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Multiple-crystal x-ray topographic characterization of periodically domain-inverted $KTiOPO_4$ crystal

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A periodically domain-inverted $KTiOPO_4$ crystal has been characterized for the first time by multiple-crystal multiple-reflection x-ray topography. The striation contrast within the domain-inverted regions has been revealed in high strain-sensitivity reflection topographs. The origin of formation of the striation contrast and the mechanism of domain inversion in $KTiOPO_4$ are discussed in terms of the structural characteristics of $KTiOPO_4$. © *1995 American Institute of Physics.*

Potassium titanyl phosphate $KTiOPO_4$ (KTP), has received intense interest for some time as a nonlinear optical material for novel applications because of several unique properties, such as a high effective nonlinear optical coefficient, a wide acceptance angle for type II noncritical phase-matching, thermal stability, and high laser damage threshold.[1–3] A considerable body of work on the physical properties and structures of crystals of the KTP family has been carried out including studies of the ferroelectric phase transition and the related formation of domains in KTP crystals.[2–11] Nevertheless, it is noted that naturally occurring domains and domain walls have never been directly observed in KTP primarily because they are 180° domains.

KTP is presently widely used for frequency doubling 1.06 μm radiation from Nd:YAG lasers to generate green light. However, extension of the applicability of KTP via reversing the domain polarization or domain inversion techniques will be valuable for other optical applications. Using domain-inversion techniques, it is possible to phase-match an arbitrary wavelength by selecting the appropriate period of modulation.[12,13] Recently, a periodically poled domain structure in a (001) section of KTP has been fabricated by electron beam scanning on the $(00\bar{1})$ face.[14] Furthermore, techniques to fabricate periodic domain inversion in $LiNbO_3$[15–18] and $LiTaO_3$,[19] as well as in KTP,[14,20,21] have been developed rapidly. However, it seems that periodically poled domain structures have not been well understood thus far. Since it is necessary to develop reliable and reproducible periodic-poling techniques for high-quality optical devices, the establishment of a structural and microstructural understanding of periodic domain inversion is of considerable importance and interest.

Multiple-crystal x-ray diffraction topography[22,23] has been extensively used for the characterization of bulk crystals or thin films of semiconductors and related materials because of its high strain sensitivity. To our knowledge, this technique has not been applied to inspecting periodic domain-inversion as yet. In the present letter, we report for the first time multiple-crystal x-ray topographic characterization of a periodically domain-inverted KTP crystal. The experimental results give a clear demonstration of the great potential of multiple-crystal topography in characterization of periodically domain-inverted nonlinear optical crystals.

Several blocks of domain-inverted regions of period 20 μm in optical grade hydrothermally grown KTP were produced by scanning an electron beam on the (001) (or-c) face.[14] The sample was then etched using a domain-selective etch at 220 °C that preferentially attacks the $(00\bar{1})$ surface. Figure 1 shows an optical transmission micrograph of the periodically domain-inverted structure in one of the grating blocks in the etched $(00\bar{1})$ face of KTP. The period of the domain inversion was revealed to be 20 μm with domain walls parallel to the (100) lattice plane. A Philips high resolution multiple-crystal multiple-reflection x-ray diffractometer,[23] which combines the advantages of a two-crystal four-reflection Ge 220 monochromator and Ge 220 analyzer, was then used for characterization of the periodically domain-inverted KTP sample. The x-ray diffraction topographs were taken using Cu $K\alpha_1$ radiation with 40 kV×30 mA, and recorded on 25 μm Ilford L4 nuclear emulsion plates.

$00\bar{4}$ and $00\bar{8}$ symmetric reflections with a three-crystal, five-reflection geometry were used for high strain-sensitivity x-ray diffraction topography. The rocking curve widths of 004 and 008 reflections from the sample are 45 and 30 seconds of arc, respectively, larger than the angular and spectral divergence of the incident beam produced by the monochromator. The defect images occur from deviation from the diffraction condition due to either a change of orientation θ or

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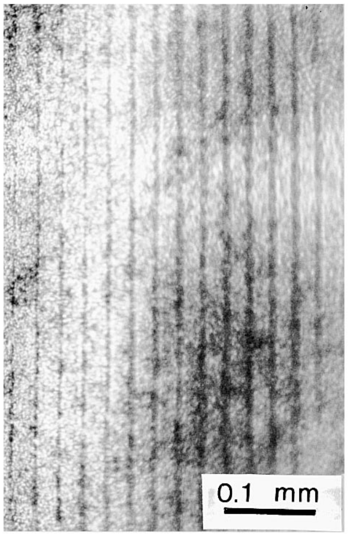

FIG. 1. Optical micrograph of periodically domain-inverted structure on the (001) face of a $KTiOPO_4$ crystal. The dark lines correspond to domain walls.

of lattice spacing d, or of both simultaneously. This can be simply written as follows[22]:

$$\Delta I = K\left(\frac{\Delta d}{d}\tan\theta_B + \delta\theta\right), \tag{1}$$

where θ_B is the Bragg angle, K is the slope of the rocking curve flanks, $\Delta d/d$ the local relative change in spacing of the diffracting planes, and $\delta\theta$ the component of the local lattice rotation with respect to the goniometer axis. The $\Delta d/d$ and $\delta\theta$ effects can be separated via two-dimensional diffraction maps.[23]

A clear demonstration of the contrast difference between the domain-inverted grating block and the untreated area (without electron-beam writing) is shown in Fig. 2, taken at the steep part of the rocking curve flanks. Figure 2(a) corresponds to a 008 diffraction topograph of the untreated or domain-uninverted region which is characterized by a relatively smooth distribution of intensity. However, sets of vertical striations in domain-inverted blocks were observed in the 004 and 008 reflections [Figs. 2(b) and 2(c)]. The left-hand side of each of these two topographs corresponds to the untreated zone and the right-hand side is the domain-inverted region. The striation features revealed in the 004 and 008 reflection topographs appear essentially the same, but the sensitivity in Fig. 2(c) is higher than that in Fig. 2(b). The enhancement of striation contrast at the border of the domain-inverted region in Fig. 2(b) is attributed to the image condensation and the local surface effect due to low Bragg angle incidence compared with the 008 reflection topograph. The steep slopes of the rocking curve flanks for the 004 and 008 reflections are 1.4×10^6 and 2.3×10^6 (cps/deg), respectively. This means that it is possible to detect low lattice strains of 10^{-7} or small rotations of 10^{-3} second of arc in the x-ray topographs. The striation contrast disappeared when x-ray topographs were taken at tails of the rocking curves, suggesting that lattice distortions are very low. The typical rocking curve widths of the 008 reflection obtained from ω and $\omega/2\theta$ scans using the triple-axis mode[23] in the domain-inverted regions are 17 and 13 seconds of arc, respectively. Such difference in the rocking curve widths was not observed in the untreated regions while we performed ω and $\omega/2\theta$ scans. Therefore, the distortions generated within the domain-inverted regions should come principally from the lattice tilt $\delta\theta$ rather than the lattice dilation $\Delta d/d$.

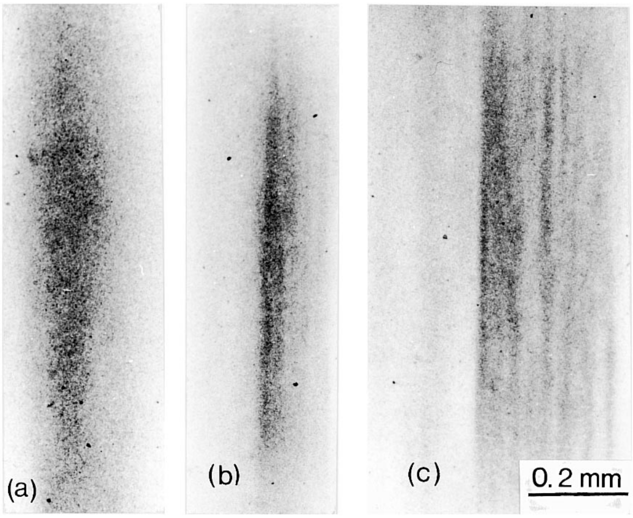

FIG. 2. Three-crystal five-reflection topographs of a periodically domain-inverted $KTiOPO_4$ crystal. Magnification ×65; (a) The untreated region, 008 reflection; (b) showing the striation contrast within the domain-inverted zone (right-handside), 004 reflection; (c) showing the striation contrast within the domain-inverted region (right-handside), 008 reflection.

Careful inspection of the images shows that the spacings of the striations revealed in the x-ray topographs are much larger than the period of the domain inversion, and that the striation distributions in different grating blocks are not identical. This suggests that the topographic striations are not identical with the contrast resulting from either the domains or domain walls. Then, what is the original of the formation of the striation contrast in the topographs in the domain-inverted regions?

It is noted that the KTP sample is strained when subjected to electron bombardment because of the converse piezoelectric effect. The piezoelectric tensor d_{ijk}, for point group $mm2$ is

$$\begin{pmatrix} 0 & 0 & 0 & 0 & d_{131} & 0 \\ 0 & 0 & 0 & d_{223} & 0 & 0 \\ d_{311} & d_{322} & d_{333} & 0 & 0 & 0 \end{pmatrix}. \tag{2}$$

In the domain-inversion experiment, the applied electric field (E_3) is along the [001] direction. So, the components of the induced strain are

$$\begin{aligned} S_{11} &= d_{311}E_3, \\ S_{22} &= d_{322}E_3, \\ S_{33} &= d_{333}E_3. \end{aligned} \tag{3}$$

This means that the electric field produced by the electron beam bombardment causes three mutually perpendicular components of the strain in the irradiated regions, together with the domain inversion. In principle, the strained and

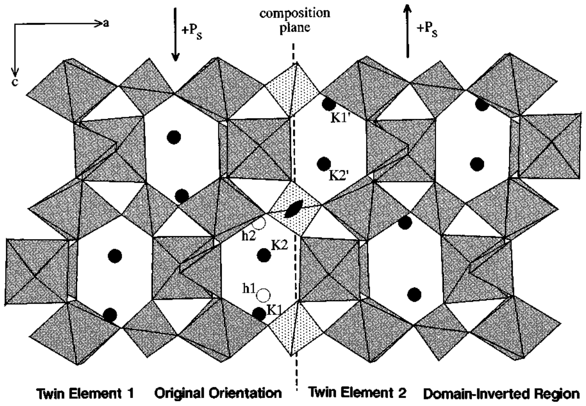

FIG. 3. [010] view of the twinned domains in $KTiOPO_4$ related by a 2[010] operation (denoted on the figure) matched along the (100) composition plane (i.e., the twin plane) through the P(1) atoms which lie on the [010] pseudo-twofold axis. Shaded elements are the TiO_6 octahedra and PO_4 tetrahedra. Solid circles are the K ions and open circles represent the hole sites. In the discussion, we consider twin element 1 as the original orientation of the structure and twin element 2 to represent the domain-inverted regions.

strain-free regions should appear alternately because of the periodic arrangement of the electron-injected and untreated zones. However, the induced strains interact with the initial strain fields in the sample so that local lattice tilts or inhomogeneous lattice strains are more easily generated around initial defects than in the near-perfect area. This is major reason why the striation spacing does not coincide with the period of the domain inversion. Similar results have been observed in domain-inverted $LiNbO_3$,[24] where the ‘‘mosaic structure’’ generated in the domain-inverted process is similar to the initial distribution of dislocations in the sample.

The observations can be put into the context of the structural characteristics of KTP. The ferroelectric phase transition of KTP is assumed to be displacive and strongly second-order,[4] involving a space–group transition from prototype symmetry Pnan to room-temperature $Pna2_1$.[9] This allows the possibility of 180° twinning via several symmetry operations. For illustration, the KTP structure and its twin formed via a 2[010] operation through $P(1)$ are shown in Fig. 3, matched along the (001) composition plane (i.e., the twin plane). We can see that each K ion is highly coordinated by oxygen atoms, and that at a short distance along the $-c$ axis from each K ion there is an empty site [$h(1)$ and $h(2)$ in Fig. 3] which can be viewed as alternative K sites. We contend that the lattice strain normally associated with domain walls is very small or negligible because the local strain of the formula units caused by twinning can be relaxed without greatly distorting the original configuration of the unit cell. This results mainly from the deformability of the large cages around K(1) and K(2). In this sense, such a domain wall in KTP should have relatively low energy.

K ions can easily move or diffuse possible via a hole mechanism along the zigzag paths, usually termed channels, winding around the [001] direction. It has been observed that domain reversal by electron beam scanning occurs because of the electric field developed because of the deposited electron beam charges at one surface. Therefore, it is reasonable to assume that the electric field primarily drives the K ions towards the negative electrode or (001) face, for example, moving K_1 and K_2 ions into K_1' and K_2' sites to form the domain-inverted structure, i.e., the other of the twin components. These movements of the K ions then provide secondary impetus for the TiO_6/PO_4 formula units to make the small adjustments necessary so that inversion of the whole structure occurs within a region injected with electrons.

In conclusion, we have applied multiple-crystal multiple-reflection high resolution x-ray topography for the first time to the characterization of domain-inverted grating in KTP fabricated by electron beam writing. Striation contrast has been revealed in high strain-sensitivity x-ray topographs, and is considered to be relevant to the domain inversion process. A possible mechanism of the domain inversion in KTP which involves a 2[010] twinning operation is proposed, from which the usual invisibility of strain contrast of the domain walls themselves can be understood.

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