Texture design for microwave dielectric (Ca$_{0.7}$Nd$_{0.3}$)$_{0.87}$TiO$_3$ ceramics through reactive-templated grain growth

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Abstract
Plate-like Ca$_3$Ti$_2$O$_7$ (CT) and Nd$_2$Ti$_2$O$_7$ (NT) particles were synthesized in molten salts and used as reactive templates for the preparation of highly textured (Ca$_{0.7}$Nd$_{0.3}$)$_{0.87}$TiO$_3$ bulk ceramics (CNT) with preferred pseudocubic $\langle 100 \rangle$ and $\langle 110 \rangle$ orientations, respectively. During flux growth CT and NT particles developed facets parallel to the pseudocubic $\{100\}$ and $\{110\}$ planes, respectively, in a perovskite unit cell, since those planes correspond to the interlayers of the layered perovskite-type crystal structures. Complementary reactants for the CNT stoichiometry were wet-mixed with the reactive templates and the slurries were tape-cast. Then stacked tapes were heat-treated for dense single-phase CNT ceramics with a distorted and A-site deficient regular perovskite-type structure. The CNT ceramics prepared with CT and NT reactive templates exhibited strong pseudocubic $100$- and $110$-family x-ray diffraction peaks, respectively, with other peaks drastically suppressed when non-perovskite sources were used as complementary reactants. The textured ceramics possess unique microstructures; as either parallel or obliquely stacked block structures with a pseudocubic $\{100\}$ plane faceted. The pseudocubic $\langle 100 \rangle$-and $\langle 110 \rangle$-textured CNT ceramics exhibited $\sim$10 and $\sim$20% higher products of the dielectric quality factor and frequency, $Q \cdot f$, respectively, than conventional ceramic sintered at the same temperature. When $Q \cdot f$ is compared based on the same grain size, the $\{100\}$-textured CNT exhibited 27% higher values than non-textured while relative permittivity and temperature coefficient of resonant frequency were of similar values. Simple geometrical relationships between electric field and penetrated pseudocubic $\{hh0\}$-type grain boundaries must lead to the reduced scattering and dielectric loss.

Keywords: microwave dielectric, textured ceramic, reactive template, grain boundary orientation

1. Introduction
Texture engineering is an approach to enhance mechanical and/or functional performances of polycrystals for materials with anisotropic properties. Processing methods for textured bulk ceramics are largely restricted to hot-working [1], colloidal processing in magnetic field [2, 3] and the use of oriented anisometric particles, such as templated grain growth (TGG) [4, 5], because of limited applicability of melting/recrystallization and plastic deformation techniques for ceramics unlike for metals and plastics. Texturing process is especially limited for materials in pseudo-cubic crystal systems such as a regular perovskite-type structure. Piezoelectric properties have been reported to be enhanced for regular perovskite-type materials such as Bi$_{0.5}$Na$_{0.5}$TiO$_3$- [6], PbTiO$_3$- [7] and K$_{0.5}$Na$_{0.5}$NbO$_3$-based systems [8] with preferred $\langle 100 \rangle_{pc}$ orientation where ‘pc’ stands for a direction or a plane expressed in pseudocubic.
measurements were conducted for \{100\}_{pc}- and \{110\}_{pc}-reactive templates. Preparation, characterization and property topochemical conversion reactions on two different types of preparation of ceramics with tailored textures through this paper we describe the chemical design strategy for the preparation of anisometric regular perovskite-type ceramics \[17\]. In bulk ceramics, however, few reports have been known for textured bulk ceramics with other preferred orientations \[11,20\]. Textured ceramics with the same target composition and the tabilized permittivity, \(\varepsilon_r (\sim 100)\), and fairly good \(Q\cdot f\) value (~17 000 GHz) \[18,19\].

Ruddlesden–Popper-type \(\text{Ca}_3\text{Ti}_2\text{O}_7\) (CT) is an isomorph of \(\text{Sr}_3\text{Ti}_2\text{O}_7\) which was synthesized in a plate-like shape by a molten salt synthesis (MSS) and used as a template for \{100\}_{pc}-textured regular perovskite-type ceramics \[11,20\]. Ruddlesden–Popper-type layered perovskite has an interlayer parallel to orthorhombic \{010\}, i.e., \{100\}_{pc} for a perovskite unit cell, where the periodic bond chain (PBC),-Ti–O–Ti–O, is terminated with a corner of TiO$_6$ octahedron. The equilibrium shape of a crystal in this family would be plate-like with its interlayer as a developed plane \[9\]. Thus the plate-like CT particles, if aligned with the developed plane parallel to one another, could be converted topochemically into the regular perovskite with its \{100\}_{pc} parallel to the original interlayer of the reactive template, schematically described in figure 1(a) \[21\].

On the other hand, \(\text{Nd}_3\text{Ti}_2\text{O}_7\) (NT) has a strontium pyro- niobate \((\text{Sr}_2\text{Nb}_2\text{O}_7)\)-type structure which has an interlayer parallel to \{110\}_{pc} for a perovskite unit cell, where the PBC is terminated with a edge of TiO$_6$ octahedron. Brahmaroutou et al reported that \(\text{Sr}_2\text{Nb}_2\text{O}_7\) particles prepared by MSS exhibited elongated plate-like morphology \[22\]. Plate-like \(\text{Sr}_2\text{Nb}_2\text{O}_7\) particles were reported to be used as reactive templates for regular perovskite-type ceramics with a preferred \{110\}_{pc} \[23\]. If NT particles also show plate-like morphology similarly to its isomorphic compound, they are also expected to be converted topochemically into a regular perovskite with its \{110\}_{pc} parallel to the original interlayer of the reactive template, schematically described in figure 1(b) \[21\].

As complementary reactants for the formation of CNT, Nd-and Ti-source materials must be mixed with CT platelets for the \{100\}_{pc} texture, whereas Ca-and Ti-source materials are needed with NT platelets for the \{110\}_{pc} texture. Three types of reaction schemes were designed with the use of reactive templates (denoted as ‘\(r_t\)’):

\[
0.203 \text{Ca}_3\text{Ti}_2\text{O}_7 \ |_t + 0.1305 \text{Nd}_2\text{O}_3 \\
+ 0.594 \text{TiO}_2 \rightarrow (\text{Ca}_0.7\text{Nd}_{0.3})_{0.87} \text{TiO}_3, \quad (1)
\]

\[
0.1305 \text{Nd}_2\text{Ti}_2\text{O}_7 \ |_t + 0.609 \text{CaCO}_3 \\
+ 0.739 \text{TiO}_2 \rightarrow (\text{Ca}_0.7\text{Nd}_{0.3})_{0.87} \text{TiO}_3, \quad (2)
\]

\[
0.1305 \text{Nd}_2\text{Ti}_2\text{O}_7 \ |_t + 0.609 \text{CaTiO}_3 \\
+ 0.130 \text{TiO}_2 \rightarrow (\text{Ca}_0.7\text{Nd}_{0.3})_{0.87} \text{TiO}_3. \quad (3)
\]

The reaction schemes (1) and (2) were designed so that the complementary reactants for A-site and B-site are supplied separately. The reaction scheme (3) was designed, to the contrary, with the use of maximum amount of complex oxide and minimum amount of simple oxide/carbonate, for the preparation of dense ceramics with minimized formation of Kirkendall voids. In the reaction (1), 40.6% of titanium is supplied by the reactive template CT, whereas 26.1% of titanium is given by the reactive template NT for the reaction (2) and (3).

2. Reaction designs for textured polycrystals

A-site deficient, distorted perovskite-type \((\text{Ca}_0.7\text{Nd}_{0.3})_{0.87} \text{TiO}_3\) (or \(\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3\), abbreviated as CNT) was selected as a target material for texture control. This composition of ceramics has been known to have a combination of high relative permittivity, \(\varepsilon_r (\sim 100)\), and fairly good \(Q\cdot f\) value (~17 000 GHz) \[18,19\].
Figure 1. Crystal structures of (a) (100)-type layered perovskite $\text{Ca}_3\text{Ti}_2\text{O}_7$, and (b) (110)-type layered perovskite $\text{Nd}_2\text{Ti}_2\text{O}_7$, schematically shown with crystal structures of distorted regular perovskite $(\text{Ca}_{0.7}\text{Nd}_{0.3})_{0.87}\text{TiO}_3$ with their TiO$_6$ octahedrons approximately aligned in the same directions as the layered perovskite reactive templates.

Table 1. Molar ratios of materials used for four batches of $(\text{Ca}_{0.7}\text{Nd}_{0.3})_{0.87}\text{TiO}_3$ ceramics.

| Batch     | MSS–CT | MSS–NT | SSR–CNT | SSR–$\text{CaTiO}_3$ | $\text{CaCO}_3$ | $\text{Nd}_2\text{O}_3$ | $\text{TiO}_2$ |
|-----------|--------|--------|---------|----------------------|------------------|------------------------|----------------|
| CP–CNT    | —      | —      | —       | —                    | —                | —                      | —              |
| CT–R–CNT  | 0.2256 | —      | —       | —                    | —                | —                      | 0.1305         | 0.5489         |
| NT–R–CNT  | —      | 0.1305 | —       | —                    | 0.609            | —                      | —              | 0.739          |
| NT–F–CNT  | —      | 0.1305 | —       | 0.609                | —                | —                      | 0.130          |

* Chemical formula of MSS–CT (a mixture of $\text{Ca}_3\text{Ti}_2\text{O}_7$ and $\text{Ca}_4\text{Ti}_3\text{O}_{10}$ platelets) was assumed as $\text{Ca}_{2.7}\text{Ti}_2\text{O}_{6.7}$ for the calculation, based on ICP analysis ($\text{Ca}/\text{Ti}=1.35$).
3. Experimental procedures

3.1. Preparation of reactive template particles

Two types of plate-like reactive template particles were prepared by MSS in a mixed KCl + NaCl flux. CaCO₃ (Kojundo Chemical Lab., 99% up) and TiO₂ (Ishihara Sangyo, Tipaque A-100, anatase, 100 nm, 99% up) were mixed with a Ca/Ti ratio of 3/2 in ethanol by ball milling for Ruddlesden–Popper-type CT. Dried powders were then mixed with the equal weight of 0.5 NaCl + 0.5 KCl as a flux and heat-treated in a platinum crucible at 1673 K for 8 h. Nd₂O₃ (Kojundo Chemical Lab., 99.9%) and TiO₂ were mixed with an Nd/Ti ratio of 1/1 in ethanol by ball milling for strontium-pyroniobate-type NT. Dried powders were similarly mixed with the 0.5 NaCl + 0.5 KCl flux and heat-treated in a platinum crucible at 1573 K for 8 h. Products were immersed in deionized water at 353 K and the flux was removed by repeated filtration until chlorine could not be detected by AgNO₃ solution. Equiaxed CT and NT particles were also prepared as reference specimens by solid-state reactions (SSRs) of CaCO₃ and TiO₂, and Nd₂O₃ and TiO₂, respectively, without flux.

3.2. Preparation and characterization of textured CNT polycrystals

Table 1 lists the source materials and compositions used for the preparation of CNT ceramics. Conventionally processed CNT ceramics (CP-CNT) were prepared by sintering of CNT powder compacts synthesized by an SSR. The SSR–CNT powder was prepared by heating mixed powder compacts of CaCO₃, Nd₂O₃ and TiO₂ with a stoichiometric ratio (Ca:Nd:Ti = 0.609:0.261:1) at 1473 K for 8 h and pulverized by ball-milling. Die-pressed (at 25 MPa) and cold-isostatic-pressed
SSR–CNT powder compacts were sintered at 1673–1823 K for 10 h in air for the preparation of CP-CNT with different grain sizes. For textured CNT, three batches of slurries were prepared by mixing molten-salt-synthesized plate-like particles with complementary reactants as well as polyvinyl butyral (PVB) as a binder and di-n-butyl phthalate (DBP) as a plasticizer dissolved in a mixed toluene–ethanol solvent. Plate-like calcium titanate, MSS–CT, identified as a mixture of Ca$_3$Ti$_2$O$_7$ and Ca$_4$Ti$_3$O$_{10}$ particles, was used as a reactive template while Nd$_2$O$_3$ and TiO$_2$ were used as complementary reactants for CT–R–CNT. Here ‘R’ stands for a specimen prepared with ‘raw material-type’ complementary reactant(s). A Ca/Ti ratio of 1.35, determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis, was used for the MSS–CT for the calculation of starting powder ratio. Plate-like Nd$_2$Ti$_2$O$_7$ particles, MSS–NT, were used as a reactive template for NT–R–CNT and NT–F–CNT where ‘F’ stands for a specimen prepared with ‘filler-type’ complementary reactant(s). As complementary reactants, CaCO$_3$ and TiO$_2$ were used for NT–R–CNT whereas pre-synthesized equiaxed CaTiO$_3$ powder by a SSR (heated at 1473 K for 8 h in air and pulverized by ball-milling) was used with TiO$_2$ for NT–F–CNT. The slurries were tape-cast by a doctor blade.

![Figure 4. XRD patterns for (a) the green sheet surface of CT–R–CNT as compared with equiaxed Ca$_3$Ti$_2$O$_7$ particles prepared by a solid-state reaction, and (b) the green sheets surfaces of NT–R–CNT and NT–F–CNT as compared with equiaxed Nd$_2$Ti$_2$O$_7$ particles prepared by a solid-state reaction.](image)

Table 2. Relative density, grain size and Lotgering’s orientation degree $F$ of (Ca$_{0.7}$Nd$_{0.3}$)$_{0.87}$TiO$_3$ ceramics.

| Batch         | Sintering temperature (K) | Relative density (%) | Average grain size ($\mu$m) | Lotgering’s $F$ for ($hkl$)$_{pc}$  |
|---------------|---------------------------|----------------------|----------------------------|-----------------------------------|
| CP-CNT        | 1673                      | 97.6                 | 47                         | —                                 |
| CP-CNT        | 1773                      | 97.8                 | 72                         | —                                 |
| CP-CNT        | 1873                      | 92.7                 | 93                         | —                                 |
| CT–R–CNT      | 1773                      | 97.2                 | 40                         | 0.998 for {100}$_{pc}$            |
| NT–R–CNT      | 1773                      | 96.8                 | 110                        | 0.983 for {110}$_{pc}$            |
| NT–F–CNT      | 1773                      | 97.6                 | 73                         | 0.184 for {110}$_{pc}$            |

*Lotgering’s orientation degree was estimated from the XRD patterns for the polished surfaces parallel to the original tape surfaces.*
and thermally etched at 1473 K.

specimens to the original tape surfaces were mirror-polished for the reaction design for RTGG processing as mentioned previously. Synthesis conditions for single-phase Ca3Ti2O7 were not found in the preliminary MSS experiment, for the MSS–CT products synthesized at 1473 and 1573 K for 8 h were single-phase CaTiO3 and mixed phases of CaTiO3 and Ca4Ti3O10, respectively, whereas a SSR from the same mixed powders of Ca/Ti=3/2 without flux produced phase-pure Ca3Ti2O7. The Ca/Ti atomic ratio for the MSS–CT particles was determined as 1.35 by ICP-AES and this value was used for the reaction design for RTGG processing as mentioned previously.

3.3. Measurements of dielectric properties

For microwave dielectric measurements, secondary lamination of 1 mm thick green bodies and subsequent sintering produced 10 mm thick specimens for highly textured CNT ceramics as well as randomly oriented CP-CNT ceramics. Cylindrical specimens 8.2 mm in diameter and 4.1 mm in thickness were machined out from the sintered bodies with their cylinder axes perpendicular to the original tape surfaces, as schematically shown in figure 2. Hakki–Coleman and Kobayashi methods [25, 26] were used to determine the microwave dielectric quality factor $Q$ and relative permittivity $\varepsilon_r$ in the TE_{011} mode at frequencies $\sim$5 GHz with a network analyzer (HP, 8757 A) at 298 K. Temperature coefficient of resonant frequency $\tau_f$ was measured between 298 and 353 K. It should be noted that the electric field is in the circular direction which is parallel to the original tape surfaces and perpendicular to the orientation axis of textured ceramics.

4. Results and discussion

4.1. Morphologies and phases of flux-grown particles

Figure 3 shows SEM images of flux-grown particles. MSS–CT particles show plate-like morphology with disordered shapes in their developed plane with sizes of 10–20 µm. MSS–NT particles show business card-like morphology with their developed plane sizes of 1–5 µm. The aspect ratios of the plate-like particles were approximately $\sim$20 and $\sim$10 for MSS–CT and MSS–NT, respectively.

XRD analysis showed that MSS–NT was single-phase Nd3Ti2O7, whereas MSS–CT was composed of Ca6Ti5O17 and Ca4Ti3O10, both Ruddlesden–Popper-type-structured compounds with two and three-layers of perovskite units, respectively. Synthesis conditions for single-phase Ca3Ti2O7 were not found in the preliminary MSS experiment, for the MSS–CT products synthesized at 1473 and 1573 K for 8 h were single-phase CaTiO3 and mixed phases of CaTiO3 and Ca4Ti3O10, respectively, whereas a SSR from the same mixed powders of Ca/Ti=3/2 without flux produced phase-pure Ca3Ti2O7. The Ca/Ti atomic ratio for the MSS–CT particles was determined as 1.35 by ICP-AES and this value was used for the reaction design for RTGG processing as mentioned previously.

4.2. Textures and microstructures of ceramics

Figure 4 shows XRD patterns for the tape casting surfaces of the CT–R–CNT and NT–R–CNT green sheets, as compared with the powder diffraction patterns of equiaxed CT and NT prepared by SSRs. It is apparent that the {010} plane of CT and the {100} plane of NT were aligned parallel to the sheet surfaces by a shear stress during tape-casting. The results indicate that they are developed planes of the plate-like template particles, as expected.

Table 2 lists the relative density, average grain size and Lotgering’s degree of orientation of the sintered specimens. All the sintered ceramics exhibited similar relative densities ranging between 96.8 and 97.8%. The lowest value (96.8%) was measured for NT–R–CNT which used a large amount of CaCO3 as a Ca source. Instead, NT–F–CNT with the use of pre-synthesized perovskite CaTiO3 as a Ca source exhibited improved density (97.6%) as designed.
Figure 5 shows XRD patterns for the sintered ceramics of CT–R–CNT and NT–R–CNT on the polished surfaces parallel to the original tape surfaces as well as an XRD pattern for the conventionally processed CP-CNT ceramic. It should be noted that (100)pc and (110)pc corresponds to (101) and (020), and (200) and (121), respectively, in orthorhombic notation. All the sintered specimens are single-phase distorted and A-site deficient regular-perovskite CNT. It is remarkable that CT–R–CNT exhibits strong {100}pc-family XRD peaks whereas NT–R–CNT is highly {110}pc-textured, with the other diffraction peaks were drastically suppressed.

The textured ceramics display unique microstructures on the sections perpendicular to the original tape surfaces when compared with a microstructure of conventionally processed CP-CNT with random orientation (figure 6(c)). The {100}pc-textured CNT ceramic shows a microstructure with parallel aligned block-shaped grains, or a brick-wall-like structure (figure 6(a)), whereas the {110}pc-textured CNT ceramic
displays ∼45° obliquely aligned block-shaped grains, like a stone-wall structure often seen in Shinto shrines (figure 6(b)). These unique microstructures are the results of in situ topo-chemical formation of a distorted perovskite from layered perovskite templates with the orientation of TiO₂ octahedrons preserved, and the successive templated growth of the oriented large-sized grains at the expense of small randomly oriented grains formed between reactive templates. A regular perovskite-type structured grains such as relaxer-PbTiO₃ generally grows with pseudocubic [100] facets [27], for the [100]pc is the slowest growth direction and the [100]pc is the plane with the lowest surface energy and its charge balanced. Similar brick-layer-like microstructure was reported for a [100]pc-textured piezoelectric KₓSn₀.₅N₀.₅O₃-based ceramic by Saito et al [8]. Templated grains of CNT also grow in an idiomorphic shape with pseudocubic [100] facets, leading to the unique microstructures, as schematically included in figure 6. It should be noted that the horizontal grain size of the [100]pc-textured CNT is only a little larger than the diameter of the original CT template while an exaggerated grain growth occurred in the [110]pc-textured CNT. The former result suggested that the grain size could be controlled for [100]pc-textured perovskite-type ceramics by the size and amount of template particles in the RTGG processing because the templated grains with [100]pc orientation grow with [100]pc facets, meet each other and stop the growth with similar surface energy conditions. We assume an ideal situation: perfect uniaxial alignment and random in-plane orientation of template-originated grains. In a [100]pc-textured perovskite, meeting of vertically growing grains with [100]pc facets parallel to each other would form a [100]pc grain boundary for both grains with no further growth. Meeting of horizontally growing grains with [100]pc facets with an arbitrary angle would form a thermodynamically stable grain boundary such as a twin boundary. For a [110]pc-textured perovskite, on the other hand, such simple meetings of two [100]pc facets rarely occur, resulting in the significant grain growth at the expense of other template-originated grains.

The NT–F–CNT ceramic exhibited, however, only a weak [110]pc texture. It is attributed to the introduction of pre-synthesized perovskite CaTiO₃. Regular perovskite phase is thermodynamically more stable than layered perovskite in general and thus diffusion-out of Nd from Nd₂Ti₂O₇ templates for CaTiO₃ particles was possibly promoted rather than diffusion-in of Ca from CaTiO₃ into Nd₂Ti₂O₇ templates, which is required for the grain growth of reactive templates.

4.3. Microwave dielectric properties of ceramics

Table 3 lists εᵣ and Q · f values for the textured and non-textured CNT ceramics. All the ceramics exhibited nearly identical relative permittivity ranging 99–102, which has a good agreement with the value (∼108) of conventionally processed Ca₀.₆₁Nd₀.₂₆TiO₃ ceramics reported by Liang et al [28]. Similar τᵣ values (∼225 ppm K⁻¹) regardless of the processing routes assure the similar composition of the three specimens sintered at 1773 K. Origins of a microwave dielectric loss are generally considered as; (1) material itself, (2) crystalline defects, and (3) microstructure of a ceramic including pores and grain boundaries. Microwave dielectric loss in ceramics generally increases as the porosity increases or the grain size decreases. The Q · f values for the conventionally processed CNT ceramics, CP-CNT, increased as the sintering temperature increased. It is because the ceramics sintered at higher temperature have larger grain size and thus fewer grain boundaries, which resulted in reduced scattering of electric field. Apparent dependence of the Q · f value on the grain size for the CP-CNT ceramics, as plotted in figure 7, reveals that the grain boundary scattering is the major determining factor for the dielectric loss in this series of CNT ceramics because they have similar relative densities and compositions but different microstructures.

The [100]pc- and [110]pc-textured CNT ceramics exhibited ∼10 and ∼20% higher Q · f values, respectively, than the conventionally processed specimen at the same sintering temperature (1773 K). The high Q · f value for the [110]pc-textured CNT can be attributed to the large grain size as shown in figure 7 although even higher property is expected if the density is identical to the non-textured. It is obvious, however, that the [100]pc-textured CNT ceramic exhibited 27% larger figure of merit than non-textured with the same grain size on the extrapolated line. Although the electric field and orientation axis were not in the same direction, three-dimensional randomness were reduced to two-dimensional randomness along the electric field in the textured CNT ceramics. Especially for the [100]pc-textured CNT ceramic, grain boundaries are, ideally, either perpendicular or parallel to the cylindrical axis of the ceramic specimen. In other words, electric field mostly penetrates (hk0)pc-type grain boundary planes which are parallel to the cylindrical axis. Simpler geometrical relationships between grains in the [100]pc-textured CNT ceramic could also lead to reduced
residual stresses and reduced scattering at grain boundaries along the electric field than in the randomly oriented polycrystals. Compared with the \{100\}_{PC}-textured, \{110\}_{PC}-textured ceramic must have more randomly oriented grain boundary distribution along the electric field.

5. Conclusions

This paper exhibits texture design and fabrication of bulk ceramics with two different pseudocubic preferred orientation directions. Texture-dependent microwave dielectric characteristic was also suggested in this study with an improved figure of merit for the \{100\}_{PC}-textured ceramic when compared with randomly oriented. It should be emphasized that the design and fabrication of favorable grain boundary orientation would be a key for microwave dielectric ceramics whereas crystallographic orientation is important for piezoelectric ceramics. Grain boundary orientation is also significantly important for ceramics with electrical conductivity [29]. Advancement in RTGG method would give ceramic engineers more freedom in design and fabrication of high performance devices regardless of the availability of a bulk single crystal with a desired composition. ‘Texture engineering’ for regular perovskite-type materials could enable polycrystalline ceramics with tailored grain and boundary orientations, leading to unique and enhanced properties for various functional devices.

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| Table 3. Dielectric properties of CNT ceramics. |
|-----------------------------------------------|
| Batch | Sintering temperature (K) | Relative permittivity | $Q\cdot f$ (GHz) | $\tau_p$, a (ppm K$^{-1}$) |
|-------|--------------------------|----------------------|----------------|-----------------|
| CP-CNT | 1673 | 99.8 | 12 340 | 228 |
| CP-CNT | 1773 | 99.6 | 13 830 | not measured |
| CP-CNT | 1823 | 99.8 | 14 970 | not measured |
| CT–R-CNT | 1773 | 101.6 | 15 140 | 225 |
| NT–R-CNT | 1773 | 99.8 | 16 395 | 222 |

a Temperature coefficient of resonant frequency was measured between 198 and 253 K.
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