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NANOCRYSTALLINE BaTiO₃ FROM GAS-CONDENSATION PROCESS

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ABSTRACT

Nanocrystalline BaTiO₃ can be prepared by the gas condensation method, which have an average particle size as small as 18nm. The stoichiometry of nanocrystalline BaTiO₃ particles can be controlled precisely and reproducibly. Nanocrystalline BaTiO₃ powders, fabricated by a novel e-beam evaporation method, show a good sintering behavior which can be sintered to a high density at a temperature as low as 1200°C and exhibit a relatively larger dielectric constant than that of coarse-grained ceramics. In addition, a thermal analysis has been also carried out to assert the lowest limit temperature for forming nanostructured BaTiO₃ from Ba/Ti oxidized clusters at ambient pressure condition.

INTRODUCTION

The fine-grained BaTiO₃ is an important electronic ceramic widely used in the manufacture of thermistors, multilayer capacitors, and electro-optic devices. The traditional ceramic processing has the difficulty in preparing morphologically homogeneous materials with fine grains, resulting in the development of several chemical solution-based methods for preparing well-crystallized submicrometer or nanocrystalline BaTiO₃ particles. These processes have the common goal of achieving product formation under mild reaction conditions (low temperatures and short reaction times) in order to limit the extent of grain growth and control particle size. BaTiO₃ particles with small and uniform particle size allow for thinner layers of the ceramic to be used in multilayer capacitors without loss of dielectric properties. In addition, small and uniform particle morphology offers the advantage of lower sintering temperature for multilayer devices, which may allow for the use of less expensive electrode materials.

Presently there are several chemical routes for synthesizing nanocrystalline BaTiO₃, such as coprecipitation procedures, sol-gel methods, and hydrothermal techniques, in which the coprecipitation procedures and hydrothermal techniques have been used to prepare commercial high purity submicrometer BaTiO₃ powders. There are two major shortcomings for coprecipitation procedures. One is the relative difficulty in introducing dopants into BaTiO₃. The other is that all the coprecipitated, single phase, complex compounds have been 1:1 for Ba:Ti [1]. As a result, the method involving a unique precursor compound applies to BaTiO₃ only and cannot be used to synthesize other compounds that are also of great technical importance in the BaO-TiO₂ system, such as BaTi₄O₉, BaTi₉O₂₀, and BaTi₃O₁₁ [2].

On the other hand, hydrothermal techniques also have many disadvantages[3-4] in that they involve several reaction steps and pressures to generate crystalline BaTiO₃ particles, and need complicated post-treatment of the powders in order to adjust the stoichiometry.

The purposes of the present work is two fold. One is to identify the feasibility of commercially synthesizing nanocrystalline multicomponent oxides, such as BaTiO₃, using the gas condensation method(GC). Unlike chemical synthesizing methods, the gas condensation method involves no solution chemistry. The other is to assert the lowest limit temperature for forming nanostructured BaTiO₃ from Ba/Ti oxidized precursors at ambient pressure condition because the reaction of Ba/Ti oxidized clusters made by a gas condensation method does not involve a hydrolysis reaction, which creates the possibility of preparing nanocrystalline BaTiO₃ at the lowest temperature at ambient pressure condition.

PROPERTIES OF NANOCRYSTALLINE BaTiO₃ FROM GC

We employed a two-source evaporation process to simultaneously produce a homogenous mixture of partially oxidized Ba/Ti clusters. The processing technique and parameters has been reported somewhere else[5].

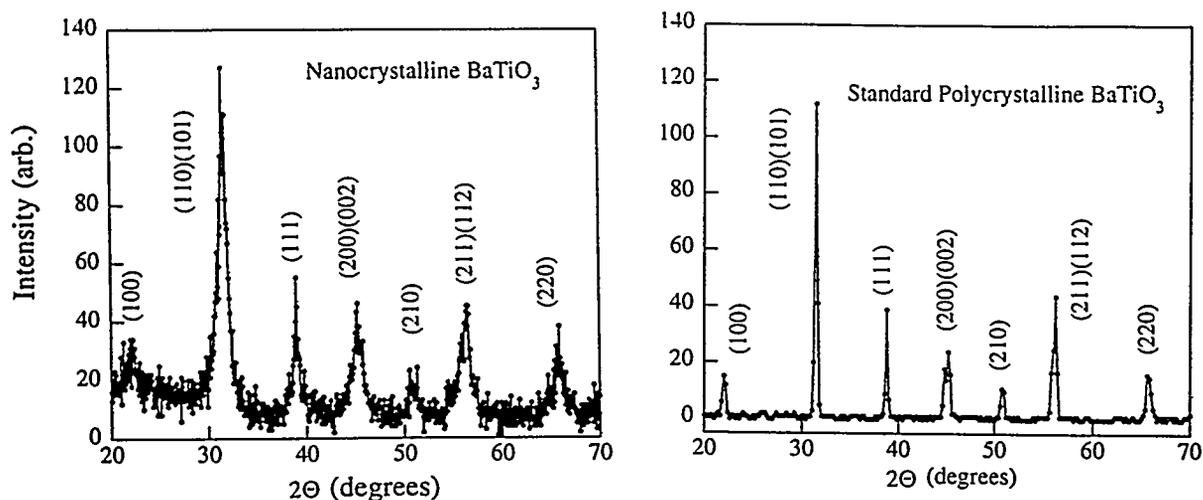


Figure 1 (a) X-ray diffraction of nanocrystalline BaTiO₃ annealed at 700 °C in air for 2 hours. (b) X-ray diffraction pattern of standard polycrystalline BaTiO₃.

After annealing the resulted mixture of Ba/Ti oxidized clusters at 700 °C in air for 1-2 hours, we can obtain well crystallized nanocrystalline BaTiO₃. Figure 1(a) is an x-ray scan for powders after annealing at 700°C for 2 hours, which indicates all the peaks belong to BaTiO₃. The dominant phase is most likely a pseudo-cubic phase, although peak broadening due to small particle size makes it difficult to distinguish the phase from the tetragonal phase typically found for coarse grained materials. The XRD observations were also reproduced by electron diffraction. Bright-field and dark field TEM images of these nanoparticles are shown in Figure 2. The average particle size is less than 20nm. The obtained nanocrystalline BaTiO₃ were pelletized by cold isostatic pressing without use of a binder.

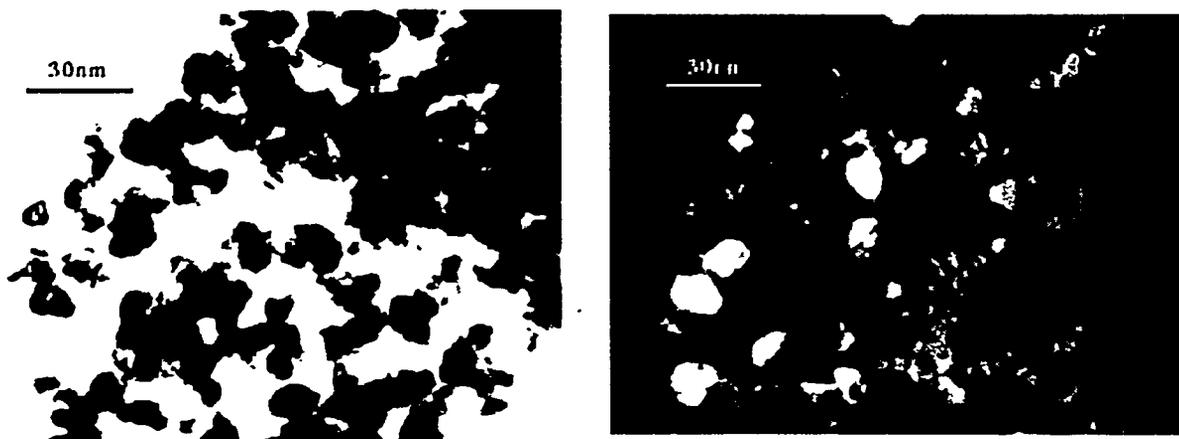


Figure 2 TEM micrographs of nano-BaTiO₃: a) Bright-field image; b) Dark-field image.

And then the pellets were sintered at different temperature ranging between 900 and 1250^oC. The densities of the samples, sintered at different temperatures, are given in Fig.3. Clearly, the well-crystallized nanocrystalline BaTiO₃ particles prepared by our GC method shows a good sinterability. Figure 4. is the plot of the dielectric constants and losses as a function temperature of the sample sintered at 1200^oC. The dielectric constants of samples were determined at 100 kHz during heating. Heating rates were 3^oC/min. Quite clearly, the phase transition behavior does not obey the Curie's law, exhibiting a rather diffused phase transition. It can be also found that the orthorhombic-tetragonal phase transformation slightly shifts up to a higher temperature, which is consistent with the recent thermal analyses done by Frey and Payne[6]. The dielectric constant of the BaTiO₃ sample made by nanocrystalline powders is larger than polycrystalline BaTiO₃ with coarse grain[7-8] at the room temperature.

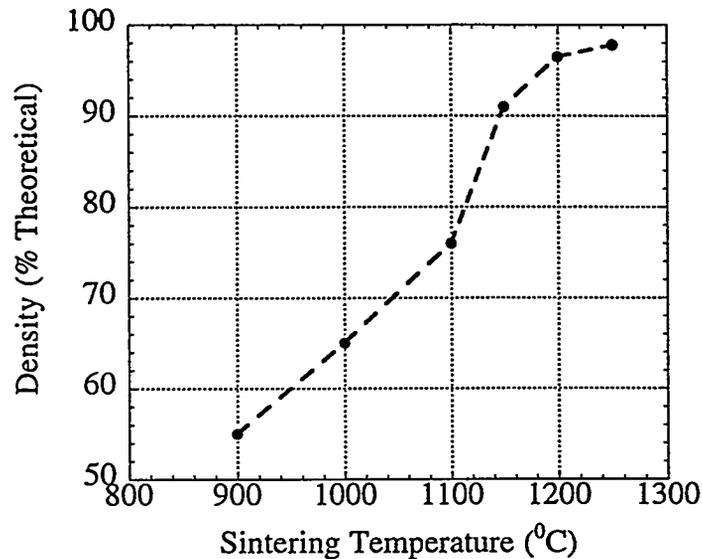


Figure 3 Plot of the density as a function of sintering temperature of nanocrystalline BaTiO₃ pellets.

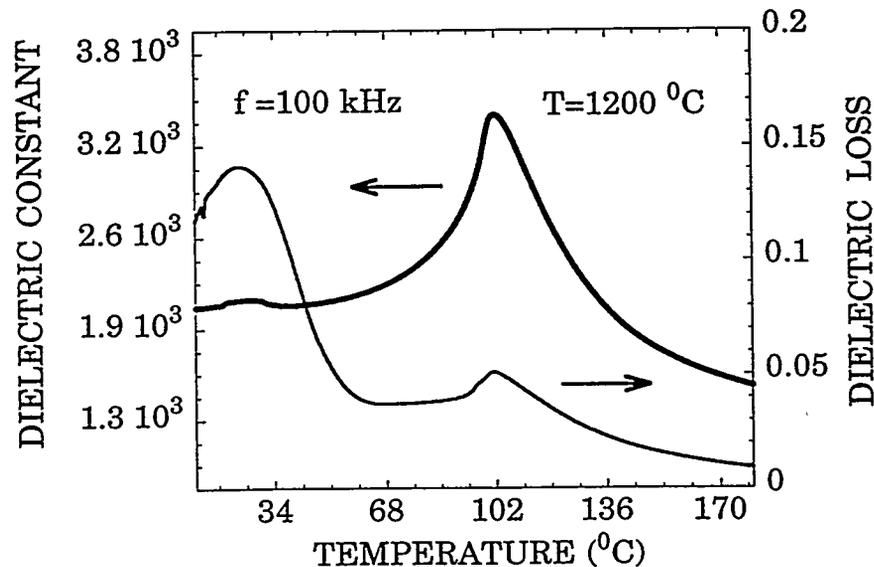


Figure 4 The dependence of dielectric constants and losses on temperature for the sample made by nanocrystalline BaTiO₃ from GC

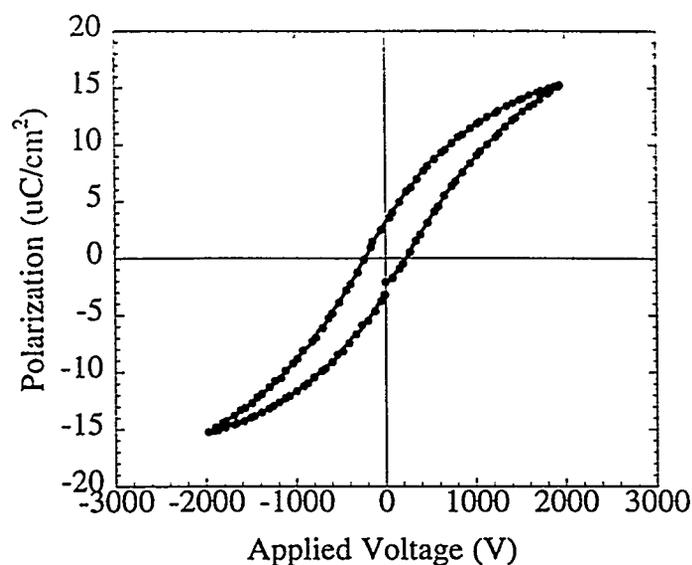
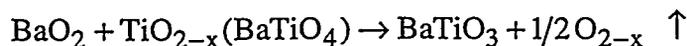
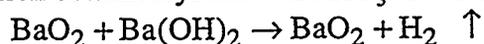


Figure 5 P vs. E hysteresis behavior of BaTiO₃ ceramics sintered at 1200 °C/2h.

However, the dielectric constants reported here are smaller than those of BaTiO₃ ceramics with ultra-fine grains reported in literature[4,8-10]. It is probably due to our incapability of fully polarizing samples prior to dielectric measurement. Fig.5 shows the polarization vs. applied electric field behavior of the samples sintered at 1200 °C. Apparently, the induced polarization are quite smaller than that of BaTiO₃ with coarse grains, even though the appearance of the classic P vs. E hysteresis is noticeable.

PRODUCTION FORMATION

Thermogravimetric analysis(TGA) and differential thermal analysis(DTA) were employed to determine the nature of the reactions that led to the formation of nanocrystalline BaTiO₃ particles. Actually the mixture of Ba/Ti precursors was first fully oxidized in air for several months. And then they were analyzed by DTA/TG at different heating rates to disclose the temperature at which exothermic/endothemic reaction took place. The heating rates from 1°C/min to 20°C/min were employed in both experiments in order to study the kinetics of nanocrystalline BaTiO₃ particles formation from Ba/Ti oxidized clusters. The results of TGA and DTA experiments are presented in Figure 6, indicating the existence of at least two stages. Stage 1, which extends up to 220°C, was accompanied by an exothermic reaction and a continuous weight loss. In stage 2, at 400°C to 600°C, depending upon heating rates, a sharp decrease in weight with apparent exothermic reaction was observed. According to the experimental results, the hypothesis reactions involved in the production of nanocrystalline BaTiO₃ are as follows:



It is expected when Ba atom clusters expose to air, they could be oxidized as Ba(OH)₂ or BaO₂ because of absorbing moisture. It should be pointed out that from thermodynamic and kinetic consideration BaO₂ is relatively more stable oxide phase at a low temperature than BaO, especially for clusters[11], although very little is known for the detailed mechanism of barium oxidation. The formation of nanocrystalline BaTiO₃ from the mixture of Ba/Ti oxidized clusters is hypothesized to proceed along the following path. At low temperature, Ba/Ti precursors consists of a mixture of Ba(OH)₂ and TiO₂. Around 100-250 °C, the Ba(OH)₂ was converted to BaO₂. Such a conversion should result in 2 % weight loss, which is in close agreement with the observed weight loss approximately.

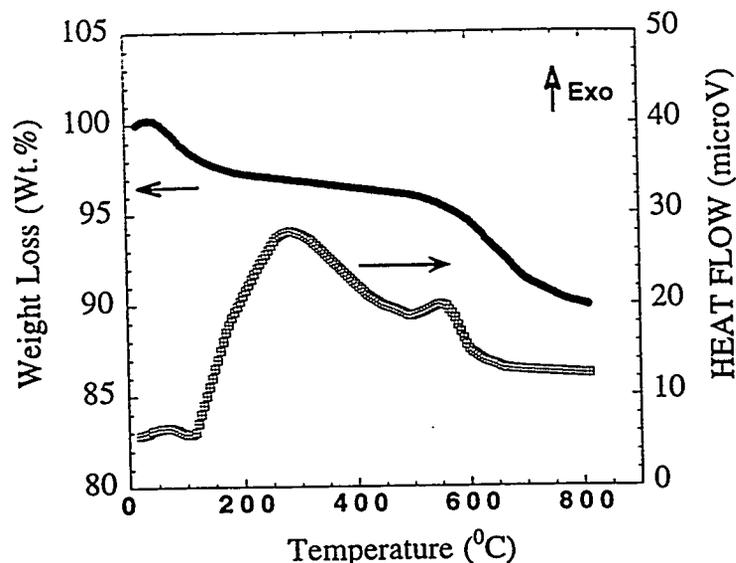


Figure 6 (a) Thermogravimetric analysis and differential thermal analysis curves of the mixture of Ba/Ti oxidized clusters.

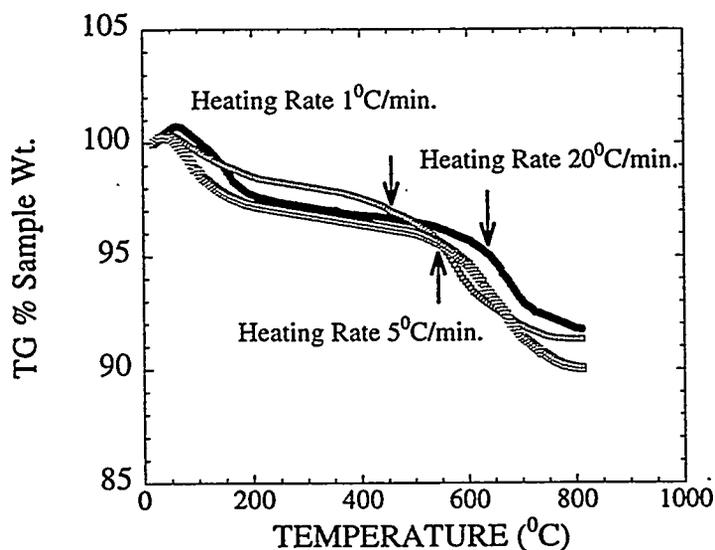


Figure 6 (b) TGA of the mixture of Ba/Ti clusters at different heating rates.

The amorphous mixture of BaO_2 and TiO_2 clusters crystallized to form nanocrystalline BaTiO_3 on heating in a temperature range from 400 to 600°C, depending upon the heating rates. Such a reaction is expected to be exothermic with a weight loss of 6-7%, in a good agreement with the experimental observations. Obviously, the faster heat rate leads to the higher temperature for nanocrystalline BaTiO_3 formation if the transformation of Ba/Ti precursors to nanocrystalline BaTiO_3 in static air is controlled by the oxygen diffusion process. The precise information of kinetics of formation nanocrystalline BaTiO_3 from Ba/Ti oxidized clusters can quantitatively obtained from Fig.(6b). From above experimental results, it is quite clearly that under ambient pressure condition well crystallized nanostructured BaTiO_3 could not be prepared from Ba/Ti oxidized clusters at a temperature below 400°C within a relatively short period of time. This result is actually consistent with the recent experimental observation by Nourbakhsh et al.[12].

It should be mentioned here that if the mixture of Ba/Ti precursors was not fully oxidized, its DTA/TGA behavior will be different from above presented results, although the mixture of Ba/Ti precursors can be still converted into nanocrystalline BaTiO₃ particles at the similar temperature range. An important aspect of our experimental results is to provide a rough assessment of the temperature limitation for synthesizing nanostructured BaTiO₃ in ambient pressure condition, by considering the kinetics characteristic of forming nanocrystalline BaTiO₃ from the mixture Ba/Ti oxidized clusters. Currently there are a number of recent literature reporting synthesizing temperature of nanostructured BaTiO₃, ranging from 200°C to 900°C[13-18]. Our experimental results presented here indicate that within a reasonable synthesizing time period the synthesizing temperature of nanostructured BaTiO₃ should be above 400°C. Otherwise, it is not possible to obtain the well crystallized nanostructured BaTiO₃. In reality, the processing temperature for synthesizing nanostructured perovskite oxides is one of foremost important issues for future microelectronic applications. Fundamentally, it is imperative for knowing the lowest possible processing temperature for synthesizing nanostructured perovskite oxides in order to use of them with standard Si processes since the interface compatibility between silicon or other semiconductors and numerous other perovskite oxides is critical for developing new generation microelectronics devices

CONCLUSION

We have successfully prepared nanocrystalline BaTiO₃ by using a gas condensation method. The physical properties of BaTiO₃ ceramic made by nanocrystalline BaTiO₃ via a gas condensation method have been reported. The obtained barium titanate powders sinter to high density at a temperature as low as 1200°C, which is favorable for the manufacture of multilayer capacitors. The possible mechanism responsible for forming nanocrystalline BaTiO₃ through the mixture of Ba/Ti oxidized clusters has been also discussed.

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REFERENCES

1. P.P Phule, and S.H. Risbud, *J. Mater. Sci.* **25**, 1169 (1990).
2. Zhimin Zhong and K. Gallagher, *J. Mater. Res.***10**(4), 945, (1995).
3. J. Menashi, R.C. Reid and L.P. Wagner, Barium Titanate Based Dielectric Compositions, U.S. Patent 4,832,939, May 23, (1989).
4. Y-S Her, E.Matijevic, and M.C. Chou, *J. Mater. Res.***10**(12), 3106-14 (1995).
5. Shaoping Li, Jeffy A. Eastman, L.T. Thompson, and P.M. Baldo, *Mat. Res. Soc. Symp. Proc.* Vol.**400**, 83-88, (1996).
6. M.H. Frey and D.A. Payne, *Phy. Rev. B* Vol.**54**(5), 3158 (1996).
7. B.W. Lee and K. H. Auh, *J. Mater. Res.***10**(6), 1416(1995).
8. K.Kinoshita and A. Yamaji, *J.Appl. Phys.* **47**, 371, (1976).
9. G. Arlt, D. Hennings, and G.deWith, *J.Appl.Phys.***58**, 1619(1985); and J.C. Niepce, *Electroceramics* **4**, Aachen, 29 (1994).
9. W.R. Buessem, L.E. Cross, and A.K. Goswami, *J.Am. Ceram. Soc.***49**, 36 (1966).
10. Technical Report from Cabot Performance Materials (1995).
11. H. J. Schmutzler, M. M. Antony, and K. Sandhage, *J. Am.Ceram.Soc.***77**, 721-29 (1994).
12. S. Nourbashsh, I.Vasilyeva, and J.N. Carter, *Appl. Phys. Lett.* **66**(21), 2804-08 (1995).
13. T. Sonogawa, et al., *Appl. Phys. Lett.***69**(15), 2193 (1996).
14. D.L. Kaiser, et al., *Appl. Phys. Lett.* **66**(21), 2801 (1995); L.A.Wills,et al., *Appl.Phys. Lett.* **60**(1) **41** (1992); and B.S. Kwak, et al., *J. Appl. Phys.* **69**(2), 767 (1991).
15. G.M. Davis and M.C. Gower, *Appl. Phys. Lett.* **55**(2), 112 (1989).
16. R.A. Mckee, et al., *Appl. Phys. Lett.* **59**(7), 789 (1991).
17. K. Iijima, et al., *Appl. Phys. Lett.* **56**(6), 527 (1990).
18. P.C.V. Buskirk, et al., *J. Mater. Res.* **7**(3), 542 (1992).