Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 38S (2012) S101–S104
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Crystal structure and dielectric properties of barium titanate–kaolinite composites

Kai Chen, Yong-Ping Pu *, Jian-Ke Liu

Key Laboratory of Auxiliary Chemistry & Technology for Chemical Industry, Shaanxi University of Science & Technology, Xi'an 710021, China

Available online 30 April 2011

Abstract

Barium Titanate–Kaolinite composites were prepared systematically by conventional solid-state method. The crystal structure and dielectric properties of samples were investigated by XRD and dielectric measurements, respectively. XRD results show that new phase $BaAl_2Si_2O_8$ was formed as kaolinite added into $BaTiO_3$. The 10 wt% kaolinite addition led to a considerable reduction in sintering temperature and a strong densification. The dielectric constant of $BaTiO_3$–Kaolinite composites tended to be stable with increasing of kaolinite content.

Keywords: B. Composites; C. Dielectric properties; D. $BaTiO_3$; D. Clays

1. Introduction

Barium titanate ($BaTiO_3$: BT) and Kaolinite are two distinct raw materials, which have far-reaching usage in today's industry. BT with perovskite structure belongs to ferroelectric materials possessing interesting dielectric properties including the high dielectric constant. However, due to the Curie peak at about 120 °C in BT ceramics, the dielectric constant of which is not stable with variations of temperature. Kaolinite is a relatively pure clay. The main product phase after firing kaolinite at high temperature is mullite, which can be formed at a temperature as low as 1100 °C [1]. Mullite is widely used as electrical insulation components for its stability and low dielectric loss, but its dielectric constant is low as well.

Composite materials combining two or more distinct constituents can take advantage of each constituent and consequently have superior properties as compared to the previous single constituent [2–4]. Recently, composites were successfully produced using kaolinite as the base matrix and BT added at several specific weight ratios [5], the resultant material exhibits both stability of kaolinite and high dielectric constant of BT ceramics. Furthermore, composites of $SrTiO_3$ powder mixed with kaolinite matrix at several particular weight ratios were prepared for the purpose of reporting on the preliminary dielectric results of the effect of $SrTiO_3$ filler in kaolinite matrix [6]. It shows that dielectric properties of the composite material do not conform to linear composite mix equation.

In the present research, BT–Kaolinite composites were prepared systematically by BT and kaolinite at various weight ratios, the crystal structure and dielectric properties of samples were investigated.

2. Experimental

Commercial BT (≥99.0%, Zhongxing Co. Ltd., Xiantao, China) and Suzhou Kaolinite (≥98.0%, Kaolinclay Co. Ltd., Longyan, China) powders were used as starting materials. $(1-x)$BT $-$ xKaolinite ($x = 0$–1) composites were prepared by solid-state method, in which x represented the weight ratio of kaolinite added into BT. These powders were weighted according to the nominal compositions, and mixed in distilled water by ball milling for 4 h. The slurries were filtered and dried at 90 °C. The powders were granulated in a 3 wt% polyvinyl alcohol solution (PVA) in a proportion of 90 wt% of powder and 10 wt% of PVA solution. Disks with 13.60 mm in diameter were prepared by unidirectional pressing (60 MPa) and baked at 600 °C for 1 h for binder removal. The samples were sintered at a certain temperature ranging from 1120 °C to 1360 °C in air. The soaking time at the sintering temperatures was 2 h.

* Corresponding author. Tel.: +86 29 86168803; fax: +86 29 86168688.
E-mail address: puyongping@yahoo.com.cn (Y.-P. Pu).

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.04.059

Crystalline phases in the resultant ceramics were identified by X-ray diffractometry (XRD; Model D/max2200pc, 2002, Rigaku, Tokyo, Japan). Patterns were recorded at 100 mA and 50 kV using Cu Ka radiation (λ = 1.54178 Å). The scan rate was 3°/min at a step size of 0.02°. For dielectric measurements, Ag paste was screen printed on both sides of the pellets and heat treated at 550 °C for 0.5 h. The frequency dependence of the dielectric constant was measured using a precision LCR Meter (Model E4980A, Agilent Technologies) over a frequency range from 20 Hz to 2 MHz at room temperature. The temperature dependence of dielectric constant was measured using a precision Impedance Analyzer (Model HP4278A, Hewlett-Packard) over a temperature range from 20 °C to 150 °C at 1 kHz.

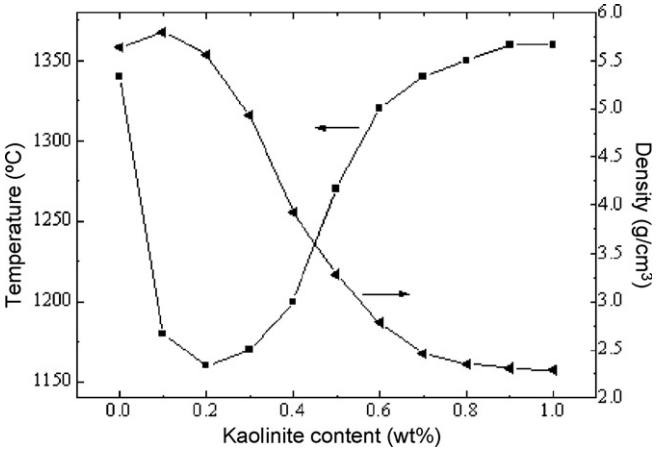

Fig. 2. Sintering temperature and density of composites as a function of kaolinite content.

3. Results and discussion

Fig. 1 shows the XRD patterns for $(1-x)$BT $-$ xKaolinite composites. The crystalline phase of pure BT was tetragonal. New phases were formed when kaolinite was added into the BT. Samples have tetragonal BT peaks with low levels of barium feldspar phases ($BaAl_2Si_2O_8$) in peaks 15.6°, 31.6° and 40.8° (when $x = 0.2, 0.3$). As kaolinite ratios increasing, the BT peaks decreases in 25.6°, 36.6°, 45.3° and 59.3°, while $BaAl_2Si_2O_8$ peaks increases a little. For mullite phase first appears at temperatures around 1100 °C, and its amount increases with the increase of temperature [1]. However, samples ($x = 0.2$, 0.3) were prepared at low temperatures (see Fig. 2), thus insufficient amount of mullite presents in samples for reaction of BT with kaolinite–mullite. When kaolinite keeps adding into BT, BT phase disappeared in samples (from $x = 0.5$), and $BaAl_2Si_2O_8$ peaks increase significantly in samples. This is presumably due to more mullite was formed for higher ratio of kaolinite and higher temperatures (see Fig. 2). In addition, there are new phases (such as $BaAl_2SiO_6$, $BaTiSi_4O_{11}$) emerged in samples (from $x = 0.5$). Furthermore, samples with higher ratios of kaolinite were investigated. These results show that $BaAl_2Si_2O_8$ peaks decreased gradually which is presumably due to relatively low amount of BT contained in samples and results in the formation of $BaTiSi_4O_{11}$. Especially, mullite phase was not found in sample until pure kaolinite. For peaks which were not denoted in figures, they were caused by the impurity contained in kaolinite, however, since there were very few impurities, those phases had little effect on the property of material. For the formation of $BaAl_2Si_2O_8$, it is considered [5] that the Ba^{2+} ions are reactive enough to form an immediate chemical bond with the kaolinite–mullite liquid state during sintering. From another point of view, for layered structure of kaolinite, it is possible that Ba^{2+} ions are capable of entering interlayer area of kaolinite–mullite liquid state and forming a temporary bond. As the composite cools down slowly, the intermediate liquid state compound rearranges itself to form $BaAl_2Si_2O_8$.

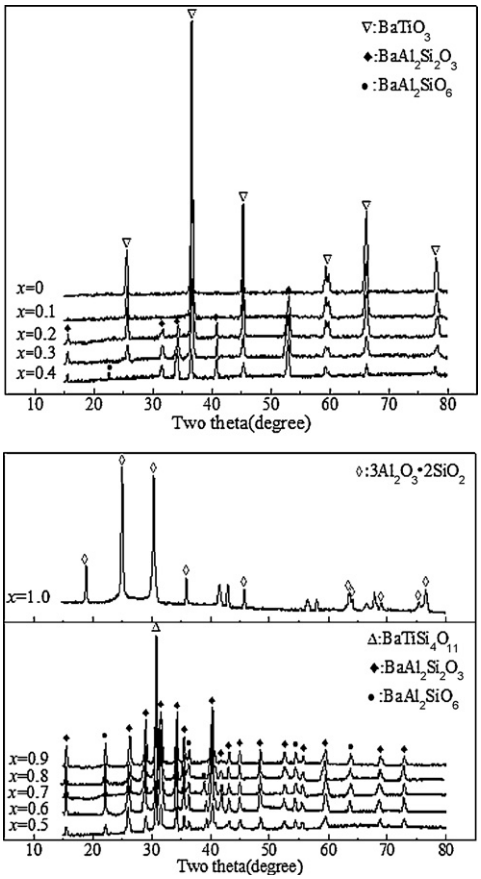

Fig. 1. X-ray diffraction patterns for $(1-x)$ BT $-$ xKaolinite composites sintered at different temperatures.

Fig. 2 shows the sintering temperature and density of composites as a function of kaolinite content. The density of the sintered samples was measured by the Archimedes method. Nearly 94.0% of the theoretical density was obtained for pure BT which was sintered at 1340 °C. With kaolinite adding into BT, there was a marked drop in sintering temperature. The maximum density for sample when $x = 0.1$ was obtained at 1180 °C. This is due to high content of Al_2O_3 and SiO_2 in kaolinite [7], which the densification of ceramics was enhanced by liquid phase sintering [8–11]. With kaolinite ratio in sample keeps increasing, the sintering temperature of ceramic arises as well, but the density of sample descends gradually. It can be

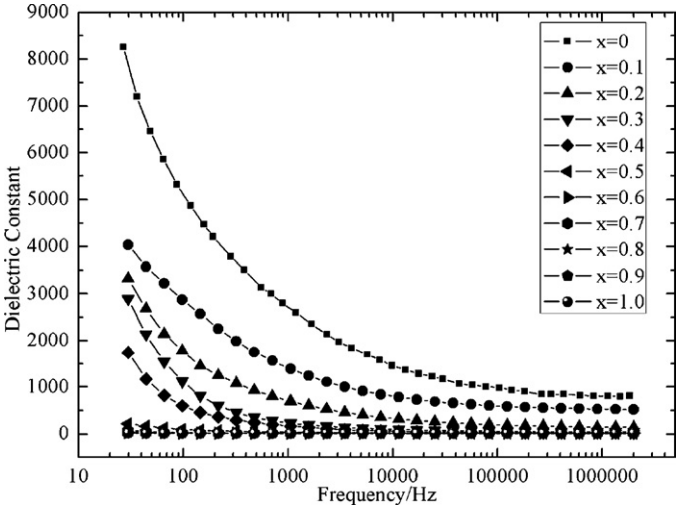

Fig. 3. Frequency dependence of dielectric constant for composites sintered at different temperatures.

attributed to the formation of $BaAl_2Si_2O_8$, which has a relatively low melting point and density, but high melt viscosity, in order to get dense ceramic, the sintering temperature needs to be increased. The theoretical density of $BaAl_2Si_2O_8$ is 2.56–2.59 g/cm^3, with increasing of kaolinite ratio, the content of $BaAl_2Si_2O_8$ in ceramic increases as well. When kaolinite ratio reaches to 80%, for there is relatively low amount of BT, $BaAl_2Si_2O_8$ in sample disappears gradually, and mullite was formed when $x = 1$.

Frequency dependence of dielectric constant for composites sintered at different temperatures is shown in Fig. 3. With increasing of frequency, dielectric constant decreases rapidly at low frequency, and tends to stabilization at high frequency. With kaolinite adding into BT ($x = 0$–0.4), dielectric constant decreases considerably. It can be considered the addition of non-ferroelectric makes the destruction of the original electric field, which results from accumulation of charges or ions in intergranular areas and, therefore, formation of macro-dipoles dispersion, which impedes polarization and leads to the decrease of dielectric constant [12]. On the other hand, according to XRD results, the main phase after reaction of BT and kaolinite is $BaAl_2Si_2O_8$, which possesses low dielectric constant [13,14], and with the increasing content of $BaAl_2Si_2O_8$, it dilutes the BT phase, which results in the decrease of dielectric constant. When BT phase disappeared in sample (from $x = 0.5$), there is little change in dielectric constant of samples, for $BaAl_2Si_2O_8$ becomes main phase in sample. In addition, mullite also possesses low dielectric constant [15,16].

Temperature dependence of dielectric constant for composites sintered at different temperatures is presented in Fig. 4. With increasing of temperature, Curie peak was obtained at about 130 °C for pure BT, but once kaolinite was added into BT, the Curie peak disappeared. It can be interpreted as high ε phase (BT) was surrounded by low ε phase ($BaAl_2Si_2O_8$) during the cooling process. Because of the significant difference in expansion coefficient between them, the low ε phase had tremendous pressure on the high ε phase [17]. However, the

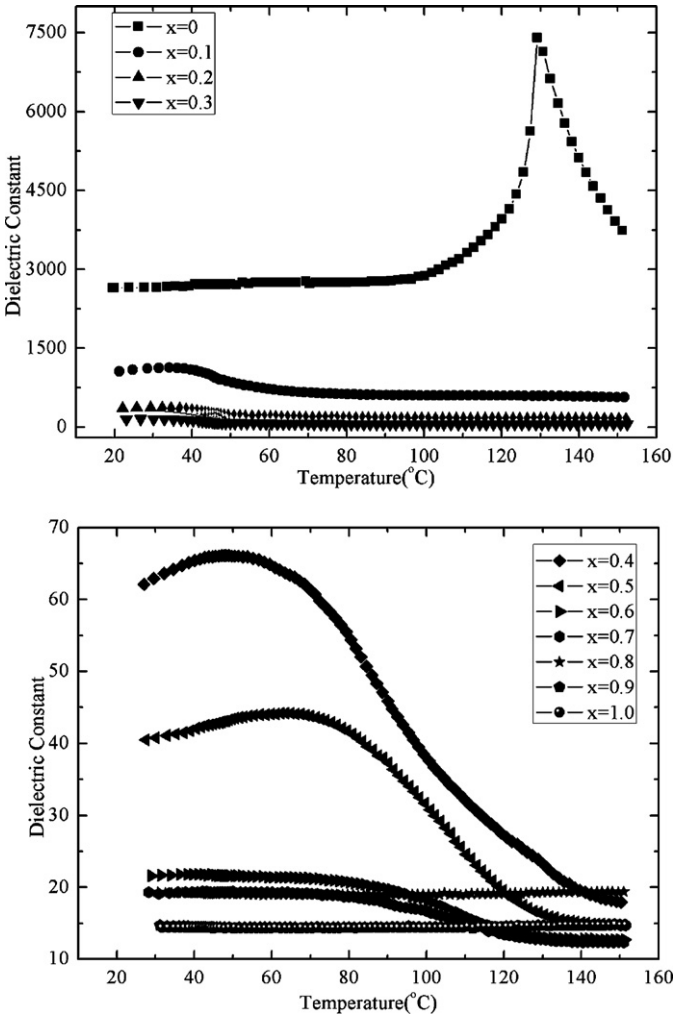

Fig. 4. Temperature dependence of dielectric constant for composites sintered at different temperatures.

Curie peak is only the reflection that electric domain is prone to be oriented along the direction of electric field, and this orientation must be accompanied by electrostriction. For BT grains were surrounded by $BaAl_2Si_2O_8$ grains, the electrostriction of BT phase was inhibited by the pressure, thus, the Curie peak was inevitably suppressed. But what is interesting is a relatively low peak was found at about 30 °C, and this peak gradually moves to high temperature as well as the intensity of this peak decreases gradually. When kaolinite content in sample is very high (such as $x = 0.8$), dielectric constant of composite nearly does not change with variations of temperature, it is due to the high content of $BaAl_2Si_2O_8$ in sample which has little variation of dielectric constant with temperature [13]. It is suggested that kaolinite can effectively work as an inhibitor of Curie peak for BT ceramic.

4. Conclusions

Barium Titanate–Kaolinite composites were prepared systematically through conventional solid-state method aiming to investigate the impact of kaolinite added into BT. The

addition of kaolinite made the formation of $BaAl_2Si_2O_8$. Low amount of kaolinite can be used as sintering aid in BT ceramics, and 10 wt% of kaolinite proved to be the optimal additive amount. Kaolinite can be worked as an inhibitor of Curie peak for BT ceramic which effectively stabilized the dielectric constant of composites.

Acknowledgements

This research has been supported by the Key Project of Chinese Ministry of Education (209126), Research projects of Science and Technology Division, Shaanxi (2010K10–14), Foundation of Shaanxi Educational Committee (112H011). This project was supported by the Graduate Innovation Found of Shaanxi University of Science and Technology.

References

[1] C.Y. Chen, G.S. Lan, W.H. Tuan, Microstructural evolution of mullite during the sintering of kaolin powder compacts, Ceramics International 26 (2000) 715–720.

[2] Y. Kobayashi, T. Tanase, T. Tabata, T. Miwa, M. Konno, Fabrication and dielectric properties of the $BaTiO_3$–polymer nano-composite thin films, Journal of the European Ceramic Society 28 (2008) 117–122.

[3] K. Naito, Y. Kagawa, S. Utsuno, T. Naganuma, K. Kurihara, Dielectric properties of woven fabric glass fiber reinforced polymer matrix composites in the THz frequency range, Composites Science and Technology 69 (2009) 2027–2029.

[4] J. Kulawik, P. Guzdek, D. Szwagierczak, A. Stoch, Dielectric and magnetic properties of bulk and layered tape cast $CoFe_2O_4$–$Pb(Fe_{1/2}Ta_{1/2})O_3$ composites, Composite Structures 92 (2010) 2153–2158.

[5] A. See, J. Hassan, M. Hashim, W.M.D.W. Yusoff, Dielectric variations of barium titanate additions on mullite–kaolinite sample, Solid State Science and Technology 16 (2008) 197–204.

[6] A. See, J. Hassan, M. Hashim, A.H. Shaari, W.M.D.W. Yusoff, Dielectric properties of strontium titanate filled mullite composites at 10 Hz–1 MHz, Solid State Science and Technology 17 (2009) 182–188.

[7] L. Feng, Z. Lin, J.T. Liu, F.K. Lu, Preparation of kaolinite/organic intercalation compounds by sonochemistry method, Journal of the Chinese Ceramic Society 34 (2006) 1226–1231.

[8] J.G. Fisher, B.K. Lee, S.Y. Choi, S.M. Wang, S.J.L. Kang, Inhibition of abnormal grain growth in $BaTiO_3$ by addition of Al_2O_3, Journal of the European Ceramic Society 26 (2005) 1619–1628.

[9] S. Jayanthi, T.R.N. Kutty, Effect of segregative additives on the positive temperature coefficient in resistance characteristics of *n*-$BaTiO_3$ ceramics, Journal of Materials Science: Materials in Electronics 17 (2006) 883–897.

[10] Z.J. Shen, W.P. Chen, J.Q. Qi, Y. Wang, H.L.W. Chan, Y. Chen, X.P. Jiang, Dielectric properties of barium titanate ceramics modified by SiO_2 and by BaO–SiO_2, Physical Review B: Condensed Matter and Materials Physics 404 (2009) 2374–2376.

[11] M.K. Kang, J.K. Park, D.Y. Kim, N.M. Hwang, Effect of temperature on the shape and coarsening behavior of $BaTiO_3$ grains dispersed in a SiO_2-rich liquid matrix, Materials Letters 45 (2000) 43–46.

[12] K. Orzechowski, T. Słonka, J. Głowinski, Dielectric properties of intercalated kaolinite, Journal of Physics and Chemistry of Solids 67 (2006) 915–919.

[13] R.A. Mccauley, Polymorphism and dielectric electric properties of Ba- and Sr-containing feldspars, Journal of Materials Science 35 (2000) 3939–3942.

[14] M.M. Krzmanc, M. Valant, D. Suvorov, The synthesis and microwave dielectric properties of $Sr_xBa_{1-x}Al_2Si_2O_8$ and $Ca_yBa_{1-y}Al_2Si_2O_8$ ceramics, Journal of the European Ceramic Society 27 (2007) 1181–1185.

[15] K. Leluk, K. Orzechowski, K. Jerie, A. Baranowski, T. Słonka, Dielectric permittivity of kaolinite heated to high temperatures, Journal of Physics and Chemistry of Solids 71 (2010) 827–831.

[16] G.M. Zhang, Z.Y. Fu, Y.C. Wang, H. Wang, W.M. Wang, Boron-doped mullite derived from single-phase gels, Journal of the European Ceramic Society 30 (2010) 2435–2441.

[17] Y.J. Kim, J.W. Hyun, H.S. Kim, J.H. Lee, Microstructural characterization and dielectric properties of barium titanate solid solutions with donor dopants, Bulletin of the Korean Chemical Society 30 (2009) 1267–1273.