Domain structure in ferroelectric PbNb₂O₆

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Abstract. Single crystals of ferroelectric PbNb₂O₆ 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 BaTiO₃ and KNbO₃. 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 BaTiO₃ and KNbO₃. The twinning can occur also on (110) plane producing a domain line at 90° with that due to twinning on (110). This gives patterns of perpendicular lines similar to those in KNbO₃ and BaTiO₃. 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 KNbO₃ carried out, in our laboratory has provided useful information. These studies are now extended to ferroelectric PbNb₂O₆, 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) niobate, PbNb₂O₆, 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 \( a = 17.51 \) Å, \( b = 17.81 \) Å and \( c = 2 \times 3.86 \) Å and at the Curie temperature \( a = 12.46 \) Å and \( c = 3.907 \) Å (Francombe and Lewis 1958). According to Labbe et al (1973) the subcell parameters are \( a = 17.65 \) Å, \( b = 17.92 \) Å and \( c = 3.87 \) 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.
There is some structural resemblances between the para-electric phase (tetragonal) of PbNb$_2$O$_6$ 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$_2$O$_6$ the Pb$^{2+}$ ions occupy five out of the six available interstitial sites formed by this framework. In spite of this structural resemblance, PbNb$_2$O$_6$ 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$_2$O$_6$, 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$_2$O$_6$ 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$_2$O$_5$ 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 × 1 × 0.3) 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 (110) planes