JOURNAL OF Materials CHEMISTRY
Communication

Preparation of translucent barium titanate ceramics from sol–gel-derived transparent monolithic gels†

Hirokazu Shimooka,*[a] Shigemi Kohiki,[a] Takeshi Kobayashi,[b] Makoto Kuwabara,[b]

[a]Department of Applied Chemistry, Kyushu Institute of Technology, 1-1 Sensui-cho, Tobata, Kitakyushu 804-8550, Japan. E-mail: shimooka@che.kyutech.ac.jp
[b]Department of Materials Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan. E-mail: kuwabara@ecl.mm.t.u-tokyo.ac.jp

Received 28th January 2000, Accepted 17th April 2000
Published on the Web 5th June 2000

Translucent barium titanate ($BaTiO_3$) ceramics with a relative sintered density of 85% have been successfully produced *via* a powderless sol–gel method, in which transparent, partially-crystallized $BaTiO_3$ monolithic xerogels (dried gels) were prepared and submitted to sintering at 1100 °C in an oxygen atmosphere. The transparent $BaTiO_3$ xerogels turned opaque upon sintering at temperatures in the range 600 to 1000 °C, but sintering at 1100 °C resulted in the formation of translucent bodies. Pore size distribution measurements demonstrate that most pores present in the translucent materials are open pores with a diameter of <10 nm.

Transparent ferroelectric ceramics like (Pb,La)(Zr,Ti)O_3 [PLZT][1] have been investigated extensively due to their importance for electro-optic applications as light shutters, modulators, color filters, image storage devices, and so on.[2] To produce such transparent ferroelectric ceramics, special sintering techniques such as vacuum sintering and pressure sintering, *e.g.* hot pressing or hot isostatic pressing, are generally required.[2] Control of the microstructure and compositional homogeneity of nanoscale ferroelectric materials has attracted much attention because of the possibility of yielding novel electro-optic properties based on grain size effects.[3] However, it is generally very difficult when a powder process is used, since contamination can easily occur during the fabrication process.

To solve the problems in powder processing, the present authors have developed a novel powderless sol–gel method using high concentration metal alkoxide solutions.[4,5] In our previous studies, transparent, partially-crystallized nanoscale $BaTiO_3$ monolithic gels with homogeneous morphology have successfully been synthesized.[6] In the present study, we have found that such transparent $BaTiO_3$ monolithic gels with a specific pore size distribution profile could be converted into translucent ceramics by sintering at a temperature of 1100 °C under atmospheric pressure.

Essentially the same powderless sol–gel method, except for the drying process involved in the method, as used in our previous studies[4,6] was used to produce transparent, partially-crystallized $BaTiO_3$ monolithic gels in the present study. In brief, highly concentrated Ba,Ti-alkoxide precursor solution (1.2 mol l^{-1}) was prepared by dissolving equimolar amounts of barium ethoxide and titanium isopropoxide in a mixed solvent of dehydrated methanol and 2-methoxyethanol (with a ratio of 60/40 by volume) at room temperature. The precursor solution was hydrolyzed under stirring with water vapor at 0 °C.[6] This hydrolysis process was continued for about 10 h so that the amount of water added in the precursor solution reached $H_2O/Ba \approx 7$ (in molar ratio). The hydrolyzed solution was aged in a sealed container kept still under the following aging conditions, where the aging temperature and time were consecutively changed: at 5 °C for 3 days, at 20 °C for 2 days, at 30 °C for 2 days and finally at 50 °C for 1 day. Gelation and syneresis (shrinkage of the gel network) reaction took place during this period, resulting in the formation of a transparent, wet monolithic gel. In our previous studies, drying of wet gels has always been performed at 90 °C in flowing N_2. In the present study, on the other hand, the wet gels were dried under flowing N_2 at 20 °C for 2 days, and then further dried under reduced pressure for 1 h at the same temperature. The obtained transparent monolithic xerogels were sintered at 1000, 1100 and 1300 °C for 2 h in flowing O_2, with a heating rate of 50 °C h^{-1} up to 400 °C and 600 °C h^{-1} above this temperature.

The transparent $BaTiO_3$ xerogels dried at 20 °C turned opaque upon firing in the temperature range 600 to 1000 °C and also at temperatures above 1200 °C, but when sintered at 1100 °C the materials turned translucent. Fig. 1 shows a typical example of translucent $BaTiO_3$ monolithic ceramics produced in the present study; the photograph was taken for a sample with a thickness of 0.34 mm. It can be seen that the $BaTiO_3$ ceramic was produced to have as much translucency to allow one to read letters typed on a paper placed beneath the ceramic. The amber color of the translucent $BaTiO_3$ ceramic may be due to light absorption edge of $BaTiO_3$ located around 3.0–3.2 eV. The optical transmittance spectra obtained for the material, taken in three different ambient media of toluene (refractive index $n=1.49$), methanol ($n=1.33$) and air ($n=1.00$), are shown in Fig. 2. From the transmittance *versus* n plot at a fixed wavelength (not shown here) the transmittance of the material itself (corresponding to the extrapolated value at $n=2.3$ for $BaTiO_3$ on the plot) is found to be in excess of 30% at wavelengths above 700 nm. Note that the transmittance value of this sample is comparable with a value of 13% (at

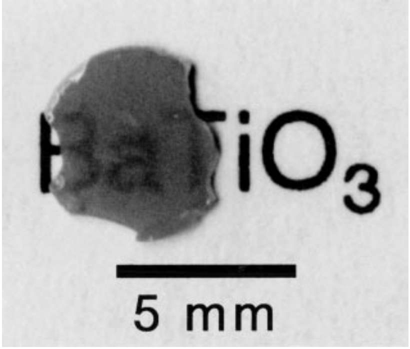

Fig. 1 Appearance of a translucent $BaTiO_3$ ceramic produced in this study: thickness = 0.34 mm.

---

†Electronic supplementary information (ESI) available: FE-SEM photographs of $BaTiO_3$ ceramics obtained at 1000 (fracture surface), 1100 (fracture surface) and 1300 °C (free surface). See http://www.rsc.org/suppdata/jm/b0/b000792g/

DOI: 10.1039/b000792g

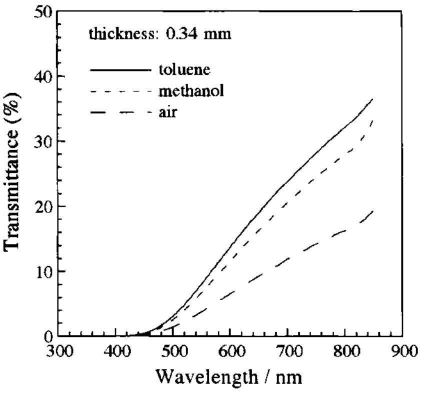

Fig. 2 Optical transmittance characteristics obtained for a translucent $BaTiO_3$ ceramic in various ambient media.

700 nm in air) reported for a hot-pressed $BaTiO_3$ sample with a thickness of 1.1 mm and a relative sintered density of >97%.[7]

In general, it may be recognized that high density is one of the requirements for translucency. However, the translucent $BaTiO_3$ ceramic obtained here had a considerably low relative sintered density of 85%, measured from its weight and volume. Another measure of the relative sintered density of the material, obtained from the porosity measurement, was also found to be around 85% (or its porosity = 15%). The result is shown in Fig. 3. Pore size distribution measurements were performed by using a nitrogen adsorption porosimeter (Quanta Chrome Co., Autosorb-1), and the plots were obtained by the Dollimore–Heal (DH) method[8] using their adsorption curves. Since the two values are in good agreement, most pores present in the material can be considered to be open ones. The obtained result indicates that pores present in the translucent ceramic had a diameter of < 50 nm, mostly of < 10 nm. FE-SEM (field-emission scanning electron microscopy) photographs (available as electronic supplementary information (ESI), see footnote†) of samples obtained at 1000 (taken on a fracture surface), 1100 (fracture surface) and 1300 °C (free surface) clearly demonstrate that the translucent sample obtained at 1100 °C had an apparently highly-dense microstructure (with no coarse pores) consisting of grains around 1 μm, while the sample at 1000 °C had a poorly sintered microstructure of much smaller grains and lots of pores. Sintering at 1300 °C resulted in a microstructure consisting of coarse grains and coarse pores; such microstructures can be seen for usual well-sintered $BaTiO_3$ ceramics. One may recognize that the samples obtained at 1000 and 1300 °C both have coarse pores ranging from sub-micron to micron scale, and this is why the two samples are opaque. Translucency of the ceramic obtained at 1100 °C suggests that open pores remaining in the sample are too small to scatter light in the visible region, although the number of open pores is considerable.

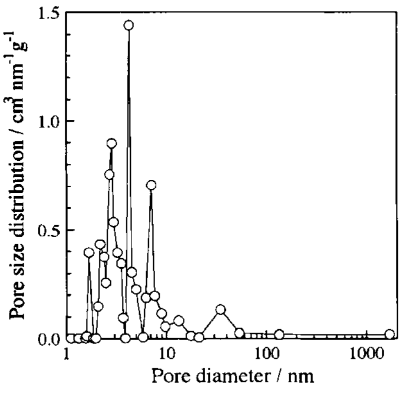

Fig. 3 Pore size distribution plot obtained for a translucent $BaTiO_3$ ceramic.

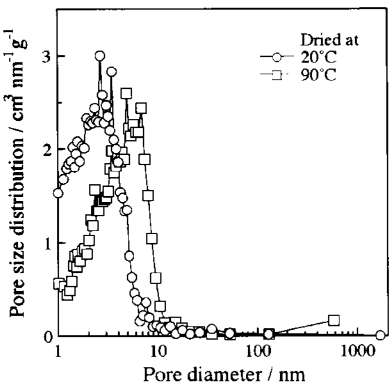

Fig. 4 Pore size distribution plots for transparent $BaTiO_3$ gels dried at 20 °C (circles) and 90 °C (squares), respectively.

In contrast to xerogels dried at 20 °C, no translucent $BaTiO_3$ ceramics could be obtained from monolithic gels dried at 90 °C produced in the present study. No precise pore size distribution measurements could be obtained for opaque ceramics obtained at 1100 °C, from gels dried at 90 °C; this is probably due to the fact that the pores remaining in the sample are closed ones, but not open ones. No appreciable difference in transparency and color was observed between the gels dried at 20 and 90 °C, but it has been found that the pore size distribution profiles of these two xerogels were different, as shown in Fig. 4. The data of Fig. 4 demonstrate that the $BaTiO_3$ gel dried at 20 °C had much smaller pore sizes (1–6 nm; average ≈ 3 nm) than that dried at 90 °C (2–10 nm; average ≈ 6 nm). The difference in the pore size distribution (average pore size and broadness) of the xerogels must be the principal reason why the translucent $BaTiO_3$ ceramic was obtained from the gels dried at 20 °C. The mechanisms of growth and inhibition of pores in the present $BaTiO_3$ xerogels at elevated temperatures are now under investigation.

In conclusion, translucent $BaTiO_3$ ceramics were successfully produced by sintering, at 1100 °C in flowing O_2, transparent monolithic xerogels dried at 20 °C, which were synthesized by a sol–gel process with a highly concentrated precursor solution ($1.2\ \mathrm{mol\ l^{-1}}$) of metal alkoxides. It has been found that pore sizes of monolithic xerogels dried at 20 °C were much smaller (1–6 nm) than those of xerogels dried at 90 °C (2–10 nm). Translucent $BaTiO_3$ ceramics were obtained only from the xerogels dried at 20 °C. A translucent $BaTiO_3$ ceramic of 0.34 mm thickness, with a density of around 85%, showed optical transmittance of more than 10% at wavelengths above 700 nm.

Acknowledgements

This work was supported in part by the Grant-in-Aid for Scientific Research, No. 09305043, given by the Ministry of Education, Science, Sports and Culture of Japan. The authors thank T. Miyabe and K. Yamada for their technical assistance in producing transparent $BaTiO_3$ monolithic gels.

Notes and references

1 G. H. Heartling and C. E. Land, *J. Am. Ceram. Soc.*, 1971, **54**, 1.
2 G. H. Heartling, *J. Am. Ceram. Soc.*, 1999, **82**, 797.
3 H. Gleiter, *Nanostruct. Mater.*, 1995, **6**, 3.
4 H. Shimooka and M. Kuwabara, *J. Am. Ceram. Soc.*, 1995, **78**, 2849.
5 H. Shimooka and M. Kuwabara, *J. Am. Ceram. Soc.*, 1996, **79**, 2983.
6 H. Shimooka, K. Yamada, S. Takahashi and M. Kuwabara, *J. Sol–Gel Sci. Technol.*, 1998, **13**, 873.
7 H. Yamamura, H. Haneda, A. Watanabe and S. Shirasaki, *Jpn. J. Appl. Phys. Suppl.*, 1985, **24-2**, 433.
8 D. Dollimore and G. R. Heal, *J. Colloid Interface Sci.*, 1970, **33**, 508.