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Plastic deformation and effects of water in room-temperature cold sintering of NaCl microwave dielectric ceramics

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Abstract

NaCl ceramics were prepared by room-temperature cold sintering using moistened NaCl powder with 4wt% water and dry pressing using dehydrated powder. When the applied uniaxial pressure is low, the relative density of dry-pressed NaCl ceramic is significantly lower than that of cold-sintered ceramic, while the former is 98.5–99.3% and much higher

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than the latter (94.3–94.6%) for high applied pressure of 200–300 MPa. The uniaxial pressure-induced plastic deformation dominates the densification of dry-pressed NaCl ceramic, and also plays a role during cold sintering as well as the dissolution-precipitation process. The lower density of cold-sintered NaCl ceramic under high applied pressure is attributed to the trapped water in ceramic body during cold sintering. Besides, the presence of water always promotes the microstructural homogeneity, which is responsible for the much higher Qf value of cold-sintered NaCl ceramic. The optimal microwave dielectric properties with ε_r = 5.55, Qf = 49,600 GHz and τ_f = -173 ppm/^{o}C are obtained in cold-sintered NaCl ceramic under the applied pressure of 300 MPa, indicating that it is a promising candidate as a microwave dielectric material.

KEYWORDS: NaCl microwave dielectric ceramics, cold sintering, plastic deformation, densification, microstructure

1 | INTRODUCTION

Cold sintering is a brand-new sintering method by which many inorganic materials can be densified at extremely low temperatures (< 300 ^{o}C) or even room temperature in presence of transient liquid phase and uniaxial pressure. [1-6] The extremely low temperature of cold sintering brings many significant advantages, such as greatly lowered energy consumption and cost, possibility to densify the ceramics that are unstable at higher temperatures, and easy conjunction between ceramics and other materials such as metal and polymer. Therefore, cold sintering has attracted much attention promptly after its appearance. Till now, cold sintering has been adopted to prepare many kinds of materials such as microwave dielectric ceramics, [1,3,4,7] ferroelectric and piezoelectric ceramics, [2,8] semiconductor ceramics, [9] solid electrolytes, [10] thermoelectric materials, [11] structural ceramics, [6,12] ceramic adhesives, [13] ceramic-polymer composites [4,9,14] and etc..

Cold sintering process in presence of transient liquid phase and uniaxial pressure can be regarded as the combination of liquid phase-enhanced and pressure-enhanced sintering methods, and it concerns many complex mechanisms that have not been well understood. [2,5] Nevertheless, the dissolution-precipitation process activated by the liquid phase is regarded as the most important mechanism for cold sintering, since it accelerates the mass transportation greatly and makes the densification at extremely low temperatures possible. [2,5] In this article, we report the uniaxial pressure-induced plastic deformation as another possible important densification mechanism during cold sintering. This mechanism is proven by comparing the densification behaviors of NaCl ceramics prepared via cold sintering and dry pressing, and the cold-sintered NaCl ceramic has been reported as a microwave dielectric material. [15] Furthermore, the effects of water on the densification, microstructure and microwave dielectric properties of NaCl ceramics prepared by cold sintering have also been investigated.

2 | EXPERIMENTAL PROCEDURE

High-purity NaCl powder (>99.99%, Shanghai Aladdin Bio-Chem Technology Co., Ltd, China) was ground with a mortar and a pestle, sieved with the mesh size of 125 μm, and then dried at 80 ^{o}C for 24 h to get rid of the absorbed moisture. The NaCl powder was moistened by mixing with 4wt% deionized water in a mortar, and the mixture was pressed at room temperature in a stainless steel mold under a uniaxial pressure ranging from 50 to 300 MPa for 10 min. The obtained sample was called cold-sintered NaCl ceramic. For comparison, the dry-pressed NaCl ceramic was also prepared by directly pressing the dehydrated powder through a similar procedure. The as-prepared NaCl ceramics were dried at 80 ^{o}C for 24 h before the following measurements. The bulk density was measured by dimension method. X-ray diffraction using Cu Kα Radiation (Rigaku 2550/PC, Rigaku, Tokyo, Japan) was conducted on the dehydrated NaCl powder and as-prepared ceramics to identify the phase constitution. The microstructure on the fractured surfaces was observed by a field emission scanning electron microscopy (S-4800, Hitachi, Tokyo, Japan). The cylindrical samples of about 12.5 mm in diameter and 6 mm in thickness were used to evaluate the microwave dielectric properties using a vector network analyzer (Agilent E8363B, Agilent Technologies Inc., Santa Clara, CA). The dielectric constant was measured by the Hakki-Coleman method [16] as well as the temperature coefficient of resonant frequency between 20 and 80 ^{o}C, and the *Qf* value was evaluated by the resonant cavity method. [17]

3 | RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of cold-sintered and dry-pressed ceramics under different applied uniaxial pressures, together with that of the dehydrated NaCl powder. All the diffraction peaks of the powder and ceramics can be indexed by sodium chloride (PDF card: 01-0994). The positions of the diffraction peaks for the cold-sintered and dry-pressed ceramics are consistent with those for NaCl powder, indicating that the presence of water and the applied uniaxial pressure have no effect on the crystalline structure or cell parameters. Furthermore, no difference is observed in the intensity of the diffraction peaks for NaCl powder and ceramics, so the preferential crystalline orientation does not occur in cold-sintered and dry-pressed NaCl ceramics.

The relative density of NaCl ceramics as a function of the applied uniaxial pressure is shown in Figure 2. For cold-sintered NaCl ceramic, the relative density is 88.4% when the applied uniaxial pressure during cold sintering is only 50 MPa. It increases to 93.1% and 93.9% when the applied pressure increases to 100 and 150 MPa, respectively. With further increasing the pressure up to 300 MPa, the relative density changes slightly in the range of 94.3–94.6%. In comparison, the dry-pressed NaCl ceramic exhibits significantly lower density of 80.0% and 89.8% for the low applied pressure of 50 and 100 MPa, respectively. Obviously, the presence of water during cold sintering promotes the mass transportation and densification of NaCl ceramic through the dissolution–precipitation process, [2,5] and is responsible for the higher final density of cold-sintered NaCl ceramic. However, the relative density of dry-pressed NaCl ceramic increases rapidly with increasing the applied pressure from 50 to 200 MPa, and it starts to exceed that of cold-sintered NaCl ceramic when the applied pressure is 150 MPa. With further increasing the applied pressure, the relative density of dry-pressed NaCl ceramic stabilizes. Surprisingly, the stable relative density of dry-pressed NaCl ceramic is as high as 98.5–99.3% when the applied pressure is 200–300 MPa, which is 4.3–4.7% higher than that of the corresponding cold-sintered NaCl ceramic. The result is inconsistent with the previous literatures, where the relative density of dry-pressed ceramic compacts is usually lower than 70%, [6,12,14] and the presence of water during cold sintering always increases the final density. [5,6,12,14] This contradiction will be discussed in detail later.

The SEM images on the fractured surfaces of cold-sintered and dry-pressed NaCl ceramics are shown in Figures 3(a)–(f). When the applied pressure is as low as 50 MPa, the dry-pressed NaCl ceramic exhibits a quite porous and inhomogeneous microstructure, and it seems like the simple packing of NaCl original particles shown in Figure 3(g). Very different and more homogeneous microstructure is observed in cold-sintered NaCl ceramic, including the appearance of typical grains in some areas, fewer pores and vanishing of original particles. This is consistent with the relative density shown in Figure 2. With increasing the applied pressure to 150 MPa for which cold-sintered and dry-pressed NaCl ceramics are of similar densities (see Figure 2), the original particles become more compact and aggregate significantly for dry-pressed ceramic, while there are still a lot of relatively small particles. Differently, well-grown grains and clear grain boundaries are observed in the cold-sintered

NaCl ceramic. With further increasing the applied pressure to 300 MPa, grains can also be observed in dry-pressed NaCl ceramic, together with a lot of small pores inside the grains and the disappearance of the relatively small original particles. For cold-sintered NaCl ceramic under the applied pressure of 300 MPa, in comparison, the larger and fewer pores locate between several grains but not inside the grains. Obviously, the cold-sintered NaCl ceramic is of more homogeneous microstructure than the dry-pressed one despite of the applied uniaxial pressure.

As discussed above, the presence of water during cold sintering always promotes the microstructural homogeneity of NaCl ceramic, and it enhances the densification for low applied pressure of 50–100MPa. This is easy to understand, since the mass transportation and densification processes are accelerated through dissolution–precipitation mechanism in presence of water, and this has been regarded as the most important mechanism of cold sintering. [2,5] However, when the applied pressure is high enough (200–300 MPa), the relative density of dry-pressed NaCl ceramic (98.5–99.3%) is much higher than that of the cold-sintered one (94.3–94.6%). It is to say, the presence of water does not enhance the densification, but lower the final density, and this is inconsistent with the previous literatures. [5,6,12,14] Furthermore, even when the applied pressure during dry pressing is as low as 50 MPa, the relative density of NaCl ceramic (80.0%) is significantly higher than those of most dry-pressed ceramic compacts (usually lower than 70%). [6,12,14] In fact, a high relative density of 84% was also reported in the Li_2MoO_4 ceramic prepared by room-temperature dry pressing under the applied uniaxial pressure of 530 MPa, which has been regarded to be attributed to the residual water that activates the dissolution–precipitation mechanism. [5] This explanation is not convincing for the present work, since the residual traced amount of water in the present dehydrated NaCl powder is far from enough for moistening, especially considering the nearly full densification of the dry-pressed NaCl ceramic under the applied pressure of 200–300 MPa. Noting that NaCl has a low Mohs hardness of 2, [18] the NaCl particles are easy to be rearranged and reshaped by mechanical force. Therefore, the uniaxial pressure-induced plastic deformation in absence of water is regarded to dominate the densification for dry-pressed NaCl ceramic. This can be proven by the microstructural evolution of the dry-pressed NaCl ceramic with increasing the applied pressure, for which the process that the relatively small original particles aggregate and transform into large grains can be observed, as shown in Figure 3. The plastic deformation should also be an important densification mechanism as well as the dissolution–precipitation process for the cold sintering of NaCl ceramic in presence of water. When the applied pressure is low, the effect of plastic deformation is not as significant as that of the dissolution–precipitation process, resulting in the higher relative density of the cold-sintered NaCl ceramic than the dry-pressed one. Under high applied pressure, the dry-pressed NaCl ceramic is almost fully densified due to the great enhancement of plastic deformation, and the similar result is also expected for cold-sintered ceramic. However, some water is trapped in the ceramic body during the cold sintering of NaCl ceramic. The trapped water results in pores after evaporating, and thus is responsible for the lower final density of cold-sintered NaCl ceramic compared to the dry-pressed one. This means that it is possible to obtain both nearly full densification and homogeneous microstructure by optimizing the water content and other experimental parameters during the cold sintering of NaCl ceramic, whose densification is co-dominated by the dissolution–precipitation process and plastic deformation.

The different relative density and microstructure of cold-sintered and dry-pressed NaCl ceramics have significant effects on their microwave dielectric properties, which are shown in Figure 4 as functions of the applied pressure. With increasing the applied pressure, the dielectric constant (ε_r) first increases rapidly, and then stabilizes for both cold-sintered and dry-pressed NaCl ceramics. The dielectric constant of cold-sintered NaCl ceramic is significantly higher than that of the dry-pressed one for the applied pressure of 50–100 MPa, while the former is lower than the latter for higher pressure, and this is consistent with the relative density shown in Figure 2. The *Qf* value also increases with increasing the applied pressure for the two ceramics, and this is attributed to the improved microstructural homogeneity and increased density for higher applied pressure (see Figures 2 and 3). Surprisingly, the *Qf* value of cold-sintered NaCl ceramic is 9,700–22,000 GHz (or 50–143%) higher than that of dry-pressed NaCl ceramic, although the relative density of the former is much lower than the latter for the high applied pressure of 200–300 MPa. Obviously, the improved microstructural homogeneity by the dissolution–precipitation process in presence of water is responsible for the much higher *Qf* value of the cold-sintered NaCl ceramic. Besides, the two ceramics exhibit a negative temperature coefficient of resonant frequency

(τ_f) of -164–-195 ppm/°C. The optimal microwave dielectric properties with ε_r = 5.55, Qf = 49,600 GHz and τ_f = -173 ppm/°C are obtained in the cold-sintered NaCl ceramic under the applied pressure of 300 MPa. The microwave dielectric properties of cold-sintered NaCl ceramic are superior to those of Li_2MoO_4 ceramic cold-sintered at room temperature to 120 °C (ε_r = 5.1–5.61, Qf = 10,200–30,500 GHz and τ_f = -160–-174 ppm/°C), [1,3,4,7,14,19] and comparable to those of Li_2MoO_4 ceramic conventionally sintered at 540 °C (ε_r = 5.5, Qf = 46,000 GHz and τ_f = -160 ppm/°C), [20] although Li_2MoO_4 is the firstly reported and most popular ceramic in the research area of cold sintering. The induced strong hygroscopicity by the high solubility (35.8 g in 100 g water at 20 °C) [21] of NaCl ceramic is the key factor that may restrict its practical applications. In fact, this is also a serious problem for many cold-sintered ceramics, such as Li_2MoO_4 with the solubility of 79.5 g. [21] It has been reported that the hygroscopicity can be significantly suppressed by spraying a thin silicone conformal coating on Li_2MoO_4 ceramic patch antenna. [22] Therefore, it is still possible to utilize the cold-sintered ceramics with high solubility for practical applications, although the coating increases the complexity.

4 | CONCLUSION

Dense NaCl ceramics were prepared by room-temperature cold sintering and dry pressing. The presence of water during cold sintering enhances the densification of NaCl ceramic when low uniaxial pressure of 50–100 MPa is applied, while it lowers the final density significantly for high applied pressure of 200–300 MPa. The densification of dry-pressed NaCl ceramic is dominated by the uniaxial pressure-induced plastic deformation, which also plays a role as well as the dissolution–precipitation process for the cold sintering of NaCl ceramic. The trapped water in ceramic body during cold sintering is responsible for the lower density of cold-sintered NaCl ceramic under high applied pressure. The presence of water during cold sintering always promotes the microsturctural homogeneity, which is responsible for the much higher *Qf* value of cold-sintered NaCl ceramic. The optimal microwave dielectric properties with ε_r = 5.55, *Qf* = 49,600 GHz and τ_f = -173 ppm/^{o}C are obtained in the cold-sintered NaCl ceramic with the applied pressure of 300 MPa, indicating that it is a promising candidate as a microwave dielectric material. Furthermore, it is expected to obtain nearly full densification, homogeneous microstructure and good properties simultaneously by optimizing the water content during the cold sintering of some ceramics, whose densification is co-dominated by the dissolution–precipitation process and plastic deformation.

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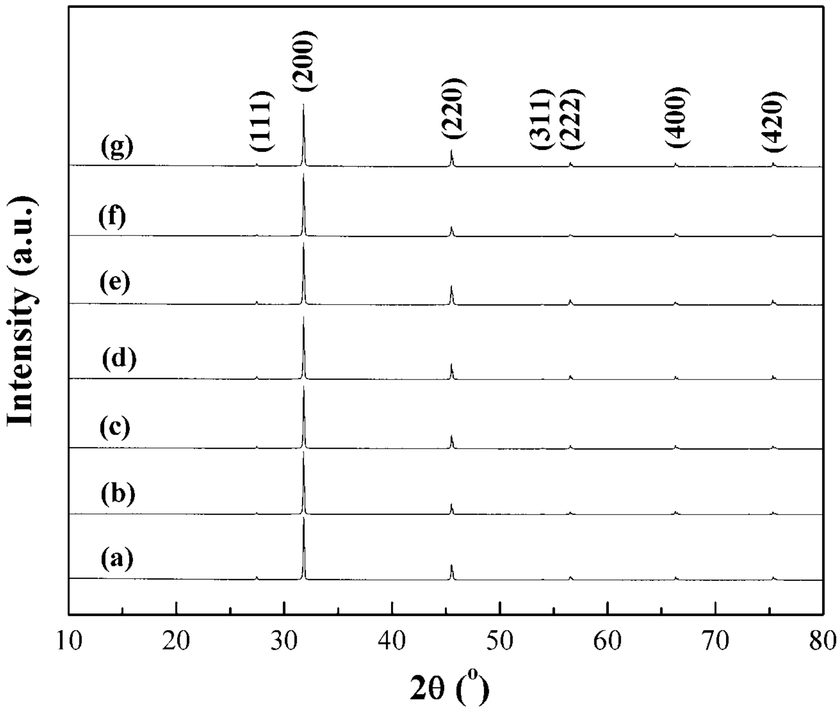
LIST OF FIGURE CAPTIONS

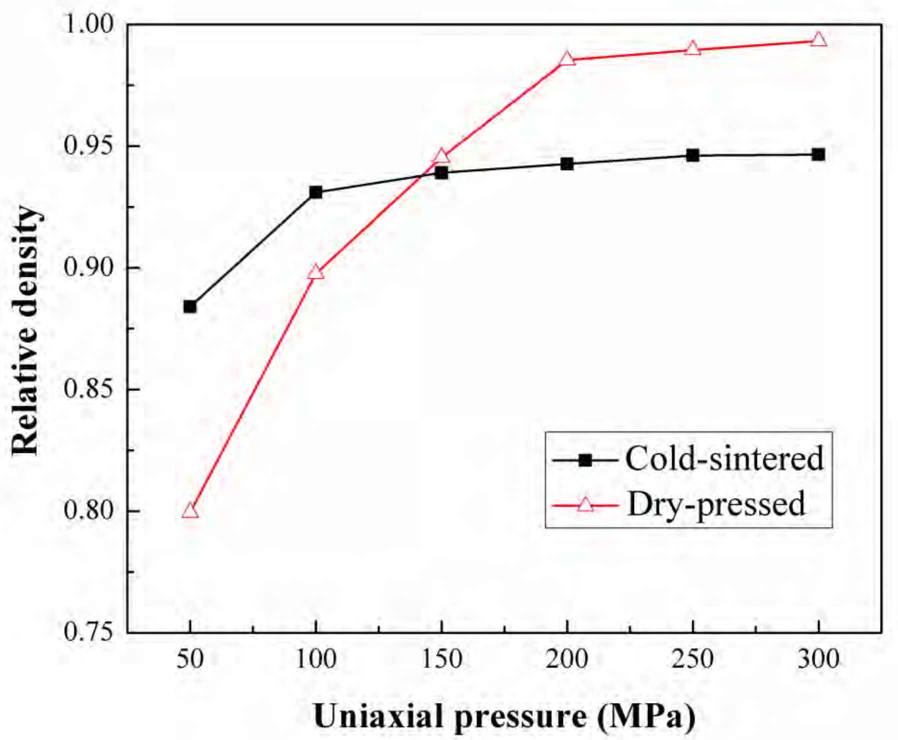
FIGURE 1 XRD patterns of (a) dehydrated NaCl powder, cold-sintered NaCl ceramics under applied uniaxial pressure of (b) 50 MPa, (c) 150 MPa and (d) 300 MPa, and dry-pressed NaCl ceramics under applied uniaxial pressure of (e) 50 MPa, (f) 150 MPa and (g) 300 MPa.

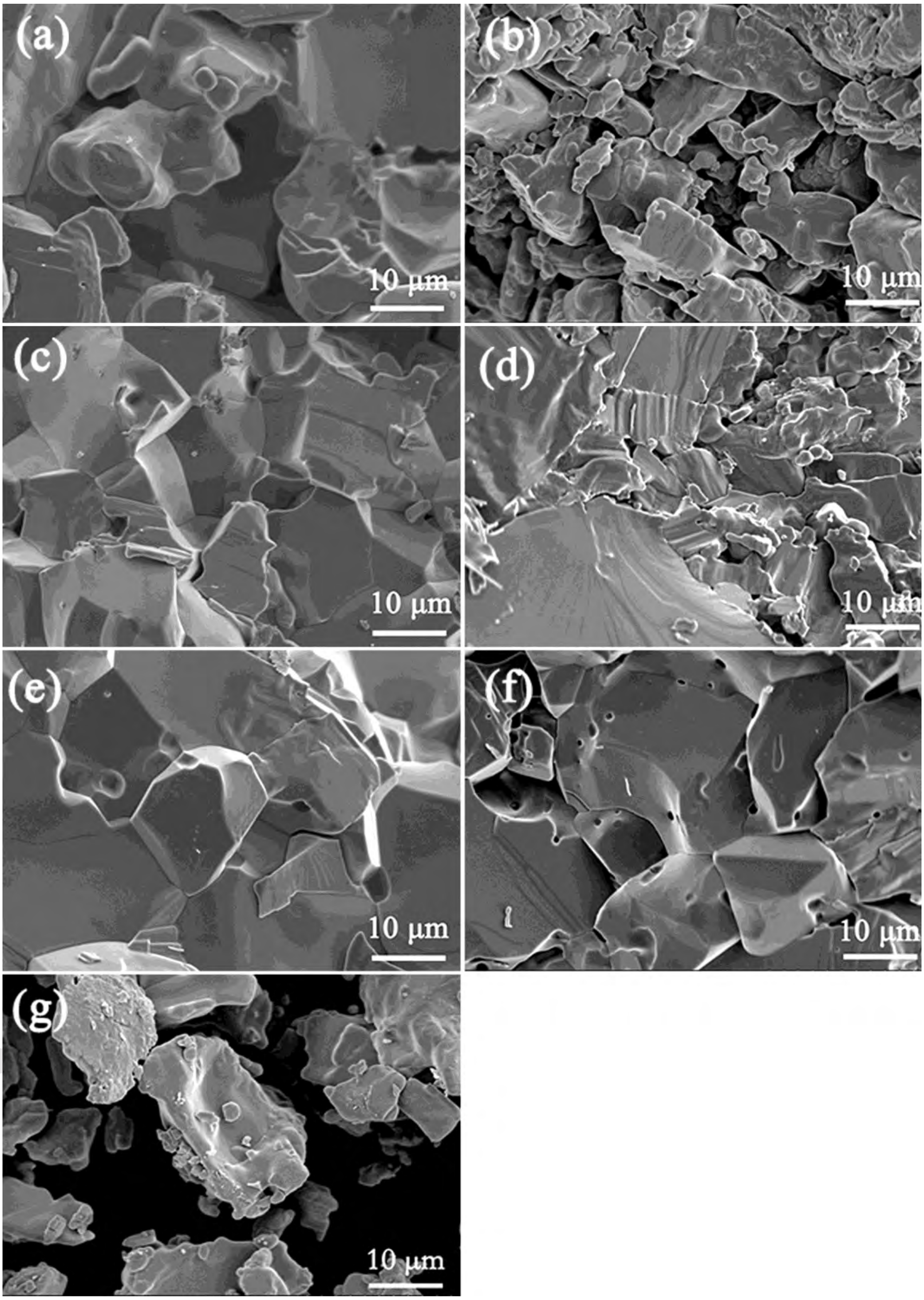
FIGURE 2 Relative density of cold-sintered and dry-pressed NaCl ceramics as a function of applied uniaxial pressure.

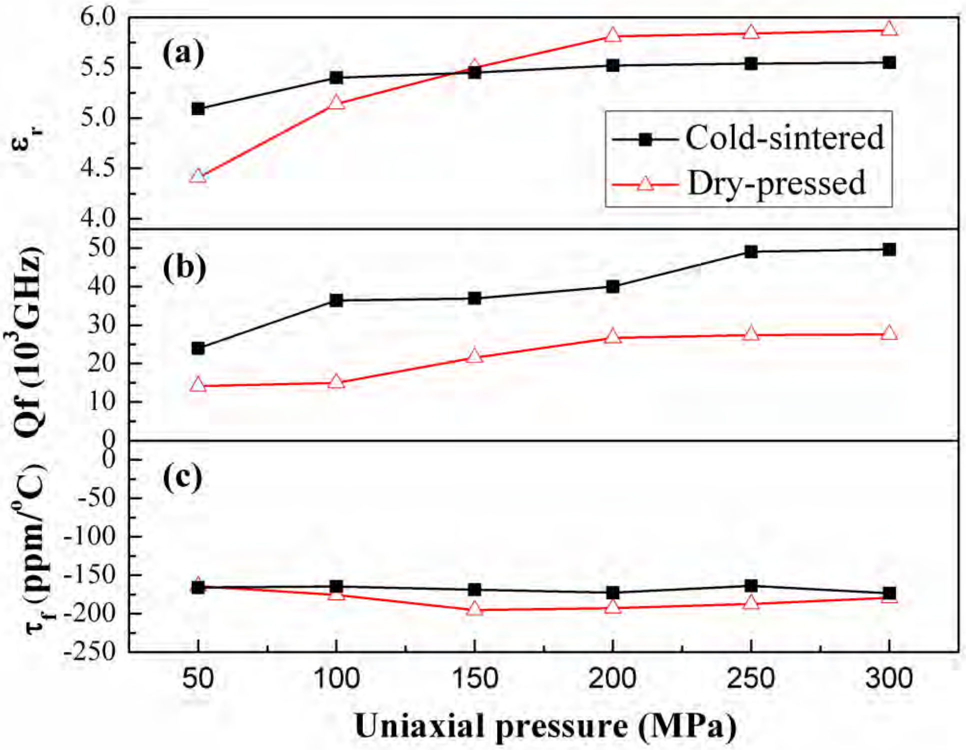
FIGURE 3 SEM images on fractured surfaces of cold-sintered NaCl ceramics under applied uniaxial pressure of (a) 50 MPa, (c) 150 MPa and (e) 300 MPa, and dry-pressed NaCl ceramics under applied uniaxial pressure of (b) 50 MPa, (d) 150 MPa and (f) 300 MPa. SEM image of dehydrated NaCl powder is shown in (g).

FIGURE 4 (a) Dielectric constant, (b) *Qf* value, and (c) temperature coefficient of resonant frequency of cold-sintered and dry-pressed NaCl ceramics as functions of applied uniaxial pressure.


(111)
(200)
(220)
(311)
(222)
(400)
(420)
(g)
(f)
(e)
(d)
(c)
(b)
(a)
Intensity (a.u.)
10
20
30
40
50
60
70
80
2θ (°)


1.00
0.95
0.90
0.85
0.80
0.75
Relative density
Cold-sintered
Dry-pressed
50
100
150
200
250
300
Uniaxial pressure (MPa)


(a)
10 μm
(b)
10 μm
(c)
10 μm
(d)
10 μm
(e)
10 μm
(f)
10 μm
(g)
10 μm


(a)
(b)
(c)
εr
Qf (10³GHz)
τf (ppm/°C)
Cold-sintered
Dry-pressed
Uniaxial pressure (MPa)
6.0
5.5
5.0
4.5
4.0
50
40
30
20
10
0
0
-50
-100
-150
-200
-250
50
100
150
200
250
300