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Fabrication of c-axis-oriented potassium strontium niobate ($KSr_2Nb_5O_{15}$) ceramics by a rotating magnetic field and electrical property

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Fabrication and property of c-axis-oriented $KSr_2Nb_5O_{15}$ (KSN) ceramics were examined. Particle-oriented KSN was fabricated by using a rotating magnetic field and subsequent sintering. KSN fine powder was prepared by conventional solid-state reaction and grinding processing. C-axis-oriented KSN green compact was fabricated in a rotating magnetic field 10 Tesla. The resulting green body was sintered at 1473 K for 6 h and then at 1525 K for 2 h to prevent exaggerated grain growth. C-axis-oriented KSN ceramics with relative density 92% was obtained. In XRD, peaks from the c-planes, such as 001 and 002, were very strong at the horizontal cross section of the sintered specimens. The ferroelectric and piezoelectric property along to c-axis was also improved to 21 $\mu C/cm^2$ and $d_{33} = 101$ pC/N by orientation structure.

Key-words : Piezoelectric material, Orientation, Magnetic field, $KSr_2Nb_5O_{15}$

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1. Introduction

Ferroelectrics of the tungsten-bronze type are very attractive as candidates for lead-free piezoelectric materials of new generation.[1)–3)] For high performance with their ceramics, however, the texture must be precisely designed.[2),4)–10)] The excellent piezoelectric property appears only in c-crystallographic axis, and this axis must be aligned in the direction of the electrical field to be applied in the application. In designing ceramics of this structure, the rotating magnetic field (RMF) orientation method is very attractive.[11)–13)] It can orient the axis of the highest diamagnetic susceptibility to one direction at least in principle as follows.[13)–17)] The diamagnetic susceptibility is different in principle axes in $KNa_2Nb_5O_{15}$, and is $\chi_c < \chi_a < 0$. Placed in a high magnetic field, the c-axis should be oriented perpendicular to the magnetic field and the a-axis aligned parallel to the magnetic field. The development of this structure has been reported. In a rotating magnetic field, the c-axis of fine $KNa_2Nb_5O_{15}$ particles (1 µm), was reported to align parallel to the axis of rotation, as shown in **Fig. 1**(a).[11)] They failed to obtain high density with this structure, however. The relative density of oriented KSN was only 85%. The low density was due to rapid grain growth before densification. Better structure design is needed for high sintered densify.[11)]

The objective of this study is to fabricate c-axis-oriented dense $KSr_2Nb_5O_{15}$ (KSN) ceramics by rotating magnetic field method, and to evaluate its electrical properties. For easy sintering, fine KSN particles with equi-axis shape must be prepared.

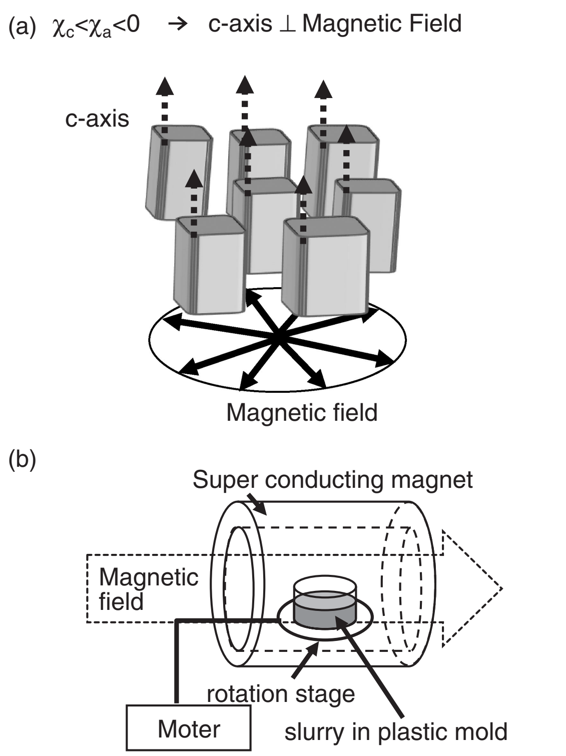

Fig. 1. Rotating magnetic field orientation. (a) Schematic illustration of orientation principle, (b) sample set in rotating magnetic field.

2. Experimental procedure

$KSr_2Nb_5O_{15}$ (KSN) powder was synthesized by conventional solid-state reaction. Powders of potassium carbonate, strontium carbonate, and niobium oxide (Nakarai Co., Ltd.) were used to synthesize KSN powder. These powders were mixed with ethanol by using a ball mill with zirconia balls for 24 h. The mixed

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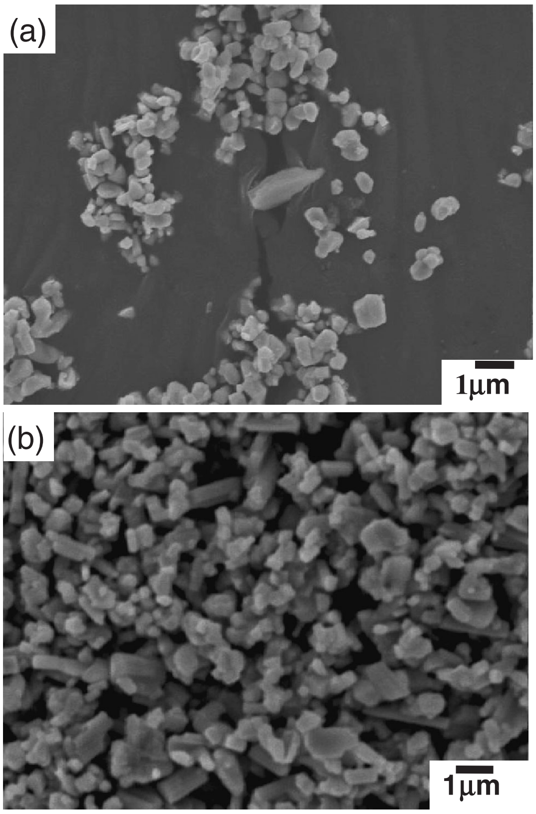

Fig. 2. Synthesized $KSr_2Nb_5O_{15}$ particles, (a) the powder synthesized in this study, (b) the powder used in the past study.[11)]

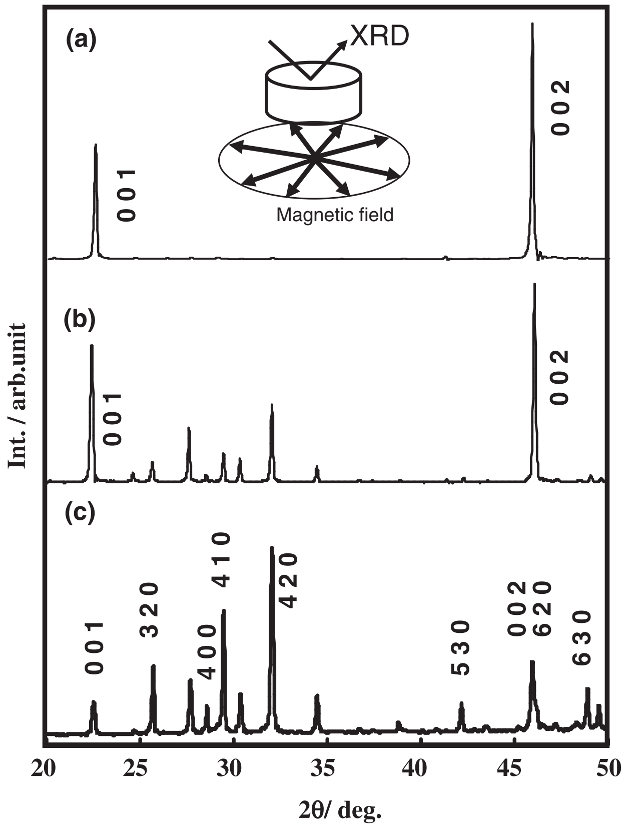

Fig. 3. XRD patterns of oriented $KSr_2Nb_5O_{15}$ (a) sintering body and (b) green body formed with rotating magnetic field, (c) sintering body prepared without magnetic field.

powders were dried then heated in an alumina crucible at 1250°C for 3 h. Crystalline phases were examined by X-ray diffraction analysis (MO3XHF22, Burker). The powder was also characterized by scanning electron microscopy (SEM) (5300LV, JEOL Co.).

The synthesized powder was mixed with distilled water and a dispersant (poly acrylic acid) in a ball-mill for 24 h to give a slurry with solid loading of 30 vol%. The slurry was poured in a plastic mould ($6 \times 10^{-6}\,m^3$) and was placed in a strong magnetic of a superconducting magnet (TM-10VH10, Toshiba). The mould was kept rotating at 30 rpm to generate the rotating magnetic field (RMF) until the slurry was dried at the room temperature, as shown in Fig. 1(b). The resultant green compact of a columnar shape, was heated at 5°C/min to 1250°C. After held for 6 h, the temperature was increased to 1350°C and held for 2 h to prevent exaggerated grain growth.

The density of the sample was estimated from its weight and dimensions. The microstructure of the specimens was examined by SEM. Grain orientation was measured by XRD. The degree of orientation was calculated semiquantitatively by the Lotgering method by using the following equation,[18)]

$$F = (P - P_0)/(1 - P_0), \quad (1)$$

where $P_0 = \Sigma I_0(00l)/\Sigma I_0(hkl)$ and $P = \Sigma I(00l)/\Sigma I(hkl)$. I and I_0 are the intensities of diffraction peaks in X-ray diffraction patterns in the ICDD data and those determined experimentally, respectively. The diffraction peaks in the range 20–50° were used for calculation.

To measure the ferroelectric properties, silver paste was painted on the surface of the sintered KSN ceramics and heated at 500°C. The hysteresis behaviour was examined at 50 Hz with a Sawyer-Tower circuit at 150°C and was recorded on a digital oscilloscope. The piezoelectric constant d_{33} was measured with d_{33} meter (ZJ-6B, Institute of Acoustic, Chinese Academy of Sciences). The specimens were poled parallel to the oriented direction under the electric field of 2.0 kV/mm for 15 min in silicone oil at 150°C, and silver electrodes were made on the major faces of these specimens.

3. Results and discussions

Figure 2 shows SEM micrographs of the new $KSr_2Nb_5O_{15}$ (KSN) powder ground by ball-milling in this study and the KSN raw powder used in the past study.[11)] In the X-ray diffraction pattern, the crystal phase of synthesized powders was identified as KSN single phase. A majority of particles had isotropic shapes or plate-like shapes in the new powder. The mean particle size was about 0.5 μm. Only few agglomerates were found in this new powder. On the other hands, some particles with rod-like shapes had been included in the powders used in the past study.[11)] Clearly, homogeneous reaction of raw materials and optimized grinding in preparing slurry contributed to the removal of rod-like particles.

Figure 3 shows X-ray diffraction patterns examined on the cross sections in parallel to the plane of the rotating magnetic field for green and sintered bodies, which are prepared with and without a rotating magnetic field (RMF). Peaks from the c-planes of the crystal, such as *001* and *002*, are very strong in RMF in Figs. 3a and 3b. Although diffraction peaks such as *320*, *410* and *420* were very strong in the raw powder, they were weak in the green specimen and absent in the sintered specimen prepared

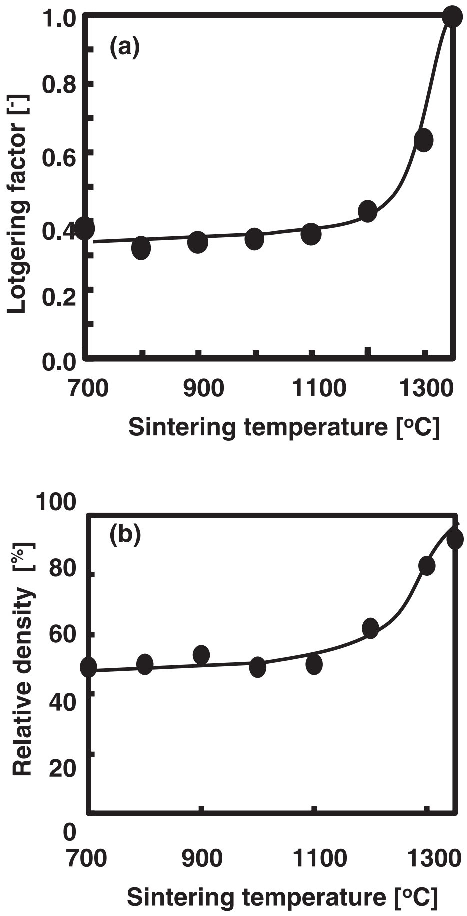

Fig. 4. (a) Lotgering factor and (b) relative density of specimens prepared with a rotating magnetic field as function of sintering temperature.

with RMF. Clearly, c-axis-oriented KSN polycrystalline ceramics were produced in RMF. This result agrees well to the past study of $KSr_2Nb_5O_{15}$.[11)]

Figure 4 shows the Lotgering factor *F* calculated with Eq. (1) and the relative density of KSN, as a function of sintering temperature. The Lotgering factor of green sample was 0.4 and increased to 0.99 as the temperature increased. The relative density was 92% at 1350°C. Fine particle without rod-like shape particles in raw materials clearly contributed to the improvement of orientation and densification.

Figure 5 shows SEM micrographs for the surfaces of the sintered specimens taken from the directions parallel and perpendicular to the plane of rotating magnetic field (RMF) after polishing and thermal etching. It also shows the microstructure for the sintered body prepared without the magnetic field. A significant difference was noted in the structures observed from two directions in the specimen prepared with RMF. The longer grains were oriented parallel to the rotation axis of the magnetic field. On the other hands, the equi-axis grains with smooth surface and some pore were observed on the face in parallel to the magnetic field (Fig. 5(a)). This microstructure suggests that the oriented particles grow preferentially along the c-axis during sintering. Tungsten-bronze-type crystals tend to have an elongate shape along the c-axis. In detailed examination, it was sound that the aspect ratio of elongated grains is smaller than that noted in the past study.[11)] Rod-like particles in raw powder had worked as seeds of grain growth during sintering. In

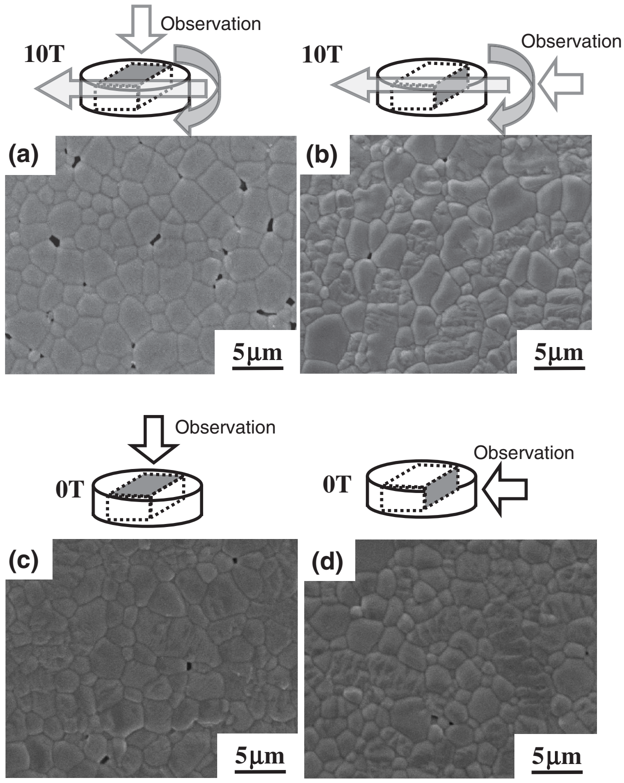

Fig. 5. Microstructure of $KSr_2Nb_5O_{15}$ ceramics, cross sections in (a) perpendicular and (b) parallel to the rotating magnetic field, (c) vertical and (d) horizontal cross sections of sintered body prepared without magnetic field.

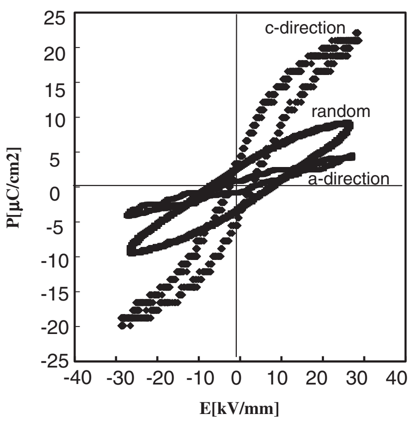

Fig. 6. Hysteresis loops of c-axis oriented and random $KSr_2Nb_5O_{15}$ specimens.

the specimen prepared without a magnetic field, the grains were randomly oriented in the microstructure.

Figure 6 shows ferroelectric properties of the c-axis-oriented KSN ceramics. P–E hysteresis behaviours were detected for both sample prepared with and without RMF. The saturation polarization was $21\,\mu C/cm^2$ in the direction of c-axis orientation. A well-developed P–E loop was noted in the c-axis oriented structure. The piezoelectric constant was 101 pC/N and approximately twice as large as that of random structure, 50 pC/N. This excellent property clearly owes to the oriented structure. However, the piezoelectric constant of 101 pC/N is slightly larger than that of a single crystal, 95 pC/N.[5)] Polarization conditions affect them, and continuous study will be needed.

4. Conclusions

Polycrystalline c-axis-oriented $KSr_2Nb_5O_{15}$ of high density was successfully fabricated by using a fine powder of excellent sintering characteristics, and a rotating magnetic field followed by conventional sintering. A high degree of orientation of 0.99, as determined from the Lotgering factor for *00l*, was achieved. The microstructure of the textured ceramics showed orientation of anisotropic grains in the direction perpendicular to the plane of the rotating magnetic field, and the sintered density was 92%. The ferroelectric and piezoelectric property along to c-axis was also improved to $21\,\mu C/cm^2$ and $d_{33} = 101\,pC/N$ by the oriented structure.

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