Journal of Nuclear Materials 393 (2009) 492–496

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Effect of CuO on $CaTiO_3$ perovskite ceramics prepared using a direct sintering process

Yi-Cheng Liou *, Chi-Ting Wu, Yuh-Lin Huang, Tzu-Chin Chung

Department of Electronic Engineering, Kun Shan University, 949, Da Wan Rd., Tainan 71003, Taiwan, ROC

ARTICLE INFO

Article history:
Received 4 August 2008
Accepted 17 July 2009

PACS:
61.10.Nz
68.37.Hk
77.80.−e
81.05.Je
81.20.Ev

ABSTRACT

Effect of CuO on $CaTiO_3$ (CT) ceramics prepared using a direct sintering process (reaction-sintering process) was investigated. The mixture of raw materials was pressed and sintered into ceramics without any calcination stage involved. Pure CT could be obtained. The degree of densification in CT via reaction-sintering process is lower than traditional oxide route but the grains grew easier in CT via reaction-sintering process. A density 3.63 g/cm^3 (90.3% of ρ_{th}) is obtained in CT pellets after 1500 °C/16 h sintering. With 3 wt.% CuO addition, density 3.92 g/cm^3 (97.5% of ρ_{th}) is obtained after 8 h sintering at 1500 °C due to the liquid phase sintering. The liquid phase at grain boundaries appeared significantly at a lower sintering temperature for longer soak time.

1. Introduction

Perovskite calcium titanate ($CaTiO_3$; CT) together with hollandite $BaAl_2Ti_6O_{16}$ and zirconolite $CaZrTi_2O_7$ are main phases in SYNROC, a titanate ceramic waste form. Most of the elements in high-level wastes can be immobilized by entering into solid solutions in the above phases [1]. Besides, CT can form solid solutions with lanthanides and actinides. It is one of the promising materials for immobilization of high-level radioactive wastes [2,3]. CT has been used for compositional modifications in $PbTiO_3$ or $BaTiO_3$ to improve their properties [4,5]. $CaTi_{1-x}Fe_xO_{3-\delta}$ ($x = 0.2–0.3$) were found with a chemical stability, a moderate thermal expansion coefficient ($\sim 12 \times 10^{-6}\,K^{-1}$) [5] and sufficient transport properties [6,7]. Therefore they had been considered as membranes for electrochemical oxygen separation [8,9] or hydrogen production [10]. The traditional process of synthesizing CT is by a solid-state reaction based on calcining the mixed oxide or carbonate powders. Other techniques such as organometallic [11], liquid mix [12], plasma spray [13] and mechanochemical [14–16] processes have also been reported.

Many oxides are added as low melting flux former to lower the sintering temperature in the preparation of ceramics. For $BaTiO_3$ ceramics, some oxides such as B_2O_3, Bi_2O_3, LiF, and SiO_2 have been used to lower the sintering temperature [17–20]. Beside these oxides, CuO has been investigated and reported to be an effective sintering aid for $BaTiO_3$ ceramics [21–26]. From the tentative phase diagram for the CuO–BaO system reported by Roth et al. [27], two binary compounds, $BaCuO_2$ and Ba_2CuO_3 are included and the latter is apparently unstable above 800 °C. $BaCuO_2$ was first synthesized by Arjomand and Machin [28]. It melts incongruently at a temperature ~1000 °C in air. Besides, there is a eutectic between $BaCuO_2$ and CuO at ~900 °C. Yang et al. [21] used the CuO–BaO mixture as a sintering aid in the fabrication of $BaTiO_3$ ceramics and studied its effects on the microstructure and densities of $BaTiO_3$ ceramics. An addition of 1 wt.% CuO–BaO mixture to $BaTiO_3$ significantly increased the sintering rate of $BaTiO_3$ at temperature between 1000 and 1100 °C. Derling et al. [29] found that CuO can be used as an effective sintering aid for $BaTiO_3$ based ceramics both as low melting flux former and as internal susceptor for microwave sintering. However, there are very few reports about the addition of CuO as a sintering aid for $CaTiO_3$ ceramics. Murashkina et al. [30] investigated $CaTi_{1-x}M_xO_{3-\delta}$ (M = Fe, Al, Cu) ceramics. They synthesized $CaTi_{1-x}Cu_xO_{3-\delta}$ at 1250 °C for 10 h and then fired at 1350 °C for 10 h. A solid solution exists in the interval of structures $0 \leqslant x \leqslant 0.1$ in $CaTi_{1-x}Cu_xO_{3-\delta}$ system. When the content of copper is more than 0.15 ($x > 0.15$) other phases are observed.

Reaction-sintering process is a simple and effective route to synthesize ceramics. Few years ago, we prepared $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) ceramics via a reaction-sintering process [31,32]. Raw materials PbO and Nb_2O_5 were mixed with $Mg(NO_3)_2$ or $Fe(NO_3)_3$ then pressed and sintered directly into PMN and PFN ceramics. These are the first successful synthesis of perovskite relaxor ferroelectric ceramics without having to go through the calcination step in the conventional solid-state route or in the columbite/wolframite route (two calcination steps were

---

* Corresponding author. Tel.: +886 6 2050521; fax: +886 6 2050250.
E-mail address: ycliou@mail.ksu.edu.tw (Y.-C. Liou).

0022-3115/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2009.07.007

involved). PMN ceramics with a density 8.09 g/cm^3 and dielectric constant 19,900 (1 kHz) were obtained. Other Pb-based complex perovskite ceramics were also produced by this reaction-sintering process successfully. In our recent studies, some microwave dielectric ceramics such as $BaTi_4O_9$, $(Ba_xSr_{1-x})(Zn_{1/3}Nb_{2/3})O_3$, $Ba_5Nb_4O_{15}$, $Sr_5Nb_4O_{15}$, $CaNb_2O_6$, and $NiNb_2O_6$ were also prepared successfully via this reaction-sintering process [33–37]. In the present study, synthesis of $CaTiO_3$ ceramics by a reaction-sintering process and the effect of CuO addition were investigated.

2. Experimental procedure

All samples in this study were prepared from reagent-grade powders: $CaCO_3$ (99.9%) and TiO_2 (99.9%). Appropriate amounts of raw materials for stoichiometric $CaTiO_3$ were milled in acetone with zirconia balls for 12 h. After dried and pulverized, the powder was then pressed into pellets 12 mm in diameter and 1–2 mm thick. The pellets were then heated at a rate 10 °C/min and sintered in a covered alumina crucible at temperatures ranging from 1330 °C to 1500 °C for 2–16 h in air. 1–5 wt.% CuO was added to improve densification and grain growth.

We analyzed the sintered pellets using X-ray diffraction (XRD) to check the reflections of the phases. Microstructures were analyzed using scanning electron microscopy (SEM). The density of the sintered pellets was measured using the Archimedes method.

3. Results and discussion

The density of CT ceramics sintered at various temperatures lower than 1400 °C and soak time for 2–6 h is shown in Fig. 1. It increased with the sintering temperature and soak time. The maximum density 2.87 g/cm^3 (71.4% of the theoretical value, ρ_{th}) is obtained after 6 h sintering at 1400 °C. In order to obtain dense CT ceramics, the sintering temperature was raised to 1500 °C. The shrinkage percentage and density values are listed in Table 1. These values increase with soak time. A density 3.63 g/cm^3 (90.3% of ρ_{th}) is obtained for 16 h sintering. Bagshaw et al. [38] obtained CT ceramics with >95% of ρ_{th} after being calcined at 1150–1250 °C and sintered at 1600 °C. Kim and Yoon [39] obtained CT ceramics with 95.41% of ρ_{th} after being calcined at 1000 °C for 3 h and sintered at 1300 °C for 3 h. Li et al. [40] obtained $Ca_{0.9}Sr_{0.1}TiO_3$ ceramics with 95.6% of ρ_{th} after sintered at 1400 °C for 2 h. From the above discussion, density of CT prepared via reaction-sintering process is lower than those via traditional oxide route. In our investigation of $SrTiO_3$ and $BaTiO_3$ prepared via reaction-sintering process, 4.99 g/cm^3 (97.5% of ρ_{th}) for $SrTiO_3$ and 5.89 g/cm^3 (97.9% of ρ_{th}) for $BaTiO_3$ was obtained after 6 h sintering at 1370 °C and 1400 °C, respectively [41]. Therefore, longer soak time and higher sintering temperature are necessary for dense CT ceramics produced using the reaction-sintering process.

Table 1
Shrinkage percentage and density CT ceramics sintered at 1500 °C for various soak time.

Soak time (h)	Shrinkage percentage (%)	Density (g/cm^3)
6	17.1	3.17
8	18.4	3.26
10	18.8	3.34
12	19.1	3.44
14	19.4	3.52
16	20.9	3.63

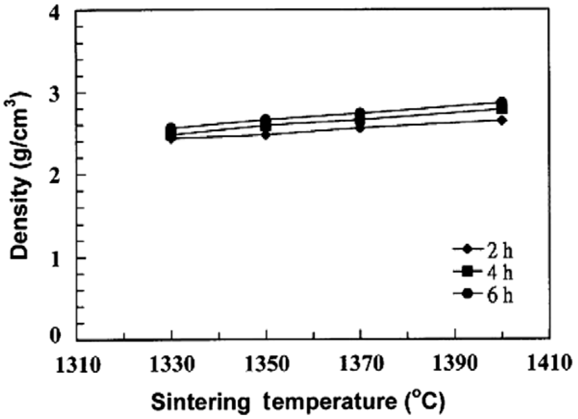

Fig. 1. Density of CT ceramics sintered at various temperatures and soak time.

The XRD patterns of CT ceramics sintered at 1500 °C for 6–16 h are shown in Fig. 2. These reflections agree with those of $CaTiO_3$ in ICDD–PDF#898033. This proves the perovskite phase $CaTiO_3$ could be obtained via the reaction-sintering process. This simple process is effective not only in preparing $BaTiO_3$, $SrTiO_3$, $NiNb_2O_6$, $BaTi_4O_9$, and Pb-based complex perovskite ceramics but also effective in preparing perovskite $CaTiO_3$ ceramics. Some intermediate phase was found in 6–12 h sintering CT and disappeared for longer soak times. The SEM photographs of as-fired CT ceramics sintered at 1350 °C–1500 °C for 6 h are illustrated in Fig. 3. Porous pellets with grain size 1–4 μm formed at 1350–1400 °C. The grain growth increased clearly at 1500 °C. For a longer soak time, grain size increased and grains of 8 μm were observed in CT sintered at 1500 °C for 16 h as shown in Fig. 4. Bagshaw et al. [38] obtained CT ceramics with grains of ~5 μm after being calcined at 1150–1250 °C and sintered at 1600 °C. Although the degree of densification in CT via reaction-sintering process is lower than traditional oxide route, the grains grew easier in CT via reaction-sintering process.

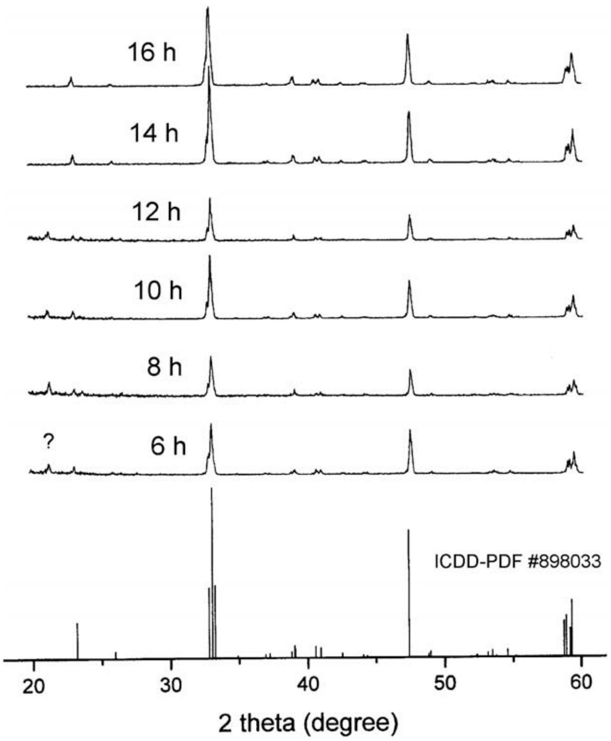

Fig. 2. XRD patterns of CT ceramics sintered at 1500 °C for 6–16 h (?: unknown phase).

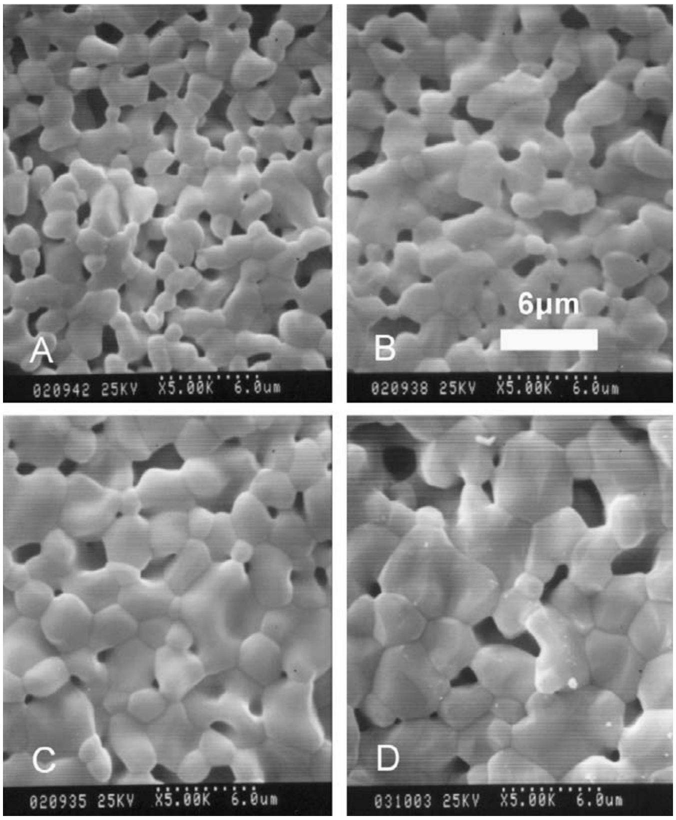

Fig. 3. SEM photographs of as-fired CT ceramics sintered at (A) 1350 °C, (B) 1370 °C, (C) 1400 °C, and (D) 1500 °C for 6 h.

The influence of sintering temperature and soak time on the density of CT ceramics with 1–5 wt.% CuO addition is shown in Fig. 5. For 1 and 3 wt.% CuO addition, density values 3.41–3.92 g/cm^3 are observed. A maximum density 3.92 g/cm^3 (97.5% of ρ_{th}) was obtained for CT ceramics with 3 wt.% CuO addition after 8 h sintering at 1500 °C. Therefore, the densification in CT pellets can be improved by adding CuO due to the liquid phase sintering and the increased diffusivity of grain boundary. A waste form must be thermodynamically resistant to leaching of radionuclides into the aqueous environment [42]. In the thermochemical studies of the ion-exchange process and the formation of dense perovskites from the open frameworks, Xu et al. [43,44] reported that the dense phases are indeed thermodynamically stable. Besides, in crystalline ceramic phases, radionuclides can be incorporated to occupy specific atomic positions in the periodic structures of constituent crystalline phases. This allows high loadings of specific radionuclides [42]. After adding 1 wt.% CuO–BaO with different CuO/BaO ratios (molar ratio, CuO/BaO = 1, 2, and 2.5) into $BaTiO_3$ + 0.5 mol% TiO_2, the sintering temperature was 200 °C lower than that for pure $BaTiO_3$. Approximately 95% of ρ_{th} could be obtained in $BaTiO_3$ + 0.5 mol% TiO_2 pellets sintered at 1150 °C [45]. Lower density values (3.03–3.63 g/cm^3) are observed in CT ceramics with 5 wt.% CuO addition due to too much liquid phase and the lowered diffusivity of grain boundary. This implies a small amount of CuO addition could raise the density of CT ceramics and too much CuO addition would result in a lower density. Similar results were observed in CuO doped $0.95(Na_{0.5}K_{0.5})NbO_3$–$0.05CaTiO_3$ ceramics. Park et al. reported the relative density was very low in pellets without CuO addition but considerably increased with CuO addition to peak at 95.4% of the theoretical density with 2.0 mol% CuO addition. They thought liquid phase sintering may have been responsible for the

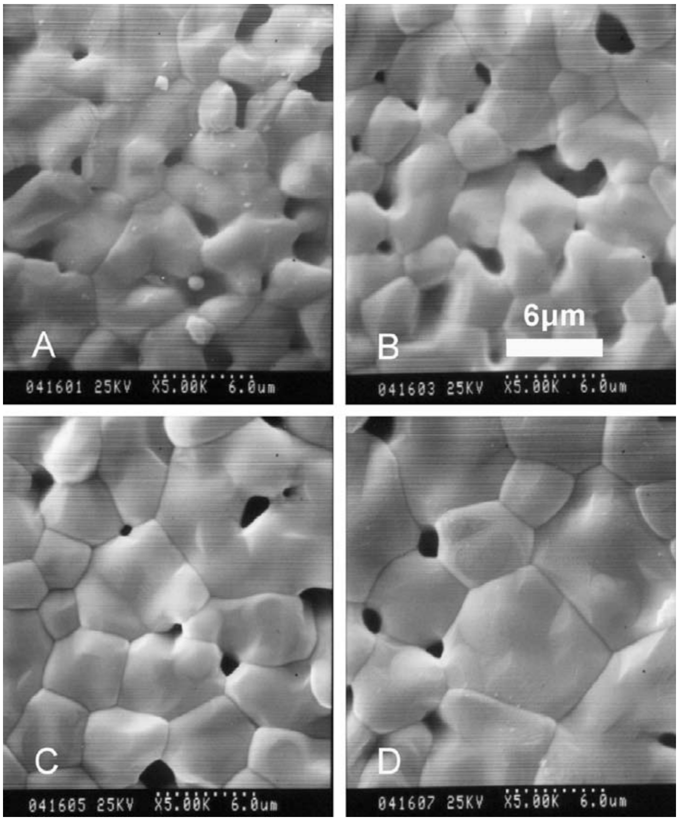

Fig. 4. SEM photographs of as-fired CT ceramics sintered at 1500 °C for (A) 10 h, (B) 12 h, (C) 14 h, and (D) 16 h.

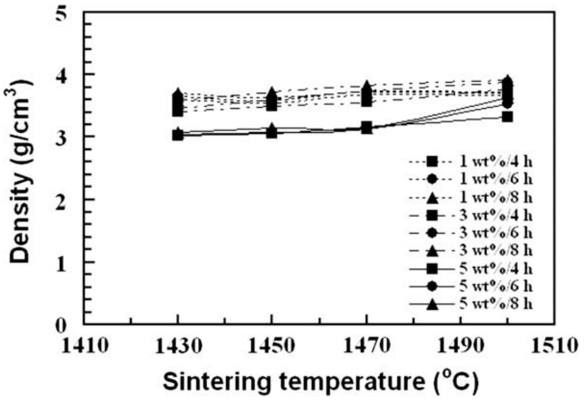

Fig. 5. Density of CT ceramics with 1–5 wt.% CuO addition and sintered at various temperatures and soak time.

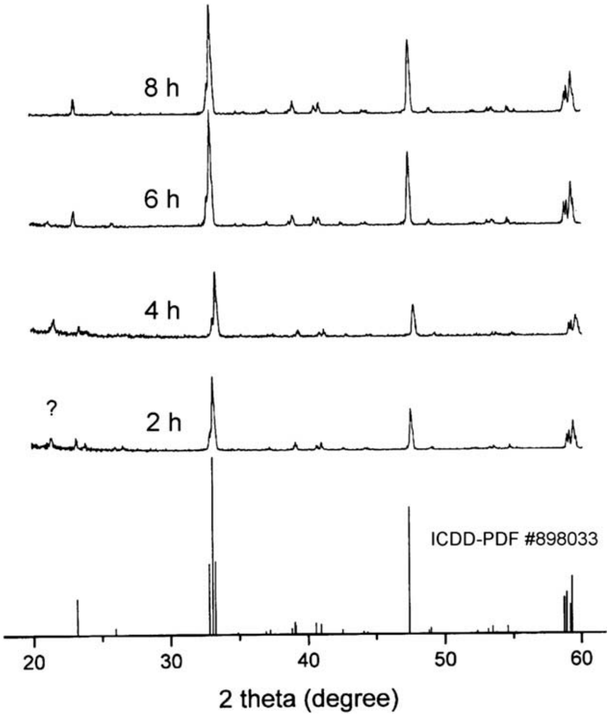

Fig. 6. XRD patterns of CT ceramics with 3 wt.% CuO addition and sintered at 1500 °C for 2–8 h (?: unknown phase).

increased relative density. The relative density slightly decreased when CuO addition exceeded 2.0 mol%, possibly due to the increased liquid phase and second phase [46]. While in $BiNbO_4$ ceramics, Huang et al. [47] reported that 0.25–1 wt.% CuO is suitable to obtain dense pellets and 2 wt.% resulted in a lower density.

The XRD patterns of CT ceramics with 3 wt.% CuO addition sintered at 1500 °C for 2–8 h are shown in Fig. 6. It is noted that the reflection of unknown phase at about $2\theta = 21.5°$ still can be found in pellets sintered for 2–6 h. The unknown phase disappeared in pellets sintered for 8 h which is 6 h shorter than CT without CuO addition as illustrated in Fig. 2. The complete formation of CT is easier as 3 wt.% CuO was added.

The SEM photographs of as-fired CT ceramics with 3 wt.% CuO addition are illustrated in Figs. 7 and 8. Pores decreased and grain size increased with sintering temperature. Grains of 5–15 μm were easily found. These are larger than CT ceramics without CuO addition as shown in Figs. 3 and 4. Liquid phase sintering is the major reason for the improvement of grain growth. Langhammer et al. [48] reported the undoped or low-doped $BaTiO_3 + 0.02BaO$ ceramics sintered at 1400 °C for 1 h exhibit normal grain growth with globular grains of 5–8 μm in diameter. For Cu addition ⩾0.3 mol%, the microstructure becomes bimodal. One fraction of grains remains globular with grain sizes only slightly increasing with Cu addition. The other fraction exhibits exaggerated grown, plate-like shaped grains with diameters 100–700 μm. With increasing percentage of the plate-like fraction, these grains touch each other during grain growth and the distinct plate-like shape vanishes gradually. The bimodal microstructure is not observed in Figs. 7 and 8. Liquid phases are occasionally found at grain boundaries in the pellet sintered for 6 h at 1450 °C and increases significantly at 1470 °C. As sintered at higher temperature 1500 °C for 6 h, the liquid phase is not found at grain boundaries. The liquid phase increased significantly for a longer sintering time of 8 h at 1450 °C and is not found in the pellet sintered at 1470 °C as shown in Fig. 8. This indicates the liquid phase at grain boundaries appeared significantly at a lower sintering temperature for longer soak time. Similar results were also observed in CuO doped $0.95(Na_{0.5}K_{0.5})NbO_3$–$0.05CaTiO_3$ ceramics. Park et al. reported that in specimens sintered for less than 10 h, grain growth did not occur and a microstructure with small grains was developed, possibly due to the small liquid phase amount. However, with increasing sintering time, the liquid phase amount increased, leading to liquid phase sintering which produced a dense microstructure with large grains. They thought a sufficient sintering time (⩾10 h) is required to produce proper liquid phase amount in order to obtain a dense microstructure in CuO doped $0.95(Na_{0.5}K_{0.5})NbO_3$–$0.05CaTiO_3$ ceramics [46].

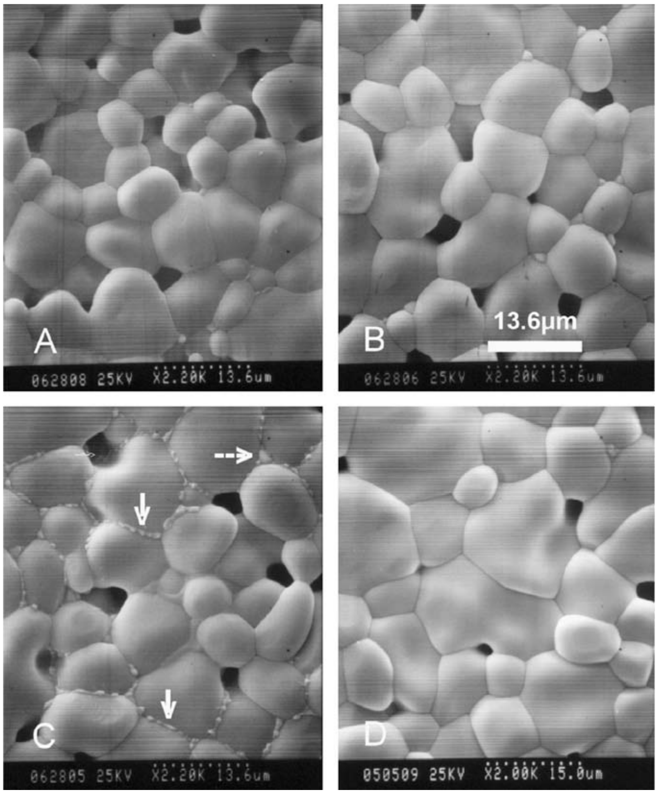

Fig. 7. SEM photographs of as-fired CT ceramics with 3 wt.% CuO addition and sintered at (A) 1430 °C, (B) 1450 °C, (C) 1470 °C, and (D) 1500 °C for 6 h (Liquid phases are indicated by arrows).

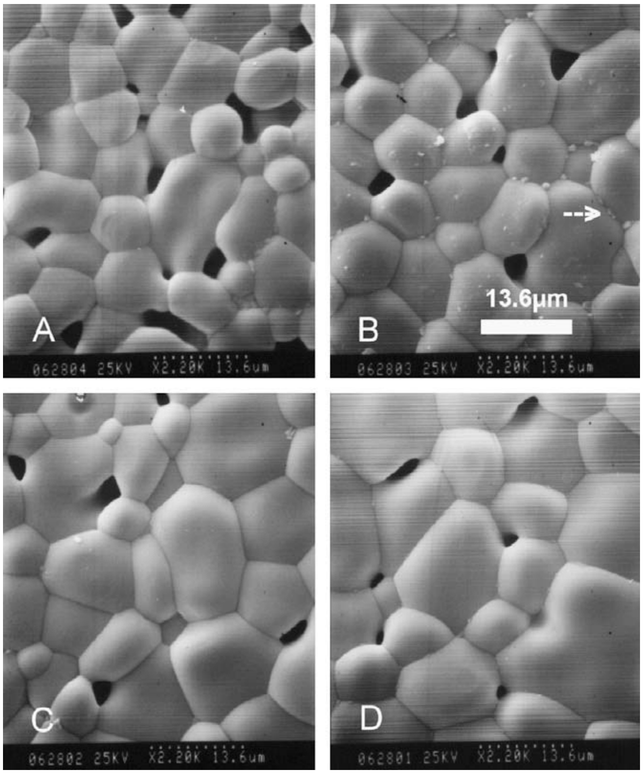

Fig. 8. SEM photographs of as-fired CT ceramics with 3 wt.% CuO addition and sintered at (A) 1430 °C, (B) 1450 °C, (C) 1470 °C, and (D) 1500 °C for 8 h (Liquid phases are indicated by arrows).

4. Conclusions

Perovskite $CaTiO_3$ ceramics could be obtained by a simple and effective reaction-sintering process successfully. A density 3.63 g/cm^3 (90.3% of ρ_{th}) was obtained after being sintered at 1500 °C for 16 h. Some intermediate phase was found in 6–12 h sintering CT and disappeared for longer soak times. With CuO addition, densification increased and a maximum density 3.92 g/cm^3 (97.5% of ρ_{th}) was obtained for CT ceramics with 3 wt.% CuO addition after 8 h sintering at 1500 °C. The intermediate phase was found only for 2–6 h sintering at 1500 °C and disappeared as sintered for 8 h. The liquid phase at grain boundaries appeared significantly at a lower sintering temperature for longer soak time.

References

[1] S.E. Kesson, A.E. Ringwood, Nucl. Chem. Waste Manage. 2 (1981) 53.
[2] G.J. McCarthy, Nucl. Technol. 32 (1977) 92.
[3] R. Roy, Radioact. Waste Disposal 1 (1982) 36.
[4] W. Wersing, K. Lubitz, J. Mohaupt, IEEE Trans. UFFC 36 (4) (1989) 424.
[5] J. Ravez, A. Simon, Solid State Sci. 1 (1999) 25.
[6] V.V. Kharton, F.M. Figueiredo, A.V. Kovalevsky, A.P. Viskup, E.N. Naumovich, J.R. Jurado, J.R. Frade, Defect Diffus. Forum 186/187 (2000) 119.
[7] H. Iwahara, T. Esaka, T. Mangahara, J. Appl. Electrochem. 18 (1988) 173.
[8] S. Xie, W. Liu, K. Wu, P.H. Yang, G.Y. Meng, C.S. Chen, Solid State Ionics 118 (1999) 23.
[9] H. Itoh, H. Asano, K. Fukuroi, M. Nagata, H. Iwahara, J. Am. Ceram. Soc. 80 (6) (1997) 1359.
[10] T. Esaka, T. Fujii, K. Suwa, H. Iwahara, Solid State Ionics 40/41 (1990) 544.
[11] Z.Z. Yang, H. Yamada, G.R. Miller, J. Solid State Chem. 41 (1985) 185.
[12] U. Balachandran, B. Odekirk, N.G. Eror, J. Mater. Sci. 17 (1982) 1656.
[13] K. Neufuss, A. Rudajevová, Ceram. Int. 28 (2002) 93.
[14] G. Mi, F. Saito, S. Suzuki, Y. Waseda, Powder Technol. 97 (1998) 178.
[15] I.R. Evans, J.A.K. Howard, T. Sreckovic, M.M. Ristic, Mater. Res. Bull. 38 (2003) 1203.
[16] G. Mi, Y. Murakami, D. Shindo, F. Saito, Powder Technol. 104 (1999) 75.
[17] I. Burn, J. Mater. Sci. 17 (1982) 1398.
[18] D.A. Tolino, J.B. Blum, J. Am. Ceram. Soc. 68 (1985) C-292.
[19] B.E. Walker, R.W. Rice, R.C. Pohanka, J.R. Spann, Am. Ceram. Soc. Bull. 55 (1976) 274.
[20] G. Desgardin, I. Mey, B. Raveau, J.M. Hausonne, Am. Ceram. Soc. Bull. 64 (1985) 564.
[21] C.F. Yang, L. Wu, T.S. Wu, J. Mater. Sci. Lett. 11 (1992) 1246.
[22] D. Hennings, Ber. Dt. Keram. Ges. 55 (1978) 359.
[23] C.F. Yang, L. Wu, T. Wu, J. Mater. Sci. 27 (1992) 6573.
[24] C.F. Yang, Jpn. J. Appl. Phys. 35 (1996) 5389.
[25] C.F. Yang, S.H. Lo, Mater. Res. Bull. 32 (12) (1997) 1713.
[26] C.F. Yang, J. Mater. Sci. Mater. Electron. 9 (1998) 167.
[27] R.S. Roth, K.L. Davis, J.R. Dennis, Adv. Ceram. Mater. 2 (3B) (1987) 295.
[28] M. Arjomand, D.J. Machin, J. Chem. Soc., Dalton Trans. (1975) 1055.
[29] S. Derling, T.H. Müller, H.-P. Abicht, K.-H. Felgner, H.T. Langhammer, J. Mater. Sci. 36 (2001) 1425.
[30] A.A. Murashkina, A.N. Demina, A.K. Demin, V.I. Maragou, P.E. Tsiakaras, Solid State Ionics 179 (2008) 1615.
[31] Y.C. Liou, K.H. Tseng, Mater. Res. Bull. 38 (8) (2003) 1351.
[32] Y.C. Liou, C.Y. Shih, C.H. Yu, Mater. Lett. 57 (2003) 1977.
[33] Y.C. Liou, C.T. Wu, K.H. Tseng, T.C. Chung, Mater. Res. Bull. 40 (9) (2005) 1483.
[34] Y.C. Liou, J.H. Chen, H.W. Wang, C.Y. Liu, Mater. Res. Bull. 41 (3) (2006) 455.
[35] Y.C. Liou, W.H. Shiue, C.Y. Shih, Mater. Sci. Eng. B 131 (2006) 142.
[36] Y.C. Liou, M.H. Weng, C.Y. Shiue, Mater. Sci. Eng. B 133 (1–3) (2006) 14.
[37] Y.C. Liou, C.Y. Shiue, Mater. Res. Soc. Symp. Proc. 848 (2005) 115.
[38] H. Bagshaw, D. Iddles, R. Quimby, I.M. Reaney, J. Eur. Ceram. Soc. 23 (2003) 2435.
[39] E.S. Kim, K.H. Yoon, J. Eur. Ceram. Soc. 23 (2003) 2397.
[40] R. Li, Q. Tang, S. Yin, H. Yamane, T. Sato, Mater. Sci. Eng. A 373 (2004) 175.
[41] Y.C. Liou, C.T. Wu, T.C. Chung, J. Mater. Sci. 42 (10) (2007) 3580.
[42] W.J. Weber, A. Navrotsky, S. Stefanovsky, E.R. Vance, E. Vernaz, MRS Bull. 34 (1) (2009) 46.
[43] H. Xu, A. Navrotsky, M.D. Nyman, T.M. Nenoff, J. Mater. Res. 15 (2000) 815.
[44] H. Xu, A. Navrotsky, M.D. Nyman, T.M. Nenoff, J. Mater. Res. 20 (2005) 618.
[45] C.F. Yang, Ceram. Int. 24 (1998) 341.
[46] S.J. Park, H.Y. Park, K.H. Cho, S. Nahm, H.G. Lee, D.H. Kim, B.H. Choi, Mater. Res. Bull. 43 (2008) 3580.
[47] C.L. Huang, M.H. Weng, C.C. Yu, Ceram. Int. 27 (2001) 343.
[48] H.T. Langhammer, T. Müller, R. Böttcher, V. Mueller, H.P. Abicht, J. Eur. Ceram. Soc. 24 (2004) 1489.