Ferroelectric domain formation and photocatalytic activity on porous alkali niobate piezoelectric ceramics

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Present study showed synthesis of novel type of porous alkali niobate piezoelectric ceramics, and the formation of domains and photocatalytic activity for the porous piezoelectric ceramics were investigated while comparing with dense ceramics to confirm enhancement of domain orientation and photocatalytic activity around pores. Porous Li₀.₀₆Na₀.₄₇K₀.₄₇NbO₃ piezoelectric ceramics were synthesized by a template method using polymethylmethacrylate as a pore former agent. Uniform pores with 6 µm in diameter were dispersed in the porous ceramics. Porous ceramics synthesized with 10 vol% of the pore former agent showed piezoelectric voltage coefficient, 29 mV/m/N, which is same as that of the dense ceramics. Smaller striped domains formed at an edge of the porous ceramics, indicating that orientation of domains was promoted by electric field concentration around the pores. Through photoreduction reaction of Ag⁺ ion, local precipitation of Ag was shown around the pores on the poled porous ceramics, whereas Ag was located over an entire surface of unpoled porous ceramics. Highest photocatalytic activity was shown for the poled porous ceramics in photodecomposition test of methylene blue. These results clearly indicated photocatalytic activity was enhanced on ferroelectric domains around pores of porous piezoelectric ceramics.

Key-words : Alkali niobates, Domain, Ferroelectrics, Photocatalyst, Piezoelectrics, Polarization, Porous

1. Introduction

Photocatalytic reaction induced by photoexcited electrons and holes is a key approach to achieve hydrogen generation, pollutant decomposition and CO₂ conversion, leading to the establishment of sustainable society. Recombination between the photoexcited electrons and holes is known to reduce efficiency of the photocatalytic reactions. Although various technologies, e.g. loading noble metal-based co-catalysts and combining two semiconductor photocatalysts,¹¹⁻¹³ have been developed to avoid losses from the recombination, there is still a high desire to look for an effective way to improve carrier transfer and photocatalytic activity. Piezoelectric materials are of significant interest in a field of photocatalysis because spontaneous polarization within a ferroelectric domain produce a charged surface, then photoexcited carriers migrate to the charged surfaces and are stabilized in the opposite direction, inhibiting the electron–hole recombination.⁵¹⁻⁵³ Furthermore, recent reports show a combination of piezocatalysis ¹⁴,¹⁵ and photocatalysis improves the catalytic performance when mechanical vibration and light irradiation are simultaneously subjected to piezoelectric materials.¹⁶,¹⁷ The catalytic activity is affected by not only the presence of spontaneous polarization but also magnitude, orientation and microstructure of domain.¹⁸⁻²² Introduction of a porous structure in piezoelectric materials is an effectual way to promote the orientation of domain and to increase magnitude of out-of-plane polarization.²³⁻²⁵ R. L. Johnson-Wilke et al. evaluated difference in domain reorientation between dense Pb(Zr₀.₃₀Ti₀.₇₀)O₃ films and porous films. The porous films exhibited approximately 12 vol% of domains reorient, and a fraction of c-axis domains with polarization laying out-of-plane and parallel to an electric field direction was larger than that of the dense Pb(Zr₀.₃₀Ti₀.₇₀)O₃ films.²⁵ It was considered that electrolytic concentration around the pores could contribute to the reorientation of domains.

Therefore, photocatalytic reaction must be enhanced around pores on porous piezoelectric materials and it depend on pore structure, distribution, size, etc. In this study, we fabricated porous alkali niobate piezoelectric ceramics by a template method and investigated domain structures and photocatalytic activities. Piezoelectric ceramics show various patterns of domain structures with orientation of spontaneous polarization aligned within grains, and they are classified as watermarks, stripe, and
herringbone pattern according to difference in the orientation. Herein, for domains around/far from pores on ceramics poled with various applied electric fields, change in the domain patterns and domain sizes were directly observed to quantify the impact of pore on the domain orientation and photocatalytic reactivity. Photodeposition of Ag is used for investigating the photoreduction activity of domains, and the photocatalytic activity was evaluated by combining the results of Ag deposition and photodegradation test of methylene blue.

2. Experimental procedure

2.1 Synthesis of dense and porous \( \text{Li}_{0.06}\text{Na}_{0.47}\text{K}_{0.47}\text{NbO}_3 \) ceramics

LiCO\(_3\) of 99.8% purity, Na\(_2\)CO\(_3\), K\(_2\)CO\(_3\) and Nb2O\(_5\) of 99.9% purity were weighed according to the formulas of \( \text{Li}_{0.06}\text{Na}_{0.47}\text{K}_{0.47}\text{NbO}_3 \) (LNKN). The starting powders were mixed by wet ball milling for 16 h with acetone as a medium. The mixed powders for LNKN were dried at 120 °C for 3 h and calcined at 910 °C for 10 h. To synthesis porous LNKN ceramics (porous-LNKN), 10 or 30 vol% of polymethylmethacrylate (PMMA, 10 μm in average particle size) was added to the calcined powder and well-ground. The calcined powder alone or the mixture of calcined powders and PMMA was pressed into pellet disks and sintered at 1003 °C for 2 h or 1003 °C for 0.5 h to obtained dense LNKN ceramics (dense-LNKN) or porous-LNKN, respectively.

2.2 Electrical property measurement and domain structure observation

The obtained ceramic disks were double-side polished, and silver electrodes were pasted on both sides of the disk. Relative permittivity of the samples was calculated using LCR meter (ZM2355, NF Corporation, Yokohama, Japan). Poling of the samples were conducted in silicone oil under applied electric field of \( E = 0.7 \text{kV/mm} \) for 30 min at 75 °C. Piezoelectric coefficient (\( d_{33} \)) of the samples poled under electric field of 3 kV/mm was measured with a quasi-static piezo meter (ZJ-6B, Institute of Acoustics, Chinese Academy of Science, Beijing, China). To determine domain structures, silver electrodes were removed by polishing of surface of the sample placed vertically in the poling direction with SiC paper and a colloidal silica. Subsequently, the polished samples were chemically etched for 20 min with a mixture of HF:HNO\(_3\):H\(_2\)O (1:1:18 by volume). Bared domain structures were observed by a confocal laser microscope (VK9700, Keyence, Osaka, Japan) and FE-SEM (JSM-7001F, JEOL, Japan).

2.3 Photocatalytic activity test

Optical absorption spectra of the products were recorded with a UV/VIS/NIR spectrophotometer (UV-1800, SHIMADZU, Kyoto, Japan), and band gap energy was calculated from their UV–vis spectra. To evaluate photocatalytic activity, unpoled or poled ceramics under applied electrical field of \( E = 5 \text{kV/mm} \) were soaked in 50 mL of 0.1 mol/L AgNO\(_3\) solution, and then the samples were irradiated with ultraviolet light with 10 mW/cm\(^2\) of irradiation intensity and 365 nm of wavelength (UV irradiation system FT-12BK, JEFCOM, Osaka, Japan). The treated ceramics were washed with water in an ultrasonic bath, and deposition of Ag particles by photocatalytic activity was confirmed by XRD analysis and an elemental mapping using an electron probe microanalyzer (JXA-8530F, JEOL, Japan) at 15 kV. For further evaluation of photocatalytic activity, methylene blue decomposition test was carried out for porous-LNKN as follows. The porous-LNKN with/without poling under applied electric field of \( E = 5 \text{kV/mm} \) were soaked in 10 mL of 10 μmol/L methylene blue solution and left for 24 h in the dark to obtain the adsorption–desorption balance. Afterwards, the samples were irradiated in the same method as above mentioned, where the irradiation intensity was 1 mW/cm\(^2\). One milliter of the solution was taken out every 20 min and was tested using the UV/VIS/NIR Spectrophotometer in 664 nm, with distilled water as a contrast. The concentration of methylene blue after photocatalytic reduction reaction was calculated according to Lambert–Beer’s law with a concentration before the reaction (10 μmol/L).

3. Result and discussion

3.1 Microstructure and electrical property of porous-LNKN

Figure 1 show SEM images of fracture surface of dense-LNKN and porous-LNKN ceramics. There were few pores in dense-LNKN synthesized without addition of PMMA [Fig. 1(a)], in contrast, pores with 6 μm in diameter formed by addition of 10 μm of PMMA [Fig. 1(b)]. Increasing PMMA ratio, a number of pores increased without increasing their size and losing the dispersibility [Fig. 1(c)]. The dense-LNKN showed 5% of porosity including open and close porosities. Addition of 10 and 30 vol% of PMMA increased open porosity to 22.9 and 30.2%, respectively. Close porosity also increased from 2.1 to 3.8% with increasing the PMMA ratio. Grain sizes of porous-LNKN ceramics synthesized with 10 and 30 vol% of PMMA were 3.5 and 4.7 μm, respectively. These sizes were smaller than that of dense-LNKN (5.6 μm). Kobayashi and co-workers reported (\( \text{Na}_{0.5}\text{K}_{0.5} \))\text{NbO}_3 powders calcined in an atmosphere with low oxygen partial pressure (\( pO_2 \)) exhibited cubic morphology with smaller particle size compared with ordinarily \( pO_2 \) (0.2 atm). In our experiment, combustion of PMMA produced low-p\( O_2 \) atmosphere during sintering steps, resulting in fine LNKN grains.

Dielectric constant (\( \epsilon \)), piezoelectric strain coefficient (\( d_{33} \)) and piezoelectric voltage coefficient (\( g_{33} \)) for the ceramics were plotted against to PMMA volume ratios (Fig. 2). The \( g_{33} \) values were calculated by dividing \( d_{33} \) with the \( \epsilon \). Increasing PMMA amounts, the \( \epsilon \) and \( d_{33} \) were decreased from 710 to 428 and from 208 to 85 pC/N, respectively. In contrast, there was no difference in \( g_{33} \) values between dense-LNKN (PMMA 0 vol% , 29 mV/m/N) and porous-LNKN synthesized with 10 vol% of PMMA (29 mV/m/N). The \( g_{33} \) value was dropped to 20 mV/m/N with increase of PMMA ratio from 10 to 30 vol%.
phenomena are considered to come from elastic compliance and dielectric constant, according to the following equations:

$$d_{33} \propto \sqrt{S_{33} \varepsilon_{33}}$$  \hspace{1cm} (1)

$$g_{33} = \frac{d_{33}}{E_{33}} \propto \sqrt{\frac{S_{33}}{E_{33}}}$$  \hspace{1cm} (2)

where $S_{33}$ indicates elastic compliance. Although the $S_{33}$ increases by introduction of pores, decreasing $\varepsilon$ with decrease of piezoelectric component (LNKN) contributed more to reduce $d_{33}$ for porous-LNKN. In contrast, according to the Eq. (2), $g_{33}$ must increase with increasing $S_{33}$ and decreasing $\varepsilon$. We previously reported highest $g_{33}$ value was obtained for specific porous structure with low $d_{33}$ value due to the high elastic compliance.\textsuperscript{30} It is therefore, in this study, the pore formation by adding 10 vol% of PMMA should increase elastic compliance, resulting in same $g_{33}$ value as dense-LNKN. In contrast, the elastic compliance does not change significantly when the polymer ratio is low.\textsuperscript{30} Furthermore, our previous results showed increase of pores causes incompleteness of poling.\textsuperscript{31} Thus, the $g_{33}$ decreased with increase of PMMA ratio from 10 to 30 vol%.

### 3.2 Domain structure observation

To verify domain structures, surfaces of the dense-LNKN and porous-LNKN were observed vertically in the poling direction. In both dense-LNKN and porous-LNKN ceramics, various domain patterns were observed and distinctively changed with increase of the applied electric field (Fig. S1). In unpoled ceramics, their domain patterns were mainly consisted of watermarks (marked with blue circle) which described as 180° walls separating regions [Figs. S1(a) and S1(e)]. Their watermarks patterns gradually disappeared with increase of the applied electric field, and a herringbone pattern (marked with yellow circle) and a striped pattern (marked with red circle) were appeared [Figs. S1(b)–S1(d) and S1(f)–S1(h)]. The situation of change in the domain structure was different between the dense- and the porous-LNKN. Watermarks patterns were still observed on dense-LNKN poled under 5 kV/mm [Fig. 3(a)], however domain structure of porous-LNKN was mainly consisted of stripe domain without watermarks patterns even though the applied poling electric field strength was same as dense-LNKN [Fig. 3(b)]. Furthermore, stripe domains around pores (marked with red arrows) were settled parallel to the pores, and their sizes were smaller than size of domains placed far from pores [Fig. 3(c)].

Ratios of these multiple types of domain structures were estimated from more than a hundred grains and...
summarized in Fig. 4. Note that the ratios were marked as 90 or 5% when most of patterns were classified as specific type or certain domain pattern was not observed, respectively. There was no difference before polling; however, watermarks pattern was less for porous-LNKN poled under 3 kV/mm (34.1%) than for dense-LNKN (44.8%). After polling under 5 kV/mm, although there was no difference in the ratios of herringbone patterns between dense- and porous-LNKN, the ratio of stripe domain for porous-LNKN were 11% larger than dense-LNKN. Watermarks patterns on the porous-LNKN were disappeared even though the dense-LNKN showed about 20% of watermarks patterns. Furthermore, a domain structure of porous-LNKN poled under 7 kV/mm was mainly consisted of striped domains, whereas the dense-LNKN still showed 20.4% of herringbone pattern.

These tendencies were also observed in electrical field strength dependencies for domain sizes (Fig. 5). The porous-LNKN had smaller domain sizes than dense-LNKN after poling treatments, especially around the pores. Comparing the samples poled at 5 kV/mm, the domain size of porous-LNKN was less than half as that of dense-LNKN. Furthermore, similar to the result of SEM observation, size of domains settled around pores was

Fig. 3. SEM observations for (a) dense-LNKN and (b) porous-LNKN poled under applied electrical field of 5 kV/mm, (c) enlarged view of pore edge on porous-LNKN.

Fig. 4. Abundances of watermark, herring bone and stripe domain pattern for (a) dense-LNKN and (b) porous-LNKN estimated from SEM observations.

Fig. 5. Average domain sizes estimated from SEM observation of domains on an entire surface of dense-LNKN, on an entire surface of porous-LNKN and around/far from pores on porous-LNKN.
smaller than size of domains located at the position far from the pores. These results indicated that domain wall motion was enhanced in porous-LNKN, especially around pores. In porous-LNKN, the electrical field must be concentrated around pores due to the difference in permittivity of the LNKN and the pores ($\varepsilon = 1$). According to the results shown in Fig. 4, it is clear that the domain orientation is enhanced by increasing the electric field strength. Therefore, the field concentration around pores enhanced the orientation of spontaneous polarization inducing the increase of stripe domains and the decrease of domain size. Additionally, the polarization around the pores should be oriented to out-of-plane direction. These specific domain structure and orientation will promote photoreduction and photodegradation reaction. To confirm our expectation, Ag deposition and methylene blue decomposition was carried out.

### 3.3 Photocatalytic activity

The band gap energy of LNKN ceramics was confirmed to be 2.97 eV by UV–visible absorption spectrum measurement, and it was lower than the energy of the irradiated UV light (3.5 eV). Figure S2 shows XRD patterns of dense-LNKN and porous-LNKN ceramics before and after AgNO$_3$ decomposition tests. These ceramics were poled under 5 kV/mm. Sharp peaks at 38.3° attributing to (111) plane for Ag was observed in all samples, indicating Ag precipitated on a surface of LNKN ceramics by their photocatalytic reduction activities. Irradiation time dependency for intensity ratio of Ag(111) plane to intensity of LNKN(101) plane was summarized in Fig. S3. For dense-LNKN, the ratio was higher for poled sample than that for unpoled sample in the reaction time of 40 min or more. In contrast, for porous-LNKN, there was no difference in the ratio between poled and unpoled samples except for the sample treated in 20 min. Figure 6 shows elemental mapping results for unpoled and poled porous-LNKN irradiated UV light for 60 min. Ag selectively precipitated around pores in the poled porous-LNKN, whereas Ag was located over an entire surface in the unpoled porous-LNKN. Based on the result of domain observations, it is considered that the photoreduction reaction was promoted around pores because the electric field concentration gave a large magnitude of polarization and a change of polarization orientation in the out-of-plane direction around the pores. W. Song et al. investigated Ag$^+$ reduction and Pb$^{2+}$ oxidation activity for polycrystalline BaTiO$_3$ with domains consisted of different orientation and magnitude of polarization. Domains with polarization nearly perpendicular to the surface showed the oxidation reaction, whereas there was no reaction on domains with polarizations nearly parallel to the surface. Also, for the reduction reaction, they reported that formation of domain with out-of-plane polarization increased the reactivity three times. These results indicate that the photocatalytic activity is enhanced even by slight changes in the out-of-plane polarization. According to the preferential formation of stripe domains around the pores shown in Fig. 3(c), it is considered that the photoreduction reaction occurred preferentially in the stripe domain. Although the correlation is not clear, it is expected that an accumulation of surfaces with different surface potentials in the stripe domains contributes to the enhancement of photoreduction. Considering neutralization of surface charges, Ag$^+$ ions should be
Considering the piezoelectric voltage output property ($d_{33}$) decreased with increase of PMMA ratio. A change of domain orientation for porous-LNKN by inducing the electric field was greater than that for dense ceramics, and the ratio of stripe domain for porous-LNKN were 11% larger than dense-LNKN poled at 5 kV/mm. Also, smaller-sized stripe domains were preferentially formed especially around the pores. The orientation of domains around the pores was promoted by electrolytic concentration, and the domains would be reoriented in out-of-plane direction with a large magnitude of polarization. Ag photoreduction under UV irradiation was confirmed to selectively occurred on the striped domains around the pores. The poled porous-LNKN ceramics showed highest photocatalytic decomposition activity (5.2 nmol/L/min) due to the high piezoelectric voltage coefficient and specific domain structures around the pores.

4. Summary

$\text{Li}_{0.06}\text{Na}_{0.47}\text{K}_{0.47}\text{NbO}_3$ ceramics with 6 $\mu$m of pores was obtained by template method using PMMA as a pore former agent. The PMMA also functioned to produce reduced atmosphere and decrease grain size from 5.6 to 3.5–4.7 $\mu$m. Piezoelectric voltage coefficient ($g_{33}$) was not changed by adding 10 vol% of PMMA even though dielectric constant ($\varepsilon$) and piezoelectric strain coefficient ($d_{33}$) decreased with increase of PMMA ratio. A change of domain orientation for porous-LNKN by inducing the electric field was greater than that for dense ceramics, and the ratio of stripe domain for porous-LNKN were 11% larger than dense-LNKN poled at 5 kV/mm. Also, smaller-sized stripe domains were preferentially formed especially around the pores. The orientation of domains around the pores was promoted by electrolytic concentration, and the domains would be reoriented in out-of-plane direction with a large magnitude of polarization. Ag photoreduction under UV irradiation was confirmed to selectively occurred on the striped domains around the pores. The poled porous-LNKN ceramics showed highest photocatalytic decomposition activity (5.2 nmol/L/min) due to the high piezoelectric voltage coefficient and specific domain structures around the pores.

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