Advances in Materials Physics and Chemistry, **2012, 2, 28-30**
doi:10.4236/ampc.2012.24B008 Published Online December 2012 (http://www.SciRP.org/journal/ampc)

The Reaction Sequence and Dielectric Properties of $BaAl_2Ti_5O_{14}$ Ceramics

Xiaogang Yao, Wei Chen, Lan Luo
Shanghai Institute of Ceramics, Chinese Academy of Science, Shanghai, China
Email: rockyao@student.sic.ac.cn

Received 2012

ABSTRACT

To investigate the correct reaction sequence of BaO-Al_2O_3-5TiO_2 system, powders calcined at different temperatures are analyzed by x-ray diffraction. The results show that the source phase $BaCO_3$ decomposes below 800°C, TiO_2 and Al_2O_3 start to consume at 900 and 1100°C, respectively. $BaTi_4O_9$ phase appears at 1000°C while $BaAl_2Ti_5O_{14}$ phase starts to reveal at 1200°C. As the temperature increases, the density, dielectric constant and quality factor of the $BaAl_2Ti_5O_{14}$ ceramic increase and keep unchanged at 1350°C. The dielectric properties of $BaAl_2Ti_5O_{14}$ ceramic sintered at 1350°C for 3h are: ε_r=35.8, Q×f=5130GHz, τ_f=-6.8ppm/°C.

Keywords: Reaction Sequence; $BaAl_2Ti_5O_{14}$; Ceramics; Dielectric Properties

1. Introduction

The rapid progress in mobile communication has created a tremendous demand for the microwave dielectric materials with high dielectric constant, low dielectric loss and near-zero temperature coefficient of resonator frequency [1,2]. As a typical high permittivity system, $Ba_{6-3x}Ln_{8+2x}Ti_{18}O_{54}$ (Ln = La, Sm, Nd) has attracted plenty of attention for the high dielectric constant over 80 [3,4]. However, the shortcoming of BLT system is its relatively high dielectric loss (low quality factor) which has restricted its commercial application.

Much work was done to lower the dielectric loss of the BLT system. Zhu improved the Q × f value of $Ba_{4.2}Nd_{9.2}Ti_{18}O_{54}$ ceramic by doping with $LnAlO_3$ (Ln = La, Nd, Sm) [5]. TiO_2 was added into $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ by Ohsato and excellent dielectric properties were obtained [6]. Our previous work has revealed that the crucial point to lower the dielectric loss of BLT system is preventing the reduction of Ti^{4+} at high sintering temperatures [7]. Al_2O_3 or MgO was used as an acceptor to suppress the reduction of Ti^{4+} in $Ba_{4.2}Sm_{9.2}Ti_{18}O_{54}$ ceramic and was very effective to improve the Q×f value of the BST ceramic. In our present work, Al_2O_3 was added into Ba-Sm-Ti and Ba-Nd-Ti systems. The dielectric loss has been reduced effectively. The common results are closely related to a new phase $BaAl_2Ti_5O_{14}$ (BAT) which is observed in both systems. No relevant information about the new BAT phase was reported.

In this paper, $BaAl_2Ti_5O_{14}$ ceramic was prepared by the solid state reaction. X-ray diffraction was used to identify the crystalline phase at each calcining temperature from 800 to 1350°C. The reaction sequence of BaO-Al_2O_3-5TiO_2 system was determined and the microwave dielectric properties of $BaAl_2Ti_5O_{14}$ ceramic were measured.

2. Experiment

The BAT ceramic powders were prepared according to the desired stoichiometry of $BaAl_2Ti_5O_{14}$ by mixing the chemical grade starting materials $BaCO_3$ (99.9%), Al_2O_3 (99.9%) and TiO_2 (99.9%). After ground in deionized water with ZrO_2 balls for 24h, the mixture was dried and then calcined at different temperatures from 800 to 1350°C in air for 1h. The optimally calcined BAT powders were milled for 24h, dried at 120°C and granulated with polyvinyl alcohol (PVA). The granules were preformed and then sintered at 1275~1375°C in air for 3h with a heating rate of 5°C/min.

The bulk densities of the BAT ceramic were measured by the Archimedes method. The crystalline phases of the calcined BAT powders and sintered BAT ceramic were analyzed by a Rigaku D/max 2550V X-ray diffractometer with a conventional Cu-Kα radiation in the range of 10~70° with a step size of 0.02°. The microstructure of the BAT ceramic was examined by a Hitachi S-4800 field emission scanning electron microscope. The dielectric properties of the polished BAT samples were tested the TE_{011} mode of an Agilent E8363A PNA series network analyzer with a frequency ranges from 3 to 4GHz. τ_f was tested in the temperature ranges from 20 to 80°C and calculated by noting the change in resonant frequency as:

$$\tau_f = (f_2 - f_1)/60 f_1 \quad (1)$$

Here, f_1 and f_2 represent the resonant frequencies at 20 and 80°C, respectively.

3. Results and Discussion

3.1. Reaction Sequence of BaO-Al_2O_3-5TiO_2 ststem

Figure 1 shows the XRD patterns of the BAT powders calcined at different temperatures from 800 to 1350°C for 1h. Here, the phases identified by X-ray diffraction at each calcining temperature are listed in **Table 1**. Six phases are observed as various temperatures are used. $BaCO_3$, Al_2O_3 and TiO_2 phases are observed at 800 °C with a new phase $BaTiO_3$ accompanied. It is easy to deduce that $BaTiO_3$ is the product of the reaction of $BaCO_3$ and TiO_2. With increasing the temperature to 900°C, no

$BaCO_3$ is residual while the trace of $BaTiO_4$ is detected. Fewer $BaTiO_3$ but a predominant $BaTiO_4$ phase is found at 1000°C. Not any change is observed until the calcining temperature is increased to 1200°C. The diffraction peaks of TiO_2 and $BaTiO_4$ are getting weak while a new phase $BaAl_2Ti_5O_{14}$ appears. Only a single $BaAl_2Ti_5O_{14}$ phase exists over 1300°C.

We can easily write down the reaction sequence of the BaO-Al_2O_3-5TiO_2 system with the increasing of calcining temperature from 800 to 1350°C.

$$\text{Below 800°C:}\quad BaCO_3 \rightarrow BaO + CO_2\uparrow \qquad (2)$$

$$\text{800°C:}\quad BaO + TiO_2 \rightarrow BaTiO_3 \qquad (3)$$

$$\text{900~1000°C:}\quad BaTiO_3 + 3TiO_2 \rightarrow BaTi_4O_9 \qquad (4)$$

$$\text{1200°C:}\quad BaTi_4O_9 + Al_2O_3 + TiO_2 \rightarrow BaAl_2Ti_5O_1 \qquad (5)$$

Figure 2 shows the DSC curve of the BaO-Al_2O_3-5TiO_2 powder heated from room temperature to 1350°C. As shown in **Figure 2**, three exothermic peaks are observed at 825, 925 and 1300°C which correspond very well to the temperatures at which the reactions (3)-(5) happen.

3.2. Dielectric Properties of $BaAl_2Ti_5O_{14}$ Ceramic

From what has been discussed above, we can draw the conclusion that the sintering temperature of the $BaAl_2Ti_5O_{14}$ ceramic is between 1300 and 1350°C. Thus, five temperature points (1275, 1300, 1325, 1350, 1375°C) are used to study the effect of temperature on the dielectric properties.

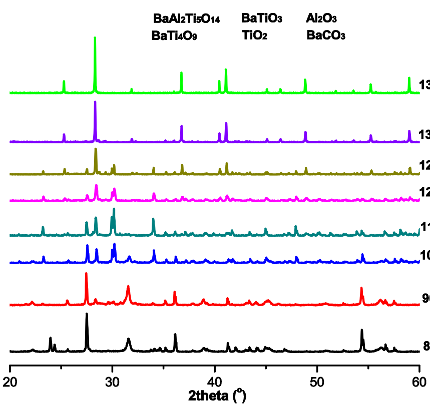

Figure 1. XRD patterns of BaO-Al_2O_3-5TiO_2 powders calcined at different temperatures from 800 to 1350°C for 1h.

Table 1. Crystalline phases exist of not exist at each calcining temperature.

T_c/°C	$BaCO_3$	TiO_2	Al_2O_3	$BaTiO_3$	$BaTiO_4$	$BaAl_2Ti_5O_{14}$
800	Y	Y	Y	Y	N	N
900	N	Y	Y	Y	Y	N
1000	N	Y	Y	N	Y	N
1100	N	Y	Y	N	Y	N
1200	N	Y	N	N	Y	Y
1250	N	Y	N	N	N	Y
1300	N	N	N	N	N	Y
1350	N	N	N	N	N	Y

Figure 3 shows the density of BAT ceramics at different sintering temperature. With the increasing temperature from 1275 to 1375°C, the density of BAT ceramics increases from 4.02 to the maximum value 4.17g/cm^3 at 1350°C, and then decreases slightly. We can conclude that the optimized sintering temperature of the BAT ceramics is 1350°C.

Figure 4 shows the SEM images of the BAT ceramic samples sintered at 1350°C for 3h. As we can see from **Figure 4(a)**, the BAT ceramic has a compact structure but a heterogeneous grain size. The average size is 10 μm, as shown in **Figure 4(b)**. Irregularly grown grains are seen in both images. The formation mechanism of these huge grains is still inexplicit and needs further research.

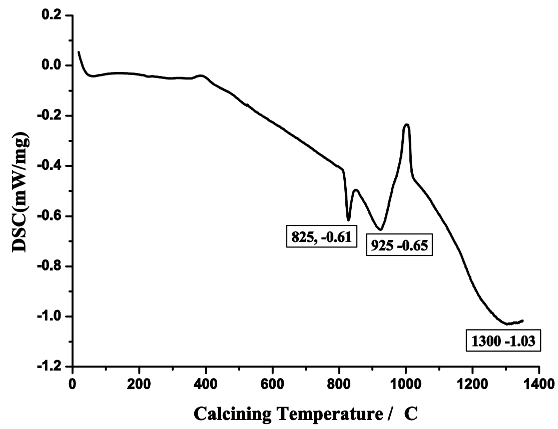

Figure 2. DSC curve of BAT powders.

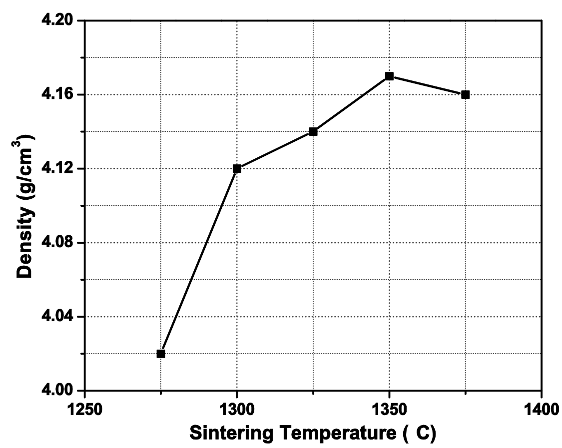

Figure 3. Density of the BAT ceramics sintered at different temperatures from 1275 to 1375°C.

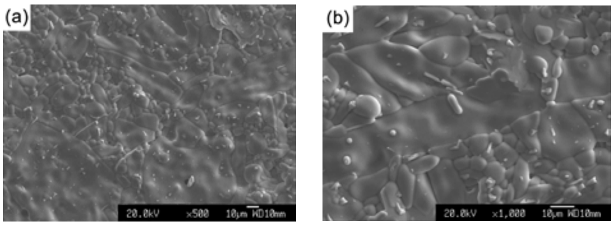

Figure 4. SEM images of the BAT ceramic sintered at 1350°C for 3h: (a) ×500; (b) ×1000.

Figure 5 shows the dielectric constant of BAT ceramics sintered at different temperatures. It is not strange that the change in dielectric constant with temperature shows the same regularity with that of density, since a more compact structure means a lower porosity. The dielectric constant of BAT ceramics reach 35.8 after sintering at 1350°C for 3h.

Figure 6 shows the Q × *f* value of the BAT ceramics sintered at different temperatures from 1275 to 1375°C for 3h. With the increasing temperature, the Q × *f* value of BAT ceramics increases from 4324GHz at 1275°C to the maximum value 5130 GHz at 1350°C. The heterogeneous grain size has very bad effect on the Q × *f* value. Huge grains can increase the dielectric loss significantly. Therefore, much work need be done to obtain a more homogenous grain distribution so as to improve the Q × *f* value of BAT ceramics.

Figure 7 shows the τ_f value of BAT ceramics sintered at different temperatures for 3h. The τ_f value of the BAT ceramics is slightly affected by the sintering temperature. BAT ceramics sintered at 1350°C for 3h has a negative τ_f value of -6.8ppm/°C.

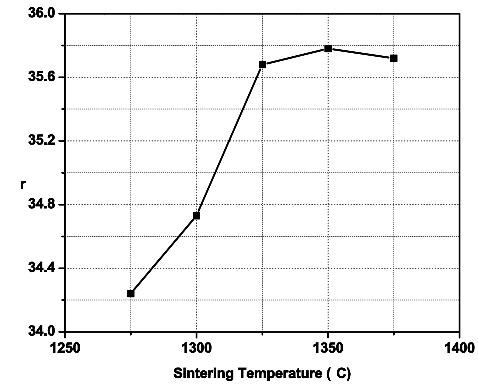

Figure 5. Dielectric constant of the BAT ceramics sintered at different temperatures from 1275 to 1375°C.

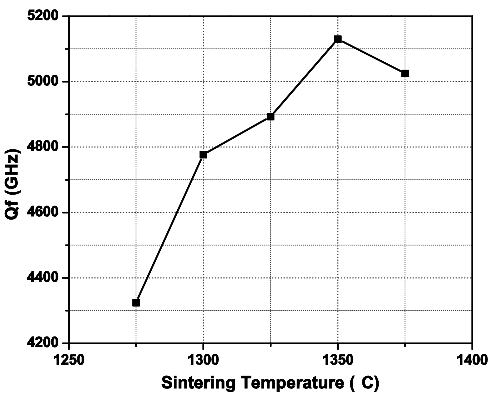

Figure 6. Q×*f* value of the BAT ceramics sintered at different temperatures from 1275 to 1375°C.

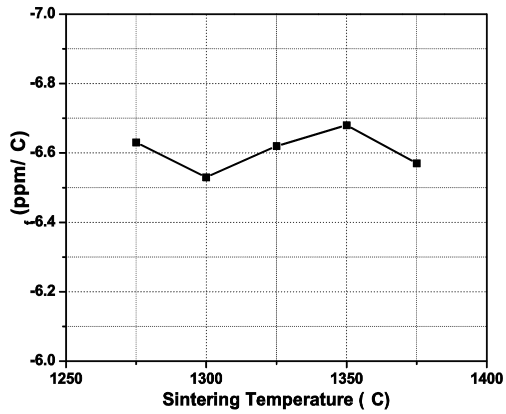

Figure 7. Resonator frequency of temperature coefficient of the BAT ceramics sintered at different temperatures from 1275 to 1375°C.

4. Conclusion

$BaAl_2Ti_5O_{14}$ ceramic is prepared by the conventional solid state reaction. The reaction sequence of BaO-Al_2O_3-$5TiO_2$ system has been established. The result shows that the ideal calcining temperature of BAT powder is 1200°C and the best sintering temperature of BAT ceramic is 1350°C. The BAT ceramic has a heterogeneous grain distribution which has very bad effect on its dielectric properties especially for the Qf value. The dielectric properties of BAT ceramic sintered at 1350°C for 3h are: ε_r=35.8, Q×*f*= 5130GHz and τ_f=-6.8ppm/°C.

REFERENCES

[1] R. Cava, "Dielectric materials for applications in microwave communications," J.Mater.Chem. pp. 54-62, 2001.

[2] I. Reaney, D. Iddles, "Microwave dielectric ceramics for resonators and filters in mobile phone networks," J.Am. Ceram. Soc.pp.2063-2072,2006.

[3] H. Ohsato, "Science of tungstenbronze-type like $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R=rare earth) microwave dielectric solid solutions," J.Euro. Ceram. Soc. pp.2703-2711,2001.

[4] H. Ohsato, M. Mizuta, "Microwave dielectric properties of tungsten bronze-type $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = La, Pr, Nd and Sm) solid solution,"J. Ceram.Soc.Jap.pp.178-182,1998.

[5] J. Zhu, E. Kipkoech, W. Lu. "Effects of $LnAlO_3$(Ln =La, Nd, Sm) additives on the properties of $Ba_{4.2}Nd_{9.2}Ti_{18}O_{54}$ ceramics," J.Euro. Ceram.Soc.pp.2027-2030,2006.

[6] H. Ohsato, A. Komura, "Microwave dielectric properties and sintering of $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R=Sm,x=2/3) solid solution with added rutile," Jpn.J.Appl.Phys. pp.5357-5359,1998.

[7] X. Yao, H. Lin, "Antireducion of Ti^{4+} in $Ba_{4.2}Sm_{9.2}Ti_{18}O_{54}$ ceramics by doping with MgO,Al_2O_3 and MnO_2," Ceram. Int. pp.3011-3016,2012.

