Colloidal processing using UV curable resin under high magnetic field for textured ceramics

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A novel colloidal processing method using UV curable resin was examined in colloidal processing under a high magnetic field. This technique can help shorten the shaping time under the magnetic field as a result of fast UV curing. We prepared the dispersed (Sr,Ca)₂NaNb₅O₁₅ (SCNN) slurry with a UV curable resin and fabricated c-axis-oriented SCNN ceramics within a short time under a rotating high magnetic field. The Lotgering factor was 0.81 for (00l) in the green compact and increased to 0.94 after sintering. The colloidal processing under the high magnetic field was thus effective not only in shortening the drying time under the magnetic field but also in obtaining highly particle-oriented structures.

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1. Introduction

Crystal-oriented polycrystalline ceramics are expected to be an alternative to single crystal materials in the industry because they provide high flexibility in shaping and their composition can be easily controlled.[1]-[3] Crystal-oriented ceramics have been prepared by several methods that involve the application of certain fields in order to control the oriented structure.[4]-[5] For example, a mechanical stress field has often been used in doctor blade techniques and hot forging processing, or an electrical field and a magnetic field have also been reported for forming processing.

Recently, colloidal processing in a high magnetic field has attracted research interest as a promising method for preparing crystal-oriented ceramics.[6]-[10] This method employs the interaction between its slight-anisotropic magnetic susceptibility and the high magnetic field. The advantages of this method include independency from particle shape and high flexibility of sample shapes. This means that conventional raw powders can be used in this method. In particular, fine particles are better for densification. This technique has been used to prepare several kinds of functional materials such as various textured ceramics, including alumina, titania, zinc oxide, and bismuth titanate.[11]-[21]

We have previously applied this technique for preparing c-axis-oriented $(\text{Sr,Ca})_2\text{NaNb}_5\text{O}_{15}$ (SCNN) ceramics, which are ferroelectrics materials of the tungsten-bronze type.[22]-[24] These are multi-functional materials that show great potential as lead-free piezoelectric and optical materials.[25]-[26] SCNN requires a c-axis-oriented texture because high piezoelectric performance is

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3 achieved only in the case of the c-crystallographic axis. In practical fabrication processing, a rotating
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6 magnetic field (RMF) is applied to attain this orientation.[27]-[29] An axis with the highest diamagnetic
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9 susceptibility is oriented to the rotating direction. As a result, the piezoelectric property is considerably
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12 improved, and the high power property is better than that of Pb systems.
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16 However, a drawback of conventional processing using a colloidal processing in a magnetic field is
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19 that the length of time required for shaping the material is high. This is because a slurry must be placed in
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22 the magnetic field until it is dried or dehydrated in this method. For example, this takes about ten minutes
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25 or more for a green sheet or a slip cased powder compact. This drawback should be in order to apply this
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28 method for large-scale manufacturing. The development of a novel solidification method is required in
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31 order to shorten the shaping time. Furthermore, continuous processing is preferable for mass production.
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35 The objective of this study is to develop a novel method to shorten the solidification time in the
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38 magnetic field and to fabricate highly particle-oriented structures. We focused on the photo polymerized
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41 reaction using a tape casting processing. Chartier et al. reported a solvent-free tape casting process, in
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44 which they studied the dispersion of particles in UV curable binder and the polymerization
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47 reaction.[30]-[31]We examined the preparation of dispersed SCNN slurry with UV curable resin and the
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50 fabrication of a c-axis-oriented SCNN green tape within a short time under a high magnetic field.
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57 **2. Experimental Procedure**

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2.1 Materials

The raw powder used in this study was synthesized $(\text{Sr,Ca})_2\text{NaNb}_5\text{O}_{15}$ (hereafter referred to as SCNN) powder, which was prepared by the conventional solid-state reaction [32]. This powder was de-agglomerated in an azeotropic mixture solvent consisting of methyl ethyl ketone (MEK) and ethanol (EtOH) (60/40 vol.) by ball-milling with zirconia media. The solvent was evaporated in an oven at 45°C for 3 h. The morphology of the powder was examined by scanning electron microscopy (SEM, JSM-5310LVB, JEOL Tokyo, Japan).

In this study, a highly concentrated SCNN slurry that was free of agglomeration was prepared. The UV curable resin that was used had a low-viscosity (100 mPa s at 20°C) polyester acrylate monomer diluted into hydroxyethyl methacrylate (Ebecryl 770, DAICEL-ALLNEX LTD., Japan) and a 2-hydroxy-2-methyl -1-phenyl-propan-1 photoinitiator (Darocur 1173, Ciba-Japan, Japan) that absorbs in the emission range of the UV lamp. To increase the volume fraction of powder while maintaining low viscosity of slurry and homogeneous dispersion, a phosphate ester (DISPERBYK-110, BYK-Chemie Japan, Japan) was used as the dispersant that acts both by electrostatic and steric repulsion.[33]

2.2 Slurry preparation

The photoinitiator and the dispersant were firstly completely dissolved in the UV curable acrylate binder, and then, the de-agglomerated SCNN powder was added into the binder. The amount of

dispersant was varied from 0.3 to 1.5 wt% (dispersant to SCNN ratio). The slurry was treated with an ultrasonic bath for 5 min and was stirred by a planetary centrifugal mixer (Awatorirentaro, Are310, Thinky, Tokyo) in the deforming mode at 2,000 rpm for 30 s and by the thin-film spin system high-speed mixer (PRIMIX, FILMIX) at 2,000 rpm for 5 min twice. Finally, the slurry was de-aired by the planetary centrifugal mixer in the deforming mode at 2,000 rpm for 30 s. Rheological measurements of the slurry were performed with a rheometer (Anton Paar, Physica MCR301) by using a cone-plate apparatus (Anton Paar, CP25-2, diameter: 24.966 mm, angle: 2.003°, truncation: 52µm) in the stress-controlled mode.

2.3 Fabrication of the green sheet with UV-curing system in high magnetic field

The UV curing process, which is photochemical, was achieved by applying ultraviolet rays emitted from a lamp (MORITEX, MUV-250U-L) at the top of the green sheet. The UV power and energy for each irradiation were measured using a UV radiometer (UIT-250, USHIO INC., Japan). The wavelength output spectra of the lamp ranged from 200 to 450 nm with a peak intensity at 365 nm. The average UV energy concentrated on the green sheet was about 360 mW/cm². The UV radiation was absorbed by the photoinitiator, which in turn generated free radicals to initiate polymerization. The photopolymerizable solution instantly hardened when it was exposed to UV radiation, entrapping ceramic particles in a polymeric matrix and forming a green sheet with high strength.

The slurry was cast into a sheet on a poly(ethylene terephthalate) (PET) film, and then placed

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3 in a magnetic field of 10 T induced by a superconducting magnet (Toshiba TM-10VH10) for 1–300 s and
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6 30 s during UV exposure. The 10 T magnetic field was applied in the direction parallel to the sheet
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9 surface, and the sheet was rotated on the axis perpendicular to the magnetic field at a revolution speed of
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12 30 rpm. After exposure to UV, c-axis-oriented green sheets were obtained (**Fig.1**). For comparison with a
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14 randomly oriented green sheet, another sample from the slurry was also exposed to UV without a
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16 magnetic field. After exposure, the liquid non-polymerized areas were removed by ethanol.
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22 **Figure 2** shows a flow chart of the preparation of c-axis-oriented green sheets by colloidal
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24 processing with the high magnetic field and UV curing.
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28 The thermal cycle of debinding of the green sheets was defined on the basis of thermogravimetric
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30 analysis of the cured green tapes. The organic species were completely removed at a temperature of
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32 500°C. The de-binding of both the c-axis-oriented and randomly oriented green sheets was performed at a
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34 heating rate of 1°C/min up to 100°C and 0.2°C/min up to 500°C. Then, the debinded tapes were sintered
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36 at a heating rate of 5°C/min up to a temperature of 1250°C for 6 h.
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44 The crystal orientations of the surfaces of the green and ceramic sheets were evaluated by X-ray
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46 diffraction (XRD) analysis (Ultima-IV, RIGAKU, Japan) using Lotgering's method. The degree of c-axis
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48 orientation was evaluated in terms of the Lotgering factor f of $[00l]$ orientation, $f = (p - p_0)/(1 - p_0)$,
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50 where $p = \sum I(00l) / \sum I(hkl)$, $p_0 = p$ for randomly oriented ceramic samples, and $\sum I(hkl)$ is the
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52 summation of the XRD peak intensities. The microstructures of both the surface and cross section of the
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sintered sheets were examined by scanning electron microscopy (SEM).

3. Results and Discussion

3.1 Synthesized SCNN powder and slurry

Figure 3 shows an SEM image of the de-agglomerated SCNN powder. The median particle size D_{50} of the powder was 1.0 μm .

The concentration of the dispersant was optimized in the slurry system, which consisted of the powder in the UV-curable resin with the phosphate ester dispersant. **Figure 4** shows the viscosity of the SCNN slurry with 30 vol% at a shear rate of 100 s^{-1} plotted against dispersant concentration. The amounts of dispersant varied from 0.3 to 1.5 wt% (dispersant to SCNN ratio). A lower viscosity, which indicates well-dispersed state, was attained for an addition of 1.2 wt% of dispersant.

The photoinitiator concentration was also examined in the slurry with 30 vol% SCNN powder and 1.2 wt% phosphate ester. The amount of the photoinitiator was varied from 1 to 6 wt% to the SCNN powder and solvent. The viscosity of the slurry at a shear rate of 100 s^{-1} is plotted in **Figure 5**. The addition of the photoinitiator led to a drastic decrease in the viscosity of the slurry. The viscosity of slurry decreased with the addition of the photoinitiator. However, the amount of the photoinitiator was 2 wt% because small amounts of the photoinitiator addition were better for fabrication.

Although slight shear thinning is observed in the viscosity curve, the behavior was almost

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3 **Newtonian.** The result shows that the particles are dispersed in the slurry. We could obtain a slurry with
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6 high solid concentration of 55 vol% under the optimized conditions. This suggests that the particles are
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9 well dispersed in the slurry prepared by using UV curable resin.
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16 3.2 Orientation of the green and sintered sheets 17 18

19 **Figure 6** show XRD patterns of the polymerized green sheets prepared for duration times of 10
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22 and 300 s with and without magnetic fields. As the duration time in the magnetic field was increased, the
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25 intensities of the peaks from the c-planes of the crystal, such as the 001 and 002 planes, become gradually
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28 high. In contrast, the diffraction peaks of the green sheet prepared without the magnetic field were
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31 coincident with the JCDD card. The degree of orientation was evaluated as the Lotgering factor f , which
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34 is calculated from the equation $f = (p - p_0) / (1 - p_0)$, where $p_0 = \sum I_0(00l) / \sum I_0(hkl)$ and
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37 $p = \sum I(00l) / \sum I(hkl)$. I_0 and I are the intensities of the XRD patterns of random and oriented
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40 samples obtained from the experiments, respectively. The Lotgering factor f was 0.81 for the sample
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43 prepared in the rotating magnetic field with a holding time of 300s. The result shows that a
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46 particle-oriented green sheet could be fabricated by the photopolymerized reaction in the rotating
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49 magnetic field. The Lotgering factor of the sample is considerably high compared to that of a sample
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52 prepared by the conventional process. This suggests that the dispersed state of particles is well attained in
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55 the slurry. Besides, the consolidation of using photo-reaction is that it is also effective for maintaining the
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particle-oriented structure, because the reaction completes quickly before the sedimentation or flocculation of particles in the slurry. This tendency is the same as the result in the case of using gel-casting processing. [21]

Figure 7 shows XRD patterns of the surface of the sintered sheets obtained by sintering of the green sheets. The duration times of the green sheets in the magnetic field were 10 and 300 s, respectively. The Lotgering factor f was 0.94 for the sample formed at a duration time of 300 s in the rotating magnetic field. The results showed that c -axis-oriented SCNN ceramics were produced by sintering of the particle-oriented green tape.

Figure 8 shows SEM micrographs of the microstructure of the sintered sheets observed from the parallel and perpendicular directions to the rotating magnetic field. The duration time in the magnetic field was 300 s. The microstructure of the sintered sheets prepared without the magnetic field is also shown in Fig. 9. A significant difference was noted in the structures observed from the two directions of the sheets prepared with the rotating magnetic field. The grains were oriented parallel to the rotation axis of the magnetic field. This microstructure suggests that the oriented particles grow in the c -axis direction during sintering, and the grain-growth of the oriented particles contributed to the enhancement of the oriented structure. [27]

4. Conclusions

A novel colloidal processing using UV curable resin has been studied. This technique can shorten the drying time in a magnetic field owing to fast UV curing and highly particle-oriented structures. The advantages of using a phosphate ester dispersant and the photoinitiator were necessary to achieve well dispersed slurry with high volume fractions of the particles. The green sheet was prepared by UV light irradiation for 30 s after a duration of 10–300 s in the field of a superconducting magnet. The oriented particles in the slurry were maintained in the polymerized green body. Thus, the Lotgering factor was 0.81 in the green compact and increased up to 0.94 after sintering. The microstructural homogeneity could be observed in the sintered body prepared by the UV curable system. Thus, the crystal orientation under a magnetic field was achieved to shorten the drying time in the magnetic field and to achieve a highly particle-oriented structure.

Acknowledgements

The authors would like to acknowledge funding from the Adaptable and Seamless Technology Transfer Program through target-driven R&D, JST and Leading Industrial Technology Development Project Grant Funds of the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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Fig.1 Schematic illustrations of experimental setting. (a) Rotation apparatus and optical fiber in the unidirectional high magnetic field induced by a superconducting magnet, and (b) an expanded view of the sheet casted on a PET film and exposure to UV light in a magnetic field.

Fig.2 Flow chart of preparation of c-axis-oriented green sheets by colloidal processing under the high magnetic field and UV curing.

Fig.3 Particle morphology of de-agglomerated SCNN.

Fig.4 Viscosity (at a shear rate of 100 s^{-1}) of slurry containing 30 vol% SCNN in UV curable resin for various amounts of phosphate ester.

Fig.5 Viscosity (at a shear rate of 100 s^{-1}) of slurry containing 30 vol% SCNN in UV curable resin and dispersant for various amounts of photoinitiator.

Fig.6 X-ray diffraction patterns obtained from green sheets for various duration times of (a) 300 s

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3 and (b) 10 s (a,b) with and (c) without a 10 T rotating magnetic field
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10 **Fig.7 X-ray diffraction patterns obtained from sintered sheets for various duration times of (a) 300**
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19 **Fig.8 Microstructure of sintered SCNN ceramics at 1250°C observed from the (a,c) perpendicular**
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22 **and (b,d) parallel directions (a,b) with a 10 T rotating magnetic field and holding time of 300 s**
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25 **and (c,d) without a 10 T rotating magnetic field.**
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