

Nucleation and evaporation of domains due to electric field at room temperature in BaTiO₃ single crystals

C M DUDHE* and P R ARJUNWADKAR

Department of Physics, Government Institute of Science, Nagpur 440 001, India

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Abstract. A study of nucleation and evaporation of 90° and 180° domains by external direct current (dc) electric field at room temperature in barium titanate single crystals has been carried out using reflecting microscope. It was observed that both the 90° and 180° domains were nucleated at some sites, while evaporated at some other sites of the crystal surface. The 90° domain follows the mechanism of micro-domain wall nucleation as well as the evaporation based on impurity dipoles, like reported for KNbO₃. The mechanism of the 180° domain nucleation is not established yet. However, in both cases, nucleation and evaporation are operative simultaneously by the same electric field, which seems to be quite interesting and which can be attributed to the different critical lengths of the domains.

Keywords. Impurity dipoles; domain walls; nucleation; evaporation; spontaneous polarization.

1. Introduction

Barium titanate (BaTiO₃) is a well-known ferroelectric material. This material is highly investigated for various possible applications.^{1–3} Above 120°C temperature, BaTiO₃ has the cubic perovskite structure. Below this temperature it remains in tetragonal phase up to 5°C having polar axis (0,0,1). In this phase the Ti and O ions move relative to Ba at the origin from their cubic positions, Ti at (1/2, 1/2, 1/2), and three oxygen at (1/2, 1/2, 0), (1/2, 0, 1/2) and (0, 1/2, 1/2), to Ti at (1/2, 1/2, 1/2 + dz_{Ti}), O_i at (1/2, 1/2, dz_{O_i}), O_{ii} at (1/2, 0, 1/2 + dz_{O_{ii}}) and (0, 1/2, 1/2 – dz_{O_{ii}}). The shifting of oxygen octahedron is very little distorted by O[–] ions displacement and no large change occurs in Ba–O bond length, but the Ti–O bond length is markedly altered, which constitutes Ti–O dipoles.⁴

In addition to Ti–O dipoles, impurity dipoles are present in the crystals as impurities are always the part of ferroelectric materials, grown by the flux melt method. In the present study, the crystals were grown by the well-known Remeika's method in platinum crucible at high temperature of around 1200°C. At such high temperature, platinum impurities are introduced very easily into the melt.⁵ Moreover, such crystals are oxygen deficient.^{6,7} Consequently, an impurity dipole will be resulted, if the oxygen vacancy exists at the site of octahedron, the impurity ion being the positive pole and vacant oxygen site being the negative pole of the impurity dipole.⁸

Several investigations have been made to investigate domain structures, domain nucleation, sidewise motion of domain walls, the domain–dislocation interaction and the impurity dipole–domain interaction.^{5,9–12} Potnis *et al*¹³ reported an excellent review of progress in the field of domain modelling and domain imaging techniques of ferroelectrics. Nowadays various advanced techniques such as atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction, second harmonic generation microscopy (SHGM), etc. are being used to investigate the domain structure. In recent times, Dudhe *et al*¹⁴ used TEM to investigate nanodomain structures in BaTiO₃ nanoparticles. A good amount of literature on the domain morphology by using simple metallurgical reflecting microscope and possible mechanisms of domain wall nucleation is widely available due to Ingle *et al*.^{8,12,15–17} Ingle and Moon⁸ reported a possible mechanism of domain walls nucleation in KNbO₃ single crystals. The mechanism proposes that the impurity dipoles tend to orient themselves in the direction of spontaneous polarization P_s of the crystal when the crystal is cooled down below the Curie temperature. However, if the orientation of the dipoles is different than that of P_s of the crystal then strain will be developed at that site and, in order to reduce this strain, a pair of domain walls will be nucleated during the paraelectric–ferroelectric phase transition such that the spontaneous polarization P_s at that site coincides the orientation of the impurity dipoles. Such nucleation of domains is possible below the Curie temperature under the influence of an external electric field. Further, it is also proposed that the mechanism of evaporation of

*Author for correspondence (chandraguptadudhe@gmail.com)

domain walls is just reversed to that of the nucleation.¹⁷ Accordingly, the reverse field for the evaporation should be 1.5 times to that of required field for the nucleation.

Although these models are better suited for the 90° domains independently for the nucleation and evaporation of domains, no explanation is given for the case when both are occurring simultaneously. Moreover, not much attention is given to the nucleation and evaporation of the 180° domains. In the present study, Ingle's model^{15,17} was applied to simultaneously occurring nucleation and evaporation of domains in BaTiO₃ crystals and results are interpreted.

2. Experimental

BaTiO₃ single crystals were grown by a well-known Remeika's flux method. The grown crystals have a smooth cleavage along the pseudocubic (001) plane; therefore, they were smoothly cut to get (001) surface (c-plates) without disturbing domain structure of the crystals. These c-plates were observed under the metallurgical reflecting microscope. Suitable site of the surface of the c-plate sample containing the 90° domains was photographed by using microscope-attachment-camera system. For the 180° domains, the c-plate sample was etched by hydrochloric acid for few seconds, and was photographed using the same system. A suitable direct current (dc) electric field E was applied perpendicular to the major surface (c-plate) of the sample for a certain period, washed with methanol and same site was again photographed.

3. Results and discussion

3.1 Nucleation and evaporation of the 90° domains

Figure 1 shows photomicrograph of pseudocubic (001) surface of the BaTiO₃ crystal. Two sets of the 90° domain walls are clearly observed, one set is parallel to the marked line CD and the other is parallel to marked line AB. Schematically they are shown in figure 2a and b, respectively, where the outside marked P_s is the directions of spontaneous polarization of the crystal as a whole, while the inside marked P_s is the direction of spontaneous polarization of independent domains present at that site (a circle with dot represents the direction of polarization perpendicular to the observed plane). On critical examination, it is concluded that the domain walls parallel to line CD are a-domains (where the P_s always lies on the plane) and the domain walls parallel to line AB are c-domains (where P_s lies alternatively on the plane and into the plane).

Same crystal surface after the application of electric field of about 5 kV cm⁻¹ for 15 min is shown in figure 3. This photomicrograph shows that the set of domains

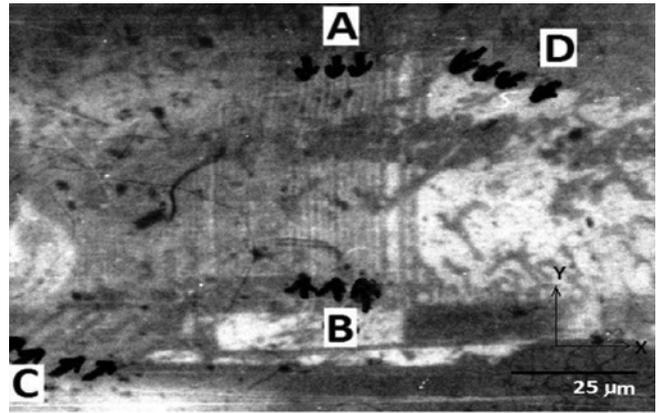


Figure 1. Photomicrograph of (001) surface of the crystal showing two set of domain walls, one parallel to AB line and the other parallel to CD line (450×).

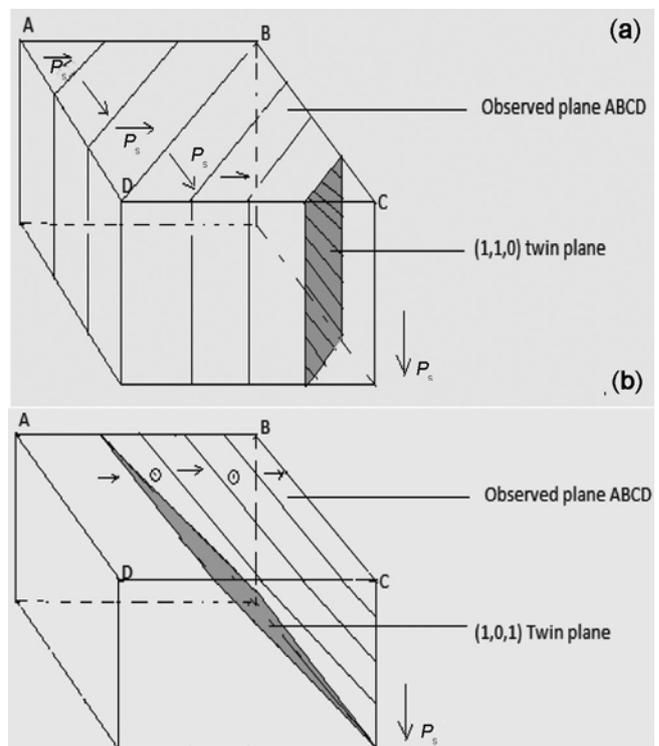


Figure 2. Schematic sketch of (a) a–b types 90° domains parallel to CD line and (b) a–c types 90° domains parallel to AB line observed in figure 1.

parallel to line CD is almost removed by the electric field due to evaporation, whereas a new line marked by MN seems to be appeared parallel to line AB. The appearance of this line indicates a process reverse to the process of evaporation, hence the marked line MN is said to be a nucleated domain wall.

The appearance of a line MN can be explained by the principle of the 90° domain wall nucleation by impurity dipoles, and by using the schematically drawn

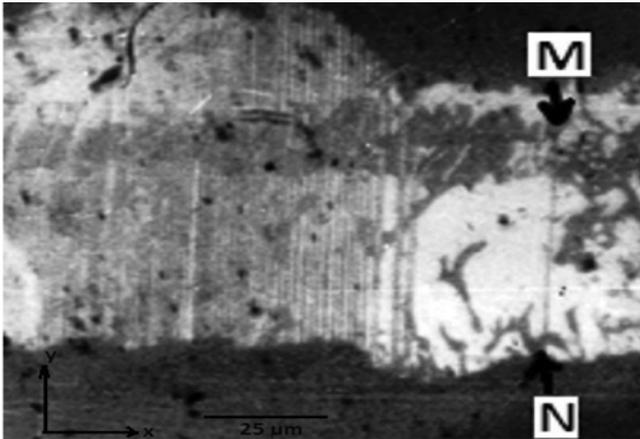


Figure 3. Photomicrograph of same surface (in figure 1) after application of dc field 5 kV cm^{-1} for 15 min showing the appearance of a new domain wall MN (450 \times).

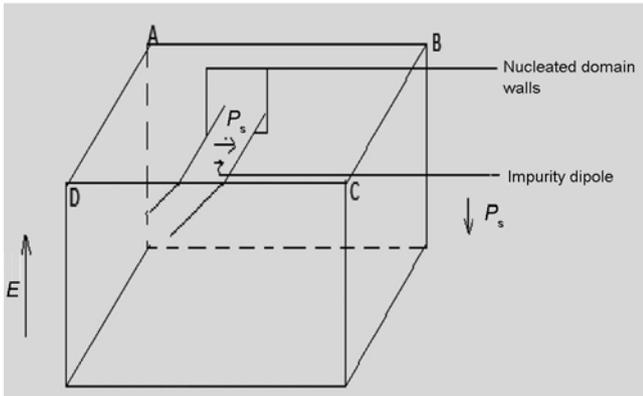


Figure 4. Schematic representation of principle of 90 $^\circ$ microdomain walls nucleation.

figure (figure 4). The applied electric field may cause the excitation of impurity ions and form impurity dipoles.¹⁶ These dipoles will try to orient themselves along the direction P_s of the crystal; if they fail, a strain is developed in the crystal at that site. To reduce this strain, a pair of microdomain walls is nucleated with the new spontaneous localized polarization P_s at that site. If there is a co-operative arrangement of the dipoles then microdomains join each other in head-to-tail manner and domain walls are formed. MN line in figure 3 is one of such nucleated 90 $^\circ$ domain walls. However, nucleation of single wall instead of pair is surprising. The single line MN may be attributed to an unresolved pair of domain walls where the thickness of the wall might be of the order of nanometre⁹ or it is an exception to the principle of domain wall nucleation, or some other mechanism might be operative in this case.

Simultaneous de-excitation of impurity dipoles was seen, for the same applied electric field, at some another site of the observed plane, resulting in evaporation of

domain walls. For example, the applied electric field acts as a reversed field for the domain walls parallel to CD line (in figure 1), giving rise to reverse strain in the crystal. The domain wall energy is then used to reduce the strain at that site. Consequently, the walls parallel to line CD are evaporated (see figure 4) and dipoles relaxed in to ionic impurities.

Quantitatively nucleation of domains can be explained by using equation suggested by Ingle *et al.*¹⁵ According to the study the critical length of nucleation of the 90 $^\circ$ domain is

$$l_{\text{cr}} = \frac{8\alpha}{3P_s(E - E_{\text{cr}})}, \quad (1)$$

where α is the domain wall energy, P_s the spontaneous polarization, E the applied electric field and E_{cr} the critical electric field for nucleation of domains. By assuming the minimum critical electric field (E_{cr}) which is about 60 V cm^{-1} for the switching of the 90 $^\circ$ domains in BaTiO₃ single crystals,¹⁸ which looks to be negligible as compared to the applied field (5 kV cm^{-1}), expression (1) can be written as

$$l_{\text{cr}} \sim \frac{8\alpha}{3P_s E}. \quad (2)$$

Using optimum values of P_s as $26 \mu\text{C cm}^{-2}$ and the 90 $^\circ$ domain wall energy (α) $\sim 80 \text{ erg cm}^{-2}$ as given in the literature,¹⁹ the critical length was estimated to be $\sim 1.7 \mu\text{m}$. This implies that the domain wall nucleated by 5 kV cm^{-1} must have a length more than $1.7 \mu\text{m}$ to form a sustainable domain structure. The length of nucleated domain MN (figure 3) is about $50 \mu\text{m}$, indicating that it is formed by joining many microdomains each of which length is higher than $1.7 \mu\text{m}$. This is possible only when there is a head-to-tail cooperative arrangement of the dipoles.

Similarly from the kinetic process of evaporation,¹⁷ it is found that

$$E' \sim \frac{3}{2E}, \quad (3)$$

where E' is the reverse electric field of evaporation of the same domain walls, which were nucleated by the electric field E .

The lines parallel to CD in figure 1a were evaporated by the electric field 5 kV cm^{-1} , indicating that they were nucleated by the opposite field less than 3.3 kV cm^{-1} by a similar cooperative manner as explained above. Since no electric field was applied before to get the photomicrograph shown in figure 1a, the required electric field was assumed to be present due to the surface charge developed while cooling the crystals in the process of crystal growth just below the Curie transition temperature. The corresponding critical length will be more than $0.24 \mu\text{m}$ for such domain structures.

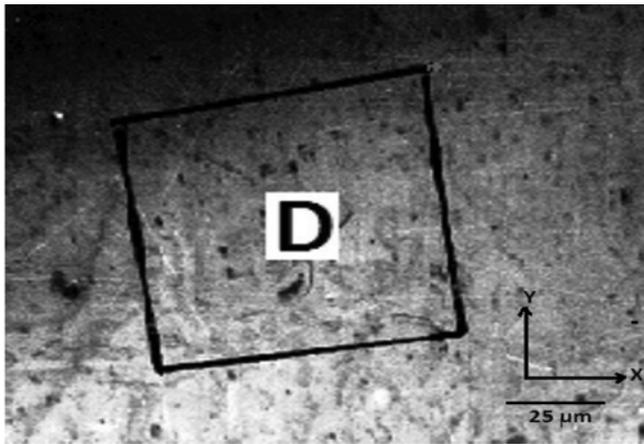


Figure 5. Photomicrograph of crystal surface showing 180° domain site marked by D (560 \times).

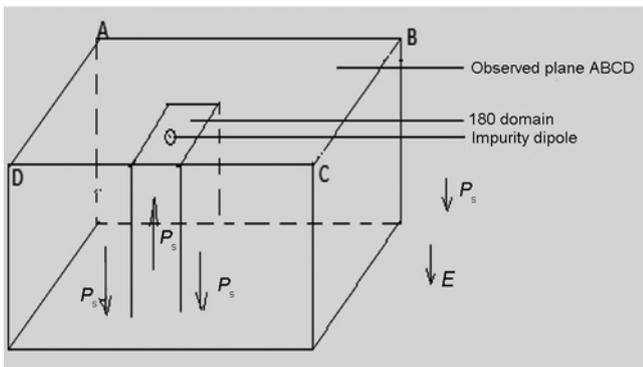


Figure 6. Schematic representation of 180° domain nucleation.

The inverse relation between the electric field and the critical length of domains suggests that the naturally occurred larger stable domains are due to the presence of smaller electric field, which is usually present just below the Curie temperature during paraelectric–ferroelectric phase transition. During transition, of course processes of nucleation and evaporation of domain walls are operative even in the absence of external electric field and finally a stable domain structures are obtained at room temperature. For smaller and smaller domain structure say of the order of nm, higher and higher electric field is required which might not be present during the phase transition when the size of the crystal is very small.

3.2 Nucleation and evaporation of the 180° domains

Hydrochloric acid is a very good etching agent which reveals 180° domains of BaTiO_3 .²⁰ The etched surface of the crystal flake by hydrochloric acid and photograph of crystal surface are shown in figure 5. The figure shows a major pseudocubic (001) surface of the flake. The D marked region enclosed in a square is a site of the 180° domain. Schematically this is shown in figure 6. After

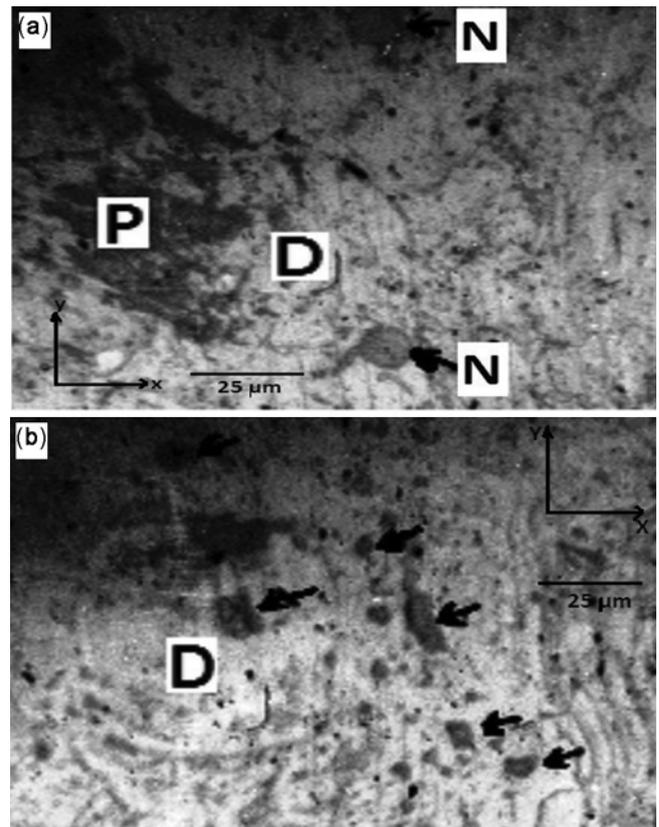


Figure 7. (a) Photomicrograph of same surface (in figure 5) after application of dc field 4 kV cm^{-1} for 10 min, etching by hydrochloric acid for 10 s and washing with methanol, the figure shows new 180° domains marked by P and N (560 \times) and (b) photomicrograph of same surface (in a) after application of dc field 7 kV cm^{-1} for 10 min, reverse direction, and after etching by hydrochloric acid for 10 s and washing with methanol showing evaporation of previously nucleated 180° domains and nucleation of another new domains marked by arrows (560 \times).

application of the electric field of about 4 kV cm^{-1} for 10 min to its major surface, subsequently etched by hydrochloric acid for 10 s and washed with methanol is shown in figure 7a. Comparison of this figure with figure 5 reveals that the earlier domain structure is altered. This photomicrograph as shown in figure 7a shows two black structures marked by N and black aggregates marked by P. These structures and aggregates are not impurity clusters; if they were, then they would have been washed out by methanol, since methanol acts as a cleaning agent and removes impurity clusters from the surfaces.²¹ This suggests that these areas marked by N and P correspond to the 180° domains.

Photomicrograph shown in figure 7b is again of the same surface as referred in figure 7a but now with the electric field of about 7 kV cm^{-1} applied in a reverse direction for 10 min. In this photomicrograph, previously nucleated N and P marked structures, observed with the forward field, disappeared and new structure marked by arrows are appeared.

This nucleation and evaporation of the 180° domains corresponding to appearance and disappearance of the structures as seen in figures 7a and b can be explained on similar line as 90° domain's nucleation and evaporation. The explanation for the mechanism involved in nucleation and evaporation of 180° domains then would be as follows: impurity ions are activated and impurity dipoles are formed because of the applied dc electric field. These impurity dipoles tend to align along the upward and/or downward directions giving rise to P_s at that site, opposite to the direction of spontaneous polarization of the crystal as a whole. Consequently, a strain site is resulted and, in order to reduce this strain, 180° domains are nucleated. Marked regions P and N, in figure 7a, are therefore newly nucleated 180° domains due to initial forward dc electric field. Conversely, if the reverse field is applied then the impurity dipoles in the nucleated 180° domains might have changed their orientation, deactivated and changed into ionic impurity form. This mechanism corresponds to evaporation of domains. Disappearance of structure N and P in figure 7b confirms the evaporation of 180° domains due to the reversed field. However, some fresh, small 180° domains are seen to be appeared (marked by arrows in figure 7b), which again confirms the simultaneous nucleation and evaporation processes of 180° domains in BaTiO₃.

Despite exact relationship of critical length of 180° domains boundary and the applied electric field, it is expected that these quantities are inversely proportional, similar to 90° domains. The higher is the applied electric field, lower is the sizes of 180° domains. The domain sizes in figure 7a and b are 4 and 7 kV cm⁻¹, respectively, when compared this fact is supported, and also goes along with the observations of Stadler and Zachmanidis.^{22,23}

4. Conclusion

Both the nucleation and evaporation of 90° and 180° domains are operative in BaTiO₃ at room temperature under the influence of dc electric field, similar to that reported in the literature, just below the Curie temperature in the absence of external electric field. The nucleation of domains is mainly due to impurity dipoles as they can be excited easily by the electric field. Bigger domain will be formed when the dipoles concerning to such domains

have head-to-tail cooperative arrangement. On the other hand, some of the domains which experiences non-cooperative reverse field get evaporated. After evaporation of domains, the dipoles related to such domains will be relaxed in to ionic form.

References

1. Lines M E and Glass A M 1977 *Principles and applications of ferroelectrics and related materials* (Oxford: Clarendon)
2. Whatmore R 2007 *Ferroelectric materials, handbook of electronic and photonic materials* (ed.) S Kasap and P Capper (Heidelberg: Springer)
3. Tayebi N and Zhang Y 2011 *Ultra-high density probe-based storage using ferroelectric thin films, ferroelectric – applications* (ed.) M Lallart (Rijeka, Croatia: InTech)
4. Megaw H D 1957 *Ferroelectricity in crystals* (London: Methuen)
5. Forsbergh P W Jr 1949 *Phys. Rev.* **76** 1187
6. Ingle S G and Joshi S C 1986 *Phys. Rev. B* **34** 4840
7. Shackelford J F and Holman R L 1975 *J. Appl. Phys.* **46** 1429
8. Ingle S G and Moon K S 1991 *J. Phys. D: Appl. Phys.* **24** 1637
9. Zhang Q and Goddard W A III 2006 *Appl. Phys. Lett.* **89** 182903
10. Tanaka M and Honjo G 1964 *J. Phys. Soc. Japan* **19** 954
11. Bradt R C and Ansell G S 1967 *J. Appl. Phys.* **38** 5407
12. Ingle S G, Moon K S and Kakade R N 1992 *Bull. Mater. Sci.* **15** 251
13. Potnis P R, Tsou N-T and Huber J E 2011 *Materials* **4** 417
14. Dudhe C M, Nagdeote S B, Khambadkar S J, Arjunwadkar P R and Patil R R 2014 *Ferroelectrics* **471** 148
15. Ingle S G, Dutta H S and David A P 1988 *J. Appl. Phys.* **64** 4640
16. Ingle S G and Kokate M V 1990 *Philos. Mag.* **A61** 543
17. Ingle S G and Moon K S 1991 *Ferroelectrics* **119** 107
18. He D Y, Qiao L J, Volinsky A A, Bai Y and Guo L Q 2011 *Phys. Rev. B* **84** 024101
19. Jona F and Shirane G 1962 *Ferroelectric crystals* (New York: Pergamon Press)
20. Hooton J A and Merz W J 1955 *Phys. Rev.* **98** 409
21. Moon K S 1992 *Role of impurity dipoles in domain formation in KNbO₃ single crystals* PhD thesis (India: Nagpur University)
22. Stadler H L and Zachmanidis 1964 *J. Appl. Phys.* **35** 2895
23. Stadler H L and Zachmanidis 1964 *J. Appl. Phys.* **35** 2625