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Domain structure in ferroelectric $PbNb_2O_6$

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Abstract. Single crystals of ferroelectric $PbNb_2O_6$ were grown employing a modification of the technique of Goodman. The results obtained on the domain structure were analysed and compared with those reported on $BaTiO_3$ and $KNbO_3$. The domain structure observed here corresponds to the twinning on (110) plane of the unit cell reported by Francombe and Lewis or the subcell reported by Labbe and others. The (001) planes were observed, as the crystal habit is such as to produce (001) planes, and the cleavage plane is also (001). Also the analysis of the observations can be done easily under these conditions. The domains observed are 90° domains with polar axis in (001) plane. Wedge shaped domains and spikes are present as in $BaTiO_3$ and $KNbO_3$. The twinning can occur also on ($\bar{1}$10) plane producing a domain line at 90° with that due to twinning on (110). This gives patterns of perpendicular lines similar to those in $KNbO_3$ and $BaTiO_3$. Crystal structure considerations show that the domain structures with polarization in and out of the observed (001) plane are not possible, and also were not observed. In this sense, it is a two dimensional ferroelectric. The studies showed a peculiar grain structure in the crystals, and it can be explained on the basis of the growth habit of the crystal. The polarizing microscope is particularly useful in analysing the domain structure along with the grain structure.

Keywords. Domain structure; grain structure; polar axis.

1. Introduction

The extensive studies on domain structure and its correlation with properties of $KNbO_3$ carried out, in our laboratory has provided useful information. These studies are now extended to ferroelectric $PbNb_2O_6$, which has some structural similarities with perovskite type oxides, and is still different in many respects.

2. Structural characteristics

The ferroelectric properties of lead (meta) noibate, $PbNb_2O_6$, were first discovered by Goodman (1953). The ferroelectric phase has orthorhombic symmetry at the room temperature, which changes to tetragonal at the Curie temperature 570°C (Goodman 1953; Roth 1957 and Francombe and Lewis 1958). The lattice parameters of the unit cell at the room temperature are $a=17{\cdot}51$ Å, $b=17{\cdot}81$ Å and $c=2\times3{\cdot}86$ Å and at the Curie temperature $a=12{\cdot}46$ Å and $c=3{\cdot}907$ Å (Francombe and Lewis 1958). According to Labbe *et al* (1973) the subcell parameters are $a=17{\cdot}65$ Å, $b=17{\cdot}92$ Å and $c=3{\cdot}87$ Å and true cell parameters $a'=2a$, $b'=b$ and $c'=2c$. The spontaneous strain according to the subcell parameters is 1·016 which agrees with the value 1·017 reported earlier (Francombe and Lewis 1958). There is some structural resemblances between the para-electric phase (tetragonal) of $PbNb_2O_6$ and the tetragonal alkali tungsten bronzes and the double oxides lie $BaTiO_3$, $KNbO_3$, etc., which have slightly distorted pervoskite structure. The NbO_6 octahedra are linked with each other through the oxygen at the corners. In $PbNb_2O_6$ the Pb^{2+} ions occupy five out of the six available interstitial sites formed by this framework. In spite of this structural resemblance, $PbNb_2O_6$ and $BaTiO_3$ or $KNbO_3$ differ substantially in their ferroelectric properties. For example, polar axes of $BaTiO_3$ and $KNbO_3$ can assume any one of the six equivalent directions (Megaw 1947) in the tetragonal phase owing to the cubic symmetry of non-polar phase, but in the case of $PbNb_2O_6$, though the direction of spontaneous polarization is not known with certainty, Francombe and Lewis (1958) have cited it as an example of two dimensional ferroelectrics. The spontaneous polarization can occur in the two directions identified with [100] and [010] axes of the orthorhombic unit cell. Subbarao *et al* (1960) suggested that the polar axis in orthorhombic $PbNb_2O_6$ can lie within the (001) plane and most probably it is parallel to the *b* axis. Recently Labbe *et al* (1973) reported that the possible polar space groups in the subcell are C2 mm and Cm2m, and in the true cell, the only possible polar space group is Bb2m, corresponding to an unambiguously determined ferroelectric axis *b*. By x-ray diffraction studies, they found small imbrications of 90° domain walls related with twinning on $\{110\}$ plane and 180° domain walls with their inversions. The purpose of this paper is to discuss the domain structures observed, their correlation with the crystal symmetry and to study their peculiarities.

3. Growth of single crystals

Single crystals of lead (meta) niobate were grown from melt by employing Goodman's technique in a slightly modified way. The constituent oxides PbO and Nb_2O_5 of analar grade in the molar ratio 1 : 1 were fused in furnace at 1300° C. Heating above 1250° C is a condition sine qua non for the achievement of ferroelectric phase (Jona and Shirane 1962). After allowing sufficient soaking time it was cooled to 1150° at the rate of 10° C/hr and again reheated to 1260° C, to follow a procedure adopted by Deshmukh and Ingle (1971a) for $KNbO_3$ single crystals. After an hour the melt was slowly cooled from 1260° C to room temperature at uniform rate of cooling. The single crystals grown by this process were plates of nearly $(1 \times 1 \times 0{\cdot}3)$ mm dimensions with pale yellow colour. The ferroelectric nature of the crystals was confirmed by observing the hysteresis loop.

4. Type of domains expected

The twinning on (110) plane of the unit cell of Francombe and Lewis (1958) or the subcell of Labbe *et al* (1973) gives rise to the geometry of domain arrangement as depicted in Figure 1(a). The 90° domain walls lie nearly at 45° and parallel to the crystal edges on (001) and (010) or (100) planes respectively, satisfying the criterion of no charge at the wall. On (001) plane, the polar axes on either side of the domain wall lie in the observed surface. If simultaneous twinning on (110) and (1I0) planes

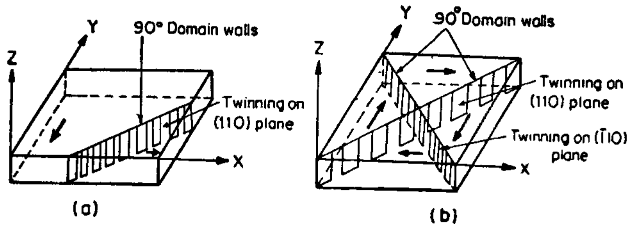

Figure 1. (a) Twinning and (b) Possible twinning on (110) and ($\bar{1}$10) planes of the true cell or subcell and the associated domain structure.

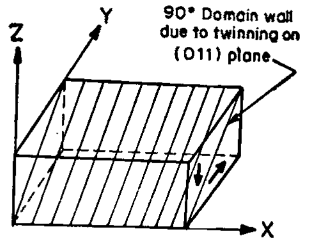

Figure 2. Disallowed 90° domain walls due to twinning on (011) planes

occur, a perpendicular pattern of 90° domain lines is produced (figure 1b). It is interesting to note here that the type of domains shown in figure 2 are not favoured. In this case, the observed plane on A domain is bounded by *a-b* axes, while that on B domain, by *a-c* axes. On account of the large difference in axial values the crystal with this type of domains will involve great strains. Domain structure is formed at 570° C when such strains in the already grown crystals are not present, and no domains of the type are expected to be formed, which was confirmed by the observations reported later in the paper.

In the case of 180° domains, planes other than (011) may serve as domain walls but there is no evidence for it so far in the literature. In the present work the domain observations were carried out optically, and hence no information of 180° domains could be collected.

5. Domain observation and discussion

5.1. *Under reflected light*

Domain walls could be observed on the naturally grown surfaces as well as on cleaved surface. The cleavage plane is (001) and the major face of the grown crystal plates is also (001). The photomicrograph in figure 3 shows a natural surface with two crystal plates *X* and *Y* separated by the grain boundary ABC. The plates *X* contain two sets of parallel domain lines perpendicular to each other. They are formed due to twinning on (110) and ($\bar{1}$10) planes as explained in the earlier section. If the twinning were to take place on (110) of the true cell (and not the subcell) of Labb *et al* (1973), the domain lines due to twinning on (110) and ($\bar{1}$10) would not be at 90° as observed, but at about 53°.

Very commonly, the perpendicular patterns of domain lines formed by twinning on (110) and ($\bar{1}$10) planes are obtained as shown in figure 4. These patterns are clearly similar to the patterns of 90° domain lines in the tetragonal $BaTiO_3$ (Bhide *et al* 1965) and of 60° domain lines in the orthorhombic $KNbO_3$ (Deshmukh and Ingle 1972b). Figure 4 also shows a pattern at 45° on the left region. It is already seen from figure 2 that in the same single crystal such patterns are not expected, as they involve a large amount of strain, which is almost prohibited for the formation of such patterns. It was found with the help of the polarising microscope (as reported later in the paper) that the part of the surface with 45° lines is on a different grain.

The grain structure as seen in figure 4 (as also in figure 3 and observed in several other crystals) is interesting in that the boundaries of the grains are mostly $\langle 110 \rangle$ and $\langle 100 \rangle$ directions. For instance, in figure 4 a closer look at the photomicrograph shows that the grain boundary ABCD is bounded by [100] directions. The reason for this particular grain structure was found in the growth habit of the crystal. The crystals are grown with (001) faces bounded by $\langle 110 \rangle$ and $\langle 100 \rangle$ directions. During the crystal growth, small crystallites get attached with each other with common (001) faces. When $\langle 110 \rangle$ or $\langle 100 \rangle$ direction of both the crystallites come parallel to each other, a coherent crystal is formed, but if a $\langle 110 \rangle$ direction of one comes parallel to $\langle 100 \rangle$ direction of other, a grain boundary with axes rotated by about 45° on either side must be the result. This type of grain structure is an important microstructure in this crystal, as also revealed later by the polarizing microscopic studies.

The photomicrograph in figure 5 shows the domain structure as in figure 4 in addition to the grains AB and CD, which are small rectangular plates. The domain structure inside the grains shows that the grain boundaries are $\langle 100 \rangle$ direction in case of both the grains. Obviously, there must be a little mismatch at the grain boundaries, otherwise a coherent crystal would have resulted. That this is so is indeed shown by the polarizing microscope, where rotations of polar axes across the grain boundaries become evident.

Owing to the spontaneous strain, the domain line AB in figure 6a is not exactly inclined at 45° with the X axis, but $90° - \tan^{-1}(b/a)$. In the case of domain structure seen in figure 6(*b*) the inclination is $90° - \tan^{-1}(a/b)$. Consequently, a wedge-shaped domain with wedge angle $\tan^{-1}(b/a) - \tan^{-1}(a/b)$ as in figure 6(c) can be formed with a domain structure as shown in the schematic sketch. This theoretical situation is found to realise in practice (figure 7). This particular photomicrograph shows several wedge-shaped domain with a wedge angle of nearly 54′ (see for example the wedges at A, B, C, etc.). One can also see in this photomicrograph 90° spikes. These spikes are similar to those observed in $BaTiO_3$ (Bhide and Bapat 1963) and $KNbO_3$ (Deshmukh and Ingle 1971b). The spikes are the domain walls terminating in the bulk of crystals with sharp tips that move forward and backward with slight change in stress or temperature. Both the wedge-shaped patterns and the spikes involve strain energy as the walls terminate in the bulk of crystals. It may be noted here that wedges and spikes do not occur so commonly in $PbNb_2O_6$ as in $KNbO_3$ (Deshmukh and Ingle 1971a, b). Secondly, the domain width is considerably larger, and the domain structure much less complicated. The extent of deviation of the domain walls from regular planes is also small. These factors indicate that the influence of the elastic energy is not as strong in this crystal as in $KNbO_3$. The studies of the dislocations and strains have, however, indicated that the role of

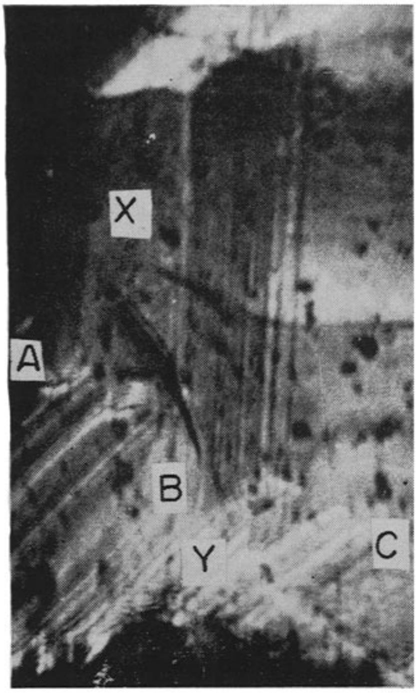

FIG. 3

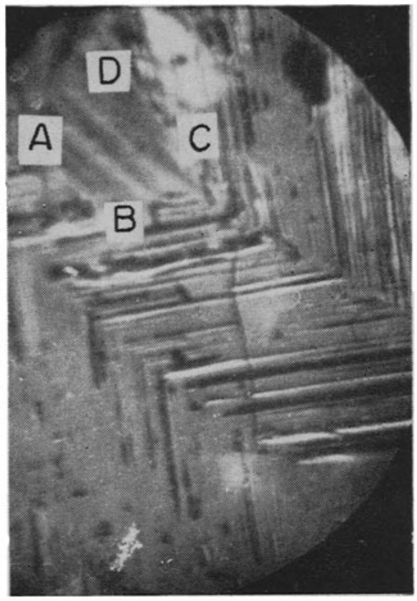

FIG. 4

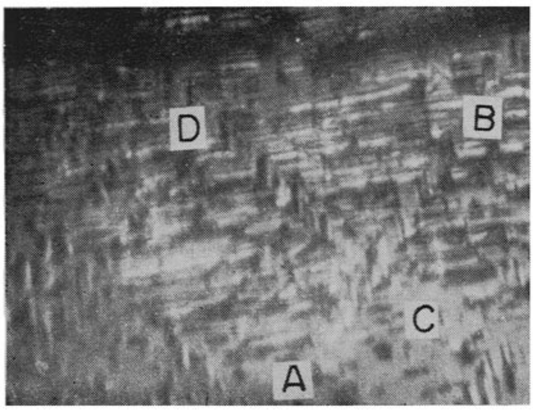

FIG. 5

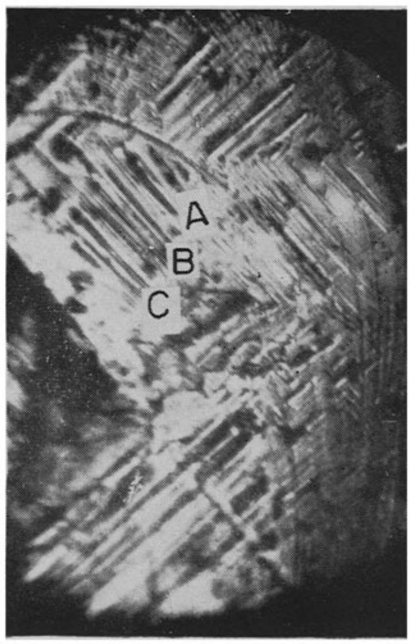

FIG. 7

Figure 3. Natural surface showing two plates X and Y. ABC is the grain boundary separating the plates X and Y (× 405)
Figure 4. Cleaved surface showing perpendicular pattern of 90° domain lines (× 270)
Figure 5. Cleaved surface showing perpendicular pattern of 90° domain lines and two small rectangular grains AB and CD (× 270)
Figure 7. Cleaved surface showing wedge-shaped domains and 90° domain spikes (× 405)

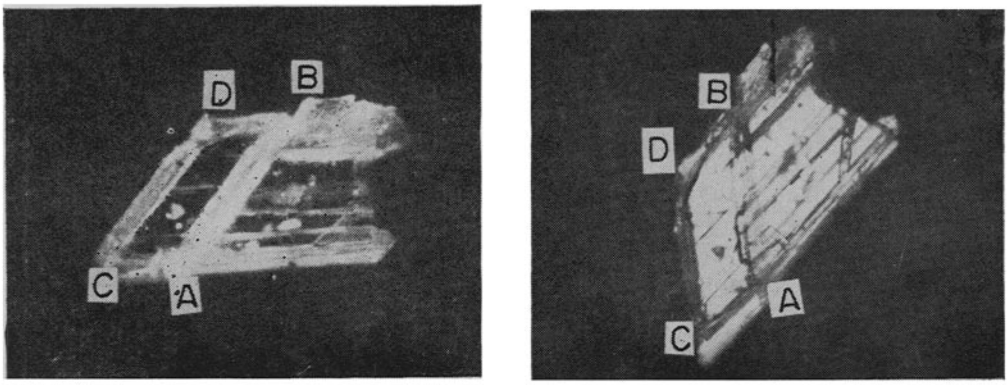

FIG. 8 (a) FIG. 8 (b)

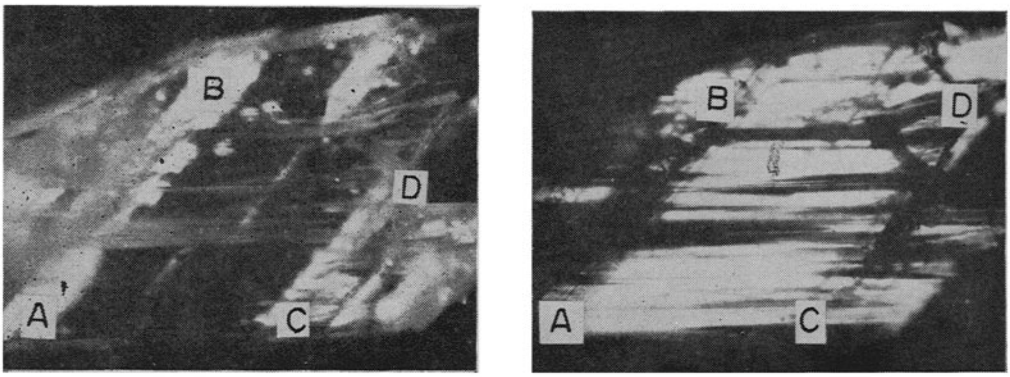

FIG. 10 (a) FIG. 10 (b)

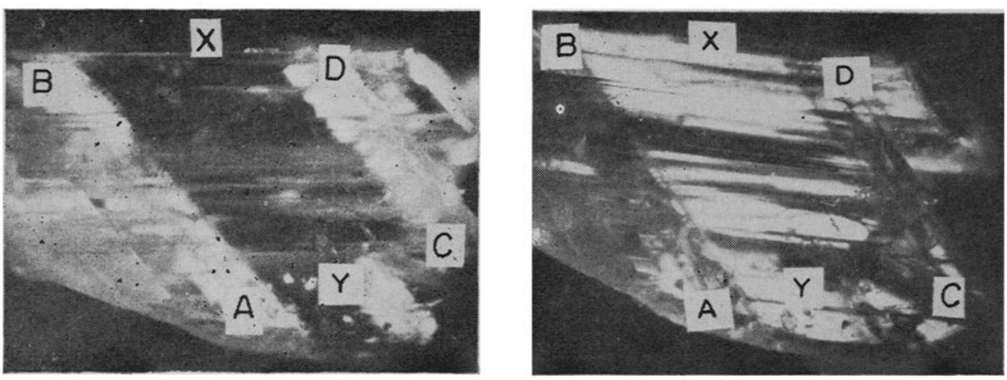

FIG. 11 (a) FIG. 11 (b)

Figure 8. Grain structure when ⟨110⟩ edge of a crystallite is joined to ⟨100⟩ edge of another crystallite. (a) parallel extinction and (b) symmetrical extinction (× 360)
Figure 10. 90° domains (a) parallel extinction and (b) symmetrical extinction (× 360)
Figure 11. 90° and 45° domain lines in the same region. 45° lines are due to mismatch of the grain (a) parallel extinction and (b) symmetrical extinction (× 360)

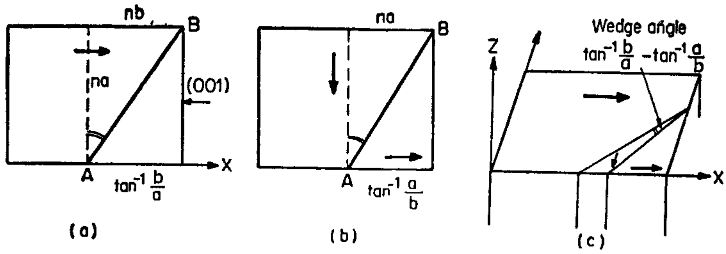

Figure 6. Domain line AB inclined with X axis at (a) $90° - \tan^{-1}(b/a)$ (b) $90 - \tan^{-1}(a/b)$ (c) Wedge-shaped domain with wedge angle $\tan^{-1}(b/a) - \tan^{-1}(a/b)$.

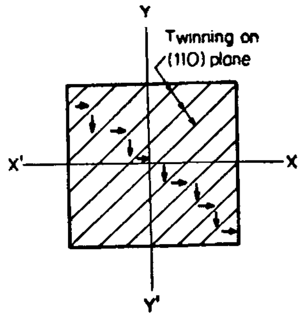

Figure 9. Domain structure present in the crystal shown in figure 8.

elastic energy in domain formation is still appreciable, especially in thick crystals, and these studies are intended to be reported later separately.

5.2. *Under polarizing light using crossed nicols*

If the polar axis is perpendicular to the plane of plate the observation of single domain will show a dark field of view between crossed nicols, but if the polar axis lies in the observed plane the plate will be bright except for the extinction positions in which the polar axis is parallel to either one of the vibrational direction of the polarizer and analyser. Obviously, if different regions extinguish at different positions, they are domains with different orientations of polar axis.

Inspection of domains was made in the two extinction positions called parallel and symmetrical. In parallel, the orthorhombic edges of a crystal flake lies parallel to the planes of polarization of nicols, and in symmetrical, the edges lie symmetrical with respect to the planes of polarization. The later position comes after rotation of crystal stage through 45° of the former.

Figure 8 shows the observations of 90° domains. In parallel extinction, as polar axis of each domain is parallel to the vibrational direction of one of the nicols, they produce dark region across the domain wall. In the symmetrical position, both the domains transmit light equally producing bright regions across the domain boundary (figure 8b). The domain structure present must be as shown schematically in figure 9.

It can be noted from figures 8a and b that the patches AB and CD do not confirm to the domain structure described in figure 9. In figure 8a the patches AB and CD transmit light whereas in the rest of the crystal both sides of domain wall are dark regions. In the symmetrical extinction photomicrograph (figure 8b) the situation is reversed. Since the domain structures with domain lines at 45° with each other is not compatible with the crystal structure as shown before the present observation of extinctions, they have to be understood in terms of the grain structure. If ⟨ 110 ⟩ edge of a crystallite is joined to ⟨100⟩ edge of another crystallite one would get the situation as observed in figure 8. The polar axes in the regions AB and CD are rotated at an angle of nearly 45° with respect to the polar axes in the central dark region of figure 8(a).

A somewhat similar situation is seen in figures 10. Figure 10a is the parallel extinction photograph and figure 10b the symmetrical extinction photograph. The difference in figures 8 and 10 is that the intensities of light in patches AB and CD in figures 8 and 10 differ considerably. This is because the polar axes in AB and CD are not nearly at 45° with respect to the polar axes in the central region as in the case of figure 8, but there is appreciable deviation from the required angle of 45°. Such deviations result depending on the way the crystallites attach with each other during growth.

One more pair of photomicrograph is produced in figure 11, mainly to emphasize the usefulness of the polarizing microscope in studying domain structures. Figure 11a is the parallel extinction photomicrograph and figure 11b the symmetrical extinction. The dark regions in XY and the domain structure involved are easy to understand being similar to those in the larger grains in figures 8 and 10, but the regions AB and CD to the left and right of the central region XY are of interest in this case. These regions show domain lines both parallel to the lines in the black region XY and at 45° with it, and are able to transmit some light also. This situation can be explained as follows. Joined to the region XY are the regions AB and CD that are mismatched by 45°, and hence the 45° lines are in them. In the parallel extinction position they transmit light, but a layer of overgrowth has occurred over those regions matching in structure with the central region XY in which the domain lines seem to be spreading from across the dark region to brighter regions. On account of this overgrowth requiring dark region, some of the intensity is reduced resulting in intensity as shown in figure 11a. In the symmetrical extinction photograph, the situation is naturally reversed. The XY region is bright and the other regions dark. Thus the polarizing microscope has been able to resolve the anomaly of observing 90° and 45° lines in the same region, a type of domain structure entirely prohibited due to large strains it would involve.

6. Conclusion

The observed domain structure does not deviate very much from the theoretically expected domain structure. One gets an interesting grain structure, and the polarizing microscope serves well to resolve the domain structure as well as the grain structure. The observed domain structures show some influence of the elastic energy on domain formation but not to the extent as it is evident in $KNbO_3$.

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