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Differential Vector Poling for Artificial Domain Control of $KNbO_3$ single crystals

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The domain structures other than 180° domains are very attractive because their boundaries or their integrated structures have versatile possibility for new applications. To control these domain structures artificially, the dependence of electric poling directions of domain generation in $KNbO_3$ single crystals was investigated. To apply electric field in several different directions, we could find that the optimum direction for poling is coincident with the direction of the difference of the spontaneous polarization vectors between original domain and controlled domain. We call this poling concept as 'Differential Vector Poling'. Using this method, we succeed in fabricating 60° domain with applying about 240 V/mm and in fabricating 90° domain with applying about 140V/mm. We could also observe the domain generation processes from the cross section using video camera. The boundaries of these controlled domain structures feel difference of refractive index, so it could become devices for refractive index control.

Key words: $KNbO_3$, 90° domain, 60° domain, electric poling

1. INTRODUCTION

Domain control technologies of single crystals, especially 180° domains, have made progress rapidly in recent years. For example a lot of periodically poled devices such as $LiNbO_3$, $KNbO_3$, and $KTiOPO_4$ were demonstrated in optical applications [1-4]. It is well known that some biaxial crystals, such as $KNbO_3$, $BaTiO_3$, have several spontaneous polarization directions [5-6]. For these biaxial materials, engineered domain structures are greatly investigated recent year because their piezoelectric and ferroelectric properties are enhanced [7-8].

If these domain structures other than 180° can be fabricated under controlled, these crystals will become a versatile performer in a lot of applications. It is important to investigate domain generation process in experimentally and theoretically. $KNbO_3$ is one of the good research targets because it has several domain structures at room temperature. Furthermore, $KNbO_3$ is very attractive in its large birefringence, high electro-optic and nonlinear constants, low optical damages, and good piezoelectric properties for surface acoustic wave (SAW) devices and bulk ultrasonic devices [2-3, 8-10].

In our group so far, electric poling method were investigated to control the several domain structures of $KNbO_3$ single crystals. We demonstrated the fabrication of 180° periodically poled $KNbO_3$ (PPKN) as nonlinear optical devices [2]. Recently, the fabrication of 60° and 90° domain structures of $KNbO_3$ have been demonstrated [11-12]. In order to control these domain structures, next two points are important. First, the direction of electric field for poling against crystallographic axis is primary important. Second, the direction of metal electrodes on the crystal surface must be made parallel to the permissible domain wall direction.

In this paper we investigate the dependence of the electric poling direction in artificial domain control of $KNbO_3$ single crystals. 'Differential vector poling' could be one of the easiest artificial fabrication methods of several domain structures in single crystals.

2. DOMAIN STRUCUTURE OF $KNbO_3$

$KNbO_3$ is a perowskite ferroelectric crystal with the same sequence of phase transitions as $BaTiO_3$. On cooling it transforms from a cubic to a tetragonal, an orthorhombic, and a rhombohedral phase at temperatures of 418, 203, and -50℃, respectively [5]. The crystal structure and point group of $KNbO_3$ at room temperature is orthorhombic and mm2, respectively. Fig. 1 illustrates a schematic view of lattice structure of $KNbO_3$ in orthorhombic phase. Domain structures of $KNbO_3$ are decided by relative position of potassium, niobium, and oxygen. In this paper, we treat the lattice constants as a=0.5695 nm, b=0.3973 nm, c=0.5721 nm, respectively [5]. To treat spontaneous polarization

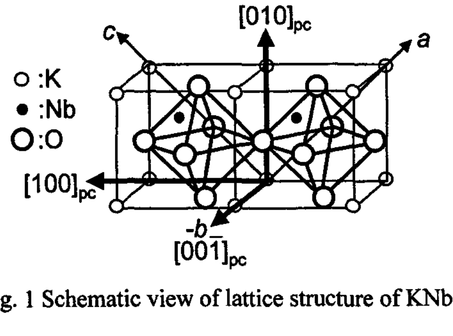


Fig. 1 Schematic view of lattice structure of $KNbO_3$

Table I The direction of polarization vector poling and differential vector poling for several domain structures.

Domains	P_s Original Domain	P_s Controlled Domain	E_c Polarization Vector Poling	E_c Differential Vector Poling
60°	$[110]_{pc}$	$[011]_{pc}$	$[011]_{pc}$	$[\bar{1}01]_{pc}$
90°	$[110]_{pc}$	$[\bar{1}10]_{pc}$	$[\bar{1}10]_{pc}$	$[\bar{1}00]_{pc}$
120°	$[110]_{pc}$	$[\bar{1}01]_{pc}$	$[\bar{1}01]_{pc}$	$[\bar{2}\bar{1}1]_{pc}$
180°	$[110]_{pc}$	$[\bar{1}\bar{1}0]_{pc}$	$[\bar{1}\bar{1}0]_{pc}$	$[\bar{1}\bar{1}0]_{pc}$

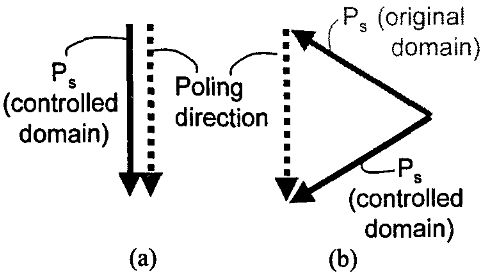


Fig. 2 Concepts of electric poling. (a): Polarization vector poling, (b):Differential vector poling.

Table II The permissible domain wall directions for several domain structures. [6]

Domain	Original Domain	Controlled Domain	Domain Wall Direction
60°	$[110]_{pc}$	$[011]_{pc}$	$(khk)_{pc}$*
90°	$[110]_{pc}$	$[\bar{1}10]_{pc}$	$(010)_{pc}$
120°	$[110]_{pc}$	$[\bar{1}01]_{pc}$	$(011)_{pc}$
180°	$[110]_{pc}$	$[\bar{1}\bar{1}0]_{pc}$	all

* $h \doteqdot 0.3$, $k=1$

direction easily, the pseudocubic axes were used. We choose [110]-direction of pseudocubic axes ($[110]_{pc}$) as the spontaneous polarization direction (*c*-axis) of KNbO$_3$. *a*-axis and *b*-axis correspond to $[\bar{1}10]_{pc}$ and $[001]_{pc}$, respectively. To consider spontaneous polarization direction, there are four directions ($[101]_{pc}$, $[10\bar{1}]_{pc}$, $[011]_{pc}$, and $[01\bar{1}]_{pc}$) for 60° domain, two directions ($[\bar{1}10]_{pc}$ and $[1\bar{1}0]_{pc}$) for 90° domain, four directions ($[\bar{1}01]_{pc}$, $[\bar{1}0\bar{1}]_{pc}$, $[0\bar{1}1]_{pc}$, and $[0\bar{1}\bar{1}]_{pc}$) for 120° domain, and one direction ($[\bar{1}\bar{1}0]_{pc}$) for 180° domain.

3. EXPERIMENTAL SETUP

3.1 Two Poling Concepts

To investigate the dependence of the electric poling direction in artificial domain control process, we chose two different electric poling concepts. Fig. 2 shows two poling concepts named as 'polarization vector poling' and 'differential vector poling'. In the case of 'polarization vector poling', the poling direction should be selected as the spontaneous polarization direction of controlled domain. On the other hand, in the case of 'differential vector poling', the poling direction should be selected as the proper direction that is coincident with the direction of the difference of spontaneous polarization vectors between original domain and controlled domain. Table I shows the poling directions of 'polarization vector poling' and 'differential vector poling' for 60° domain ($[011]_{pc}$), 90° domain ($[\bar{1}10]_{pc}$), 120° domain ($[\bar{1}01]_{pc}$), and 180° domain ($[\bar{1}\bar{1}0]_{pc}$).

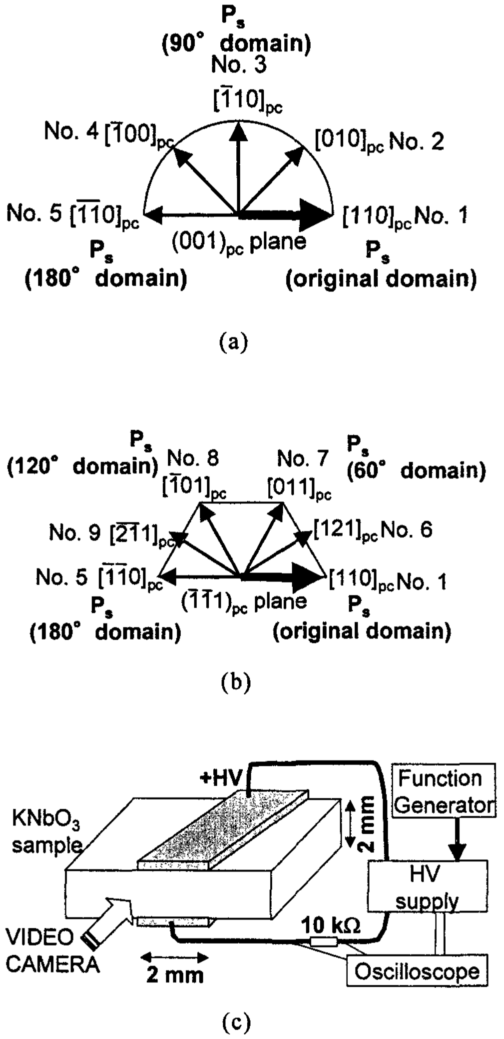


Fig. 3 Experimental setup. (a) and (b) show the directions of prepared samples, and (c) shows poling circuit.

3.2 Domain Wall Direction

The permissible domain wall directions were described by Fousek and Wiesendanger [6,13]. There are two types of domain walls, charged wall and uncharged wall. Uncharged wall is more stable than charged wall. The permissible uncharged domain wall directions of KNbO$_3$ for each domain structure are shown in Table II [6]. To fabricate arbitrary domain structures, it is effective to make electrodes parallel to permissible domain wall direction because it could be avoided to generate unwanted strains during fabrication process.

3.3 Sample Preparation

A $KNbO_3$ crystal was grown by the top seeded solution growth (TSSG) method and was cut into cubic blocks parallel to *a* -, *b*-, and *c*-axis about 15mm×15mm×15mm. These blocks were poled by applying the electric field (200V/mm) at 215℃ and then annealed 120 hours at 195℃ to make it single crystal.

To investigate dependence of electric poling direction in fabrication of several domains, plates 2 mm in thickness cut as 9 different directions were prepared as shown in Fig. 3(a) and (b). Both surfaces were optically polished. Electrodes were made parallel to permissible domain wall direction by silver paste with about 2 mm in width. The side surfaces of samples were also optically polished to observe domain generation processes observing magnified optical images by video camera.

3.4 Experiment System

Fig. 3(c) illustrates the schematic view of poling systems. The electric field was applied between two electrodes using HV supply (Matsusada Precision Inc, Model HEOPT-20B10) controlled by arbitrary function generator (Yokogawa Electric Corp. Model AG2200). Domain generation processes were measured by electric current using oscilloscope and by optical images using video camera.

To avoid generation of unwanted domains, triangle or trapezoid voltage patterns were applied.

4. RESULTS AND DISCUSSION

Fig. 4 shows an example of measured electric current waveforms as poling. We could recognize the threshold voltage of the domain generation from these forms. In the cases of poling directions those were tilted at an angle 90° or more to the original spontaneous polarization direction (No. 3, 4, 5, 8, and 9), electric current peaks were observed like Fig. 4. Fig. 5 shows an example of measured optical images of before and after domain generation. In most of cases, generation processes were observed when applied voltage achieved threshold voltage. The measured threshold voltages were reproducible with an error in about 10%. Table III shows the results of measured threshold voltages and observed domain structures. In 60° - and 90° domain case, the threshold voltages of 'differential vector poling' were lower than those of 'polarization vector poling'. It is expected that 'differential vector poling' is easiest way for artificial domain control.

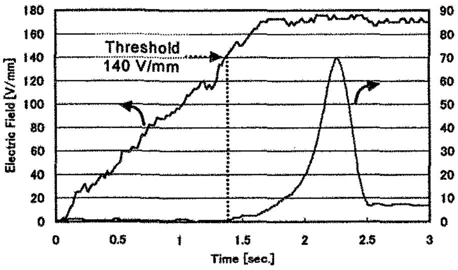
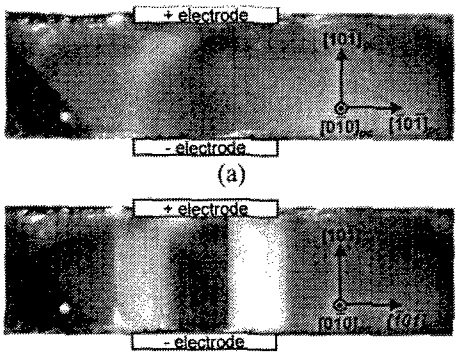


Fig. 4 Typical electric current waveform. (The case of differential vector poling for 90° domain (poling direction No. 4)).



(a)

(b)

Fig. 5 Optical images of 60° domain generation process in the case of differential vector poling (Poling direction No. 8). (a) and (b) are images before and after poling, respectively. The area between the two white regions, those are domain walls tilted to the observing $[0\bar{1}0]_{pc}$ surface, is fabricated 60° domain structure.

Table III Measured threshold voltages and observed domain structures for several poling directions.

	Polarization Vector Poling			Differential Vector Poling		
Domain	Poling Direction	Observed Domain	Threshold Voltage [V/mm]	Poling Direction	Observed Domain	Threshold Voltage [V/mm]
60°	No.7 $[011]_{pc}$	No Change	——	No.8 $[\bar{1}01]_{pc}$	$[011]_{pc}$ (60°)	240
90°	No.3 $[\bar{1}10]_{pc}$	$[\bar{1}10]_{pc}$ (90°)	235	No.4 $[\bar{1}00]_{pc}$	$[\bar{1}10]_{pc}$ (90°)	140
120°	No.8 $[\bar{1}01]_{pc}$	$[011]_{pc}$ (60°)	245	No.9 $[\bar{2}\bar{1}1]_{pc}$	$[011]_{pc}$ (60°) $[\bar{1}\bar{1}0]_{pc}$ (180°)	215
180°	No.5 $[\bar{1}\bar{1}0]_{pc}$	$[\bar{1}\bar{1}0]_{pc}$ (180°)	250	No.5 $[\bar{1}\bar{1}0]_{pc}$	$[\bar{1}\bar{1}0]_{pc}$ (180°)	250

After poling, the fabricated domain structures were evaluated by measuring surface profile images and optical microscope images, and by using etching technique [2,11,12,14]. The controllability of each domain was investigated in the following.

4.1 180° domain

180° domain is visualized by surfaces profiles after etched by 50% hydrofluoric acid solution at room temperature [2]. In 180° domain case, the directions of 'polarization vector poling' and 'differential vector poling' are identical same. The threshold voltage of 180° domain is larger than that of other domain structures.

4.2 90° domain

90° domain walls were confirmed by surface profiles, domain wall directions, and transparence optical microscope using birefregence effect [11,14]. In 'differential vector poling' case, a lot of domain walls were generated under electrode. After applying over threshold voltage for about 10 minutes, several domain walls are merged and sharp clear domain walls were obtained only at the edges of electrode. In 'polarization vector poling' case, a lot of domain walls were generated under and around electrode and some of them were remained as shown in Fig. 6. The threshold voltage of 'polarization vector poling' is larger than that of 'differential vector poling'. From these result, it is expected that the direction of the 'differential vector poling' is suitable direction to fabricate 90° domain structures.

4.3 60° domain

60° domain walls were confirmed by surface profiles, and domain wall directions [12]. In 'differential vector poling' case, 60° domain walls ($(1/0.3/1)_{pc}$ walls) generated when about 230 to 250V/mm was applied and sharp clear domain walls were obtained only at the electrode edges after several seconds poling as shown in Fig. 5.

On the other hand, in 'polarization vector poling' case, no changes were observed up to E_c~1000V/mm. Over 1000V/mm applied, electric discharging in the sample was occurred. From these result, it is also expected that the direction of the 'differential vector poling' is also suitable direction to fabricate 60° domain structures..

Compared to the domain generation process of 90° domains, the threshold voltage of 60° domains in 'differential vector poling' case is higher than that of 90° domains but the velocity of domain wall movement of 60° domains is faster than that of 90° domains.

4.4 120° domain

In 'differential vector poling' case for 120° domain, sample area under electrodes was become milky color when threshold voltage (about 215 V/mm) were applied. In the milky color region, 60° domain walls were observed by optical microscope image. Using etching technique by hydro fluoride acid, 180° domains were observed in most of milky color region. Permissible 120° domain wall ($(101)_{pc}$ walls) were rarely observed. This tendency is similar to Wiesendanger's report [6]. Although 120° domains were observed in some area, 120° domain was not generated under control. On the other hand, in 'polarization vector poling' case, 60° domains were generated as mentioned in 4.3. From these results, fabrication of 120° domains without generation of other domain structures by electric poling method is difficult.

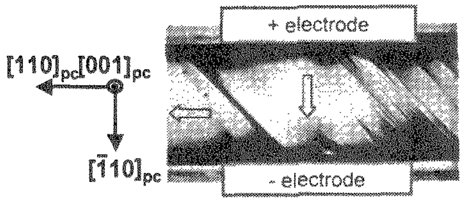


Fig. 6 Residual domain walls in fabricating 90° domains (The case of poling direction No. 3). Arrows mean spontaneous polarization directions of after poling.

In the cases of poling directions those were tilted at an angle within 90° to the original spontaneous polarization direction (No. 1, 2, 6, and 7), no remarkable changes were observed in current profiles and optical images when applied electric field achieved 1000V/mm. From these results, it is expected that the domain structures were difficult to change when some elements of applied electric field contain the same direction of the original spontaneous polarization.

5. CONCLUSION

The dependence of the electric poling direction in artificial domain control process of $KNbO_3$ single crystals was investigated. Using 'differential vector poling' and consider permissible domain wall direction, we could control 60° domain, 90° domain and 180° domain structures of $KNbO_3$ single crystals artificially. This concept could be applied to other materials that have several domain structures such as $BaTiO_3$. The boundaries of these controlled domain structures feel difference of material constants such as refractive index, so it will be expected new functional devices.

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