**, 1287 (1972)
[3] S G Ingle and N M Patil, *Jpn. J. Appl. Phys.* **39**, 2670 (2000)
[4] S G Ingle and N M Patil, *Ferroelectrics* **274**, 143 (2002)
[5] S G Ingle, H S Dutta and A P David, *J. Appl. Phys.* **64**, 4640 (1988)
[6] S G Ingle, *Principles of ferroelectricity and intriguing domain behaviour of* $KNbO_3$ (Himalaya Publishing House, Mumbai, Delhi, Bangalore, Nagpur, 1999)
[7] S G Ingle and N M Patil, *Jpn. J. Appl. Phys.* (to be published)
[8] S G Ingle and R N Kakde, *J. Appl. Phys.* **78**, 104 (1995)
[9] S G Ingle and M V Kokate, *Philos. Mag.* **A61**, 443 (1990)
[10] S G Ingle and J G Dupare, *Pramana – J. Phys.* **36**, 167 (1991)
[11] S G Ingle and K S Moon, *J. Phys.* **D24**, 1637 (1991)
[12] S G Ingle and K S Moon, *J. Phys. Chem. Solids* **53**, 61 (1992)
[13] P V Lambeck and G H Jonkar, *Ferroelectrics* **22**, 1 (1978)
[14] G T Joo, J Ravej, J C Grenier, L Fourries and P Hagnmullar, *Mater. Res. Bull.* **21**, 535 (1986)
[15] S G Ingle and N M Patil, *Indian J. Pure Appl. Phys.* **41**, 598 (2003)
[16] S G Ingle and B M Bangre, *Indian J. Pure Appl. Phys.* **16**, 1059 (1978)
[17] S G Ingle and N M Patil, *Ferroelectric Lett.* **30**, 1 (2003)
[18] S G Ingle and N M Patil, *Ferroelectrics* (accepted)