Dielectric Properties of Thermo-Sensitive Hydrogels Containing Ferroelectric Nanoparticles

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強誘電性ナノ粒子を含有した感温性ハイドロゲルの誘電特性

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ABSTRACT

Ferroelectric nanopowders of 10% KF-doped $BaTiO_3$, which show very large dielectric constant at room temperature, were synthesized by a sol-gel method. We embedded the powder into PNIPAm hydrogels, which have a discontinuous volumetric phase transition at $T_C \sim 34$ ℃. The dielectric constant of the gels in water was measured at 40 MHz in a temperature range between 23 and 43 ℃. The gel shows a dielectric anomaly at T_C and the gel's dielectric constant increases up to 28% after the post-embedment, in comparison with that of the distilled water. The results indicate that the nanopowders are useful for heating the gel using radio frequency radiation.

【Keywords: Dielectric constant, PNIPAm hydrogel, KF-doped $BaTiO_3$, ferroelectric nanoparticles, sol-gel method】
【キーワード：誘電率，PNIPAm ハイドロゲル，KF- 添加 $BaTiO_3$，強誘電ナノ粒子，ゾル・ゲル法】

1. Introduction

Barium titanate ($BaTiO_3$, abbreviated as BT) is a typical ferroelectric material and is widely used in electric devices such as multi-layer ceramic capacitors and piezoelectric actuators. Recently, we have revealed that the single crystals of 10% KF-doped BT ($Ba_{0.9}K_{0.1}TiO_{2.9}F_{0.1}$: abbreviated as $KF_{10\%}$-BT) have a large dielectric constant reaching 15,000 at room temperature, because the composition locates near the tricritical point [1-3]. Moreover, we have successfully synthesized the 10% KF-doped BT powders by a sol-gel method [4, 5].

Such dielectric powder, which has a large dielectric constant at room temperature, will be used as absorbers of electro-magnetic waves in a radio frequency (RF) range; for example, as an agent for local heating in hyperthermia [6]. Poly(*N*-isopropylacrylamide) (PNIPAm) hydrogel has been shown to have a discontinuous volumetric phase transition at $T_C \sim 34$℃ [7]. If we use the PNIPAm hydrogel embedded with the dielectric powder, we will be able to control the T_C by external RF radiation and use it as a drug delivery system. Our goals for this research were to study and determine the most effective ways to control the heating of the gels using RF.

In this report, we carried out following experiments in order to obtain fundamental data for medical application: 1) embedding of the $KF_{10\%}$-BT powders into the PNIPAm hydrogel, and 2) temperature dependence of the dielectric constant of the plain gel and the post-embedment gel.

2. Sample Preparation

Titanium tetraisopropoxide ($Ti[OCH(CH_3)_2]_4$), barium diethoxide ($Ba(OC_2H_5)_2$) and KF powders (Merck, 99%) were used as the sources for Ti, Ba and KF, respectively [4, 5]. At a molar ratio of 1.0 : 0.9 : 0.1, they were dissolved in sequence in a mixed solution of methanol and 2-methoxyethanol in a dry glove box with an N_2 gas flow, to form a clear yellow solution of 1.0 mol/L. Hydrolysis was carried out by spraying with distilled water after the solution was cooled to 0 ℃ while being magnetically stirred. A transparent gel was formed and was dried at 50 ℃ for 24 h, then at 90 ℃ for 3 days. The resultant yellow dry precursor-gel was pulverized and fired at various temperatures. In this study, the precursor-gel powders were calcined at 650 ℃ for 12 h in order to evaporate organic matters, and after repeated pulverization, were fired again at 800 or 1,000 ℃ for 2 h.

PNIPAm hydrogels were formed using a free-radical polymerization process. NIPAm monomer (N-isopropylacrylamide) was mixed with H_2O in a 1:9 weight ratio. BIS cross-linker (N,N'-Methylenbisacrylamide) was then added at roughly

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0.3 mol% of the NIPAm water mixture. In the case of dielectric dispersed gels, the dielectrics were added to the monomer solution at this time. Our experiments used 10 wt% of the total monomer solution. The monomer solution was mixed for over 2 h while being chilled to a temperature of roughly 3 ℃. After mixing, the solution was then infiltrated with a N_2 gas flow for greater than 1 h at a low rate to remove O_2, a retardant for the polymerization process. The O_2-reduced monomer solution was then chilled to ~1 ℃. The last step is to add chilled initiator (ammonium persulfate) and accelerator (N,N,N',N'-tetramethyl-ethylenediamine) in the amount of 1 mol% each of the NIPAm in the chilled monomer solution. The final solution should be intermittently shook and inserted into crushed ice or a water-ice mixture that is at 0 ℃ until polymerization occurs.

3. Experimental Results and Discussion

Figure 1(a) shows XRD patterns of the $KF_{10\%}$-BT powders calcined at 650 ℃ and subsequently fired at 800 or 1,000 ℃. The XRD pattern of the 650 ℃-calcined powders has crystalline diffraction peaks indexed by the cubic structure of BT, as shown in Fig. 1(a). Further firing at 800 or 1,000 ℃ results in sharper, stronger, and well-resolved diffraction peaks, indicating the full crystallization of the gel precursor. Figures 1(b)-(c) show TEM images for the $KF_{10\%}$-BT fine particles calcined at 650 ℃ and further fired at 800 ℃ respectively. It can be noticed that the 650 ℃-calcined powders are homogeneous in size, approximately 70 nm in length, and show a cubic form. However, the 800℃-fired powders grow to a large size and aggregate; they do not show the crystal habit. While most particles grow as large as 200 nm in size, fine particles as small as 70 nm still exist. The 1,000 ℃-fired powders also show similar shape and size to those of the 800 ℃-fired powders. Judging from the FWHM of XRD pattern and the physical appearance, the crystal quality of the particles becomes worse at 1,000 ℃, because of some evaporation of F^-. The powders calcined only at 650 ℃ were white in color; however, those fired at 800 or 1000 ℃ were colored pale yellow as shown in Fig. 1(d); we call these powders as KFBT650, KFBT800, and KFBT1000, respectively.

The dielectric constant of each sample was measured using an RF Impedance/Material Analyzer (HP 4291A) in the rage 1-1000 MHz. The sample holder was a Teflon ring with a thickness of 2 mm, capped with copper tape to make electrodes. To calibrate the dielectric constant for unknown samples, measurements of the empty cell capacitance as well as the cell filled with the standard materials of H_2O, 1-Buthanol, and Acetone capacitances were taken. Using the following equation [8]: $C/C_0 = (\varepsilon + \alpha)/(1+\alpha)$, where C is the capacitance of the cell filled with sample, C_0 is the capacitance of the empty cell, ε is the dielectric constant of sample, and α is a constant related to the sample holder itself, a linear relation between the dielectric constant ε and the ratio of capacitances could be found. From the standard values of ε at 40 MHz (H_2O = 78.30, 1-Buthonol = 17.51, and Acetone = 20.07), the cell constant α was estimated: the equation determined for our sample cell is $\varepsilon = 9.2483C/C_0 + 9.4286$. Subsequent capacitances from the unknown samples were then plugged into the equation to solve

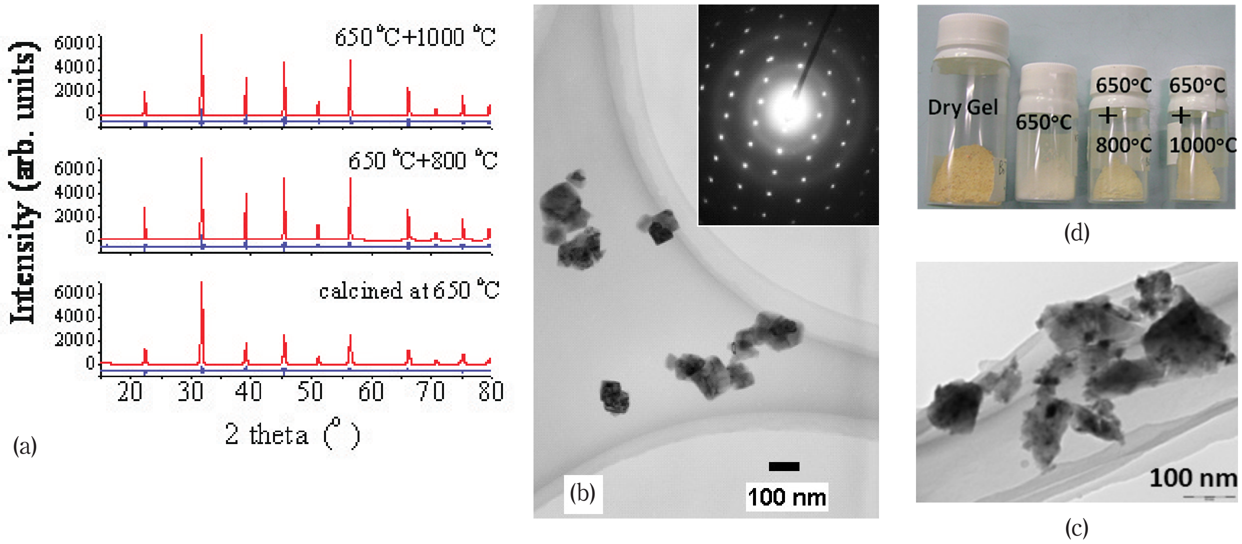

Fig. 1 $KF_{10\%}$-BT powders fired at several temperatures: (a) XRD patterns with CuKα radiation, (b) TEM photographs of 650 ℃-calcined powders, (c) of 800 ℃-sintered powders, and (d) a photograph of the powders. The inset in (b) is a diffraction pattern of the particle.

for ε. For measurements of the sample properties while under the effects of heating, a resistance heater was placed on the dielectric test-fixture (HP16453A) shown in Fig. 2, then the whole apparatus was electrically and thermally insulated. During heating related experiments, data was recorded at 40 MHz every 30 seconds.

As the pictures in Fig. 3 show, PNIPAm polymer hydrogels possess the unique property of a discontinuous volumetric phase change at roughly 34 ℃, its critical temperature T_C. Below T_C, the gel is hydrophilic, and is interstitially filled with an ambient liquid. Above T_C, the gel becomes hydrophobic, and expels the ambient liquid from its polymer network. For the polymer-to-water weight ratio measurement, the weight of the gels were measured then placed into a furnace at 100 ℃ for greater than 24 h. In the case of polymer-to-water weight ratio, only gels without any extra materials were used. The average weight ratio is close to 95% water and 5% polymer material.

The dielectric constants of each sample were measured over the temperature range of ∼23 to ∼43 ℃. Measurement was taken every 30 seconds at 40 MHz. All samples exhibit a decreasing behavior in the dielectric constant with increasing temperature. The change is not consistent between all samples, not even samples of the same type. Because of this change, it is impossible to give a definitive dielectric constant value for each sample. We can, however, deduce basic properties and behaviors as they related to water, our standard.

As seen in Fig. 3, the dielectric constant of water decreases in a linear manner, as the temperature increases. Plain gel exhibits a similar decrease, but shows a sharp change in behavior around 34-35 ℃. The slope change is not uniform for all samples, but does occur in all samples. From this, we conclude a change in

Fig. 2 Teflon sample holder was inserted between the electrodes of the test-fixture HP16453A, rolled by a heater. Temperature was measured by a thermocouple set near the sample holder.

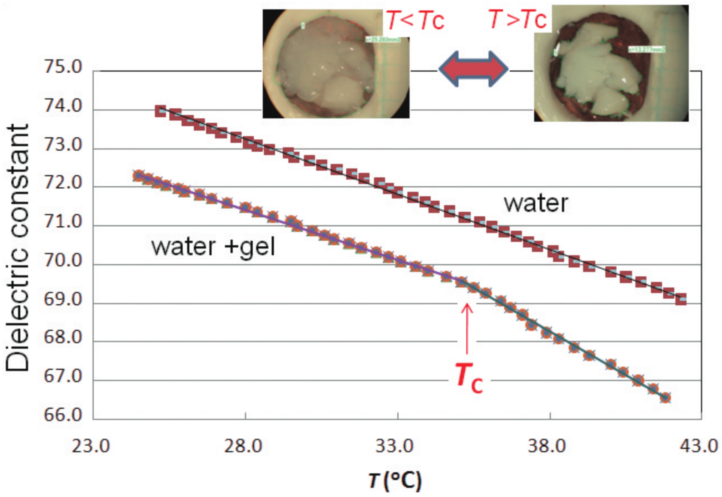

Fig. 3 Temperature dependence of the dielectric constant of the PNIPAm hydrogels at around the volumetric phase change at T_C. For comparison, result of water is shown. Pictures show the hydrogels in a Teflon sample holder above and below T_C.

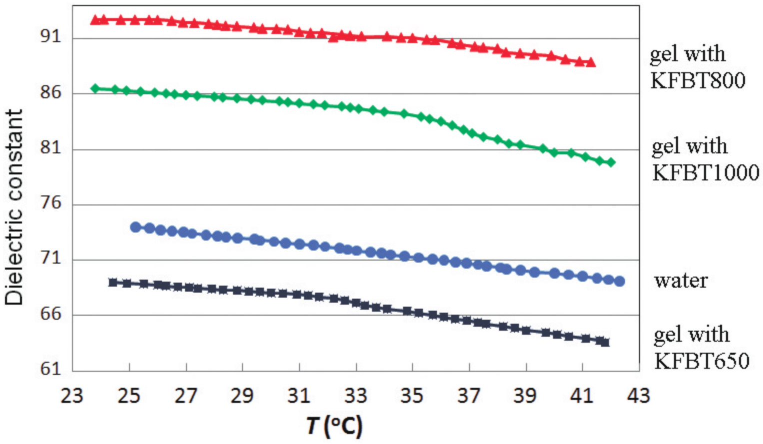

Fig. 4 Temperature dependence of the dielectric constant of PNIPAm polymer hydrogels with different 10% KF-doped $BaTiO_3$ powders.

dielectric constant occurs around 34-35 ℃, which is very near the phase transition temperature of the PNIPAm hydrogel. The data also show that the dielectric constant of the hydrogel is essentially lower than that of water.

Temperature dependence of the dielectric constant of PNIPAm hydrogel embedded of different $KF_{10\%}$-BT powders, consists of KFBT650, 800 and 1000, is shown in Fig. 4. The gel with KFBT1000 maintained a higher dielectric constant than water, and two distinct slopes appear, though not as clearly as plain gel. Comparison of the below/above T_C images shows that the KFBT1000 gel does not shrink as much as plain gel. The gel embedded of KFBT800 powders show the highest dielectric constant, about 28% larger than that of water, but did not show any gel-like behavior. In the cases where the sample holder was filled completely with the KFBT800 gel, the dielectric constant displayed a plateau type behavior. As mentioned above, KBT800 powders have the highest quality on the crystal property (see Fig. 1), and most pronounced dielectric constant. It is possible that the quality of the crystal enlarges the dielectric constant of the gel. Finally, concerning the gel embedded with KFBT650, which has poor crystal property: the dielectric constant of the gel remained lower than water. The slope behavior varied from sample to sample, but was consistently unstable. That is to say, none of the KFBT650 samples showed a single slope similar to water or two distinct slopes similar to plain gel. One possible cause of the instability in the behavior is an interaction between the smaller KFBT650 particles and the polymer network.

4. Summary

Ferroelectric nanopowders of 10% KF-doped $BaTiO_3$ were successfully synthesized by a sol-gel method. We embedded the powder into PNIPAm hydorogels, which have a discontinuous volumetric phase transition at T_C ～34 ℃. The dielectric constant of the gels in water was measured at 40 MHz in a temperature range between 23 and 43 ℃. The plain gel in water shows a dielectric anomaly at T_C and the gel's dielectric constant is lower than that of the water. The dielectric constant of the hydrogels embedded with different $KF_{10\%}$-BT powders consists of KFBT650, 800 and 1000 was measured. The dielectric constant increases up to 28% after the post-embedment of KFBT800 in comparison with that of the distilled water. Application of this material in hyperthermia treatment of biological tissues with the goal of tumor therapy may be possible.

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論文要旨

室温で大きな誘電率を持つ強誘電体であるKF10％添加$BaTiO_3$のナノ粒子を、ゾル・ゲル法を用いることで、合成することができた。このナノ粒子をT_C = 34℃で不連続な体積相転移を示すPNIPAmハイドロゲルに埋め込み、ハイドロゲルの誘電率を、水中23－43℃の温度域で、40 MHzの周波数で測定した。ゲルはT_Cにて誘電異常を示す、そしてゲルの誘電率はナノ粒子を埋め込むことによって、蒸留水の誘電率に比べ約28％上昇する。この結果は、このナノ粒子がラジオ周波数での電磁波加熱に有効であることを、示唆している。

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