Ceramics International 28 (2002) 685–688

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effect of $BaTi_4O_9$ fibers on dielectric properties of $0.64BaTi_4O_9+0.36BaPr_2Ti_4O_{12}$ composites

Ying Song[a,b,*], Fuping Wang[a], Zhaohua Jiang[a], Yu Zhou[c]

[a]*Department of Applied Chemistry, Harbin Institute of Technology, Harbin 150001, People's Republic of China*
[b]*Department of Electronics Science and Technology, Harbin Institute of Technology, Harbin 150001, People's Republic of China*
[c]*School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, People's Republic of China*

Received 15 June 2001; received in revised form 21 September 2001; accepted 17 January 2002

Abstract

$BaTi_4O_9$(f)/($0.64BaTi_4O_9$–$0.36BaPr_2Ti_4O_{12}$) composites are prepared for a new kind of microwave dielectric ceramics with modified dielectric constant, low dielectric loss and small temperature dependence. The phase composition, dielectric properties, the chemical state of Ti element and abundance of the constituent elements on the sample surface were characterized by X-ray diffraction (XRD), LCR meter method and X-ray photoelectron spectroscopy (XPS). The results show that this system is composed of two phases, i.e. $BaTi_4O_9$ and $BaPr_2Ti_4O_{12}$. The content of Ti^{3+} and Ti^{2+} decrease and that of oxygen element increases in the BPT system composites due to the addition of $BaTi_4O_9$ fibers, which greatly improve the dielectric properties of this system. BPT10 sample, which has 10% $BaTi_4O_9$ fibers, has the best dielectric properties in this system ($\varepsilon_r=64$, $tg\,\delta=1\times10^{-4}$, at 1 MHz), and might be a potential candidate for microwave dielectric ceramics.

Keywords: C. Dielectric properties; $BaTi_4O_9$ fibers; $BaTi_4O_9+BaPr_2Ti_4O_{12}$

1. Introduction

The rapid growth of mobile telecommunication systems created the need for a large variety of new microwave dielectric materials. In order to obtain the desired dielectric properties, the technique of mixing two low loss materials with positive and negative dielectric temperature coefficients, has become well known [1]. As one of possible choices, the microstructure and microwave dielectric properties of the $BaTi_4O_9$–$BaPr_2Ti_4O_{12}$ system were investigated [2,3]. The results show that this system is composed of two phases: $BaTi_4O_9$ and $BaPr_2Ti_4O_{12}$, with a modifiable dielectric constant, low dielectric loss and small temperature dependence, and in this case it is possible to predict the dielectric properties of the mixture from the dielectric properties of each component, and furthermore, the lattices of each phase are well matched at the interfaces, and which are considered to influence the dielectric properties of this system.

The dielectric properties of $0.64BaTi_4O_9$–$0.36BaPr_2Ti_4O_{12}$ are $\varepsilon_r=57$ and $Q=1890$ at 5 GHz, and they are moderate in this system.

This paper presents the study of the microstructure and dielectric properties of a new kind of dielectric ceramics—$BaTi_4O_9$(f)/($0.64BaTi_4O_9+0.36BaPr_2Ti_4O_{12}$) composites, and concludes that $BaTi_4O_9$ fibers in this system improve the dielectric properties of materials.

2. Specimen preparation and experimental procedure

Ceramic samples were prepared with high purity $BaTiO_3$, TiO_2, Pr_6O_{11}, and $BaTi_4O_9$ fibers of 20–30 μm long and 1–3 μm in diameter, which are prepared in our lab [4]. The compositions of the $BaTi_4O_9$(f)/($0.64BaTi_4O_9+0.36BaPr_2Ti_4O_{12}$) composites listed in Table 1 were investigated. The powder was weighed so as to agree with the composition of $0.64BaTi_4O_9+0.36BaPr_2Ti_4O_{12}$, mixed by a ball mill, dried and calcined at 1050 °C for 2 h. After addition of $BaTi_4O_9$ fibers, the mixture was pressed by cold isostatic pressing and sintered at 1300 °C in air for 2 h.

The bulk density was evaluated by Archimedes method with sintered samples. The phase identification of samples prepared in this way was characterized by X-ray diffraction (XRD) using Cu K_α radiation, and the chemical state and abundance of the constituent

* Corresponding author.

0272-8842/02/$22.00
PII: S0272-8842(02)00028-7

elements on the sample surface were studied by X-ray photoelectron spectroscopy (XPS), using a VG Scientific ESCALAB MarkII spectrometer equipped with two ultrahigh-vacuum (VHV) chambers. The pressure in the chambers during the experiments was about 10^{-7} Pa. Mg K_α X-ray photoelectron spectra were referenced to the C1s peak (Eb = 284.80 eV) resulting from the adventitious hydrocarbon (i.e. from the XPS instrument itself) present on the sample surface. The surface of samples was sputter-etched for 600 s using 5 KeV argon-ions at a beam current of 40 mA.

The measurements of dielectric constant and dielectric loss were made at 1 MHz using an HP4192A LCR meter. Silver paste was used as the electrode.

3. Results and discussion

Fig. 1 shows the XRD patterns of $BaTi_4O_9$(f)/($0.64BaTi_4O_9 + 0.36BaPr_2Ti_4O_{12}$) composites sintered at 1300 °C in air for 2 h. It is well known that in the BaO–TiO_2 system numerous phases, e.g. $BaTi_3O_7$, $Ba_4Ti_{13}O_{30}$, $BaTi_4O_9$, $Ba_2Ti_9O_{20}$, exist. Furthermore, various phases are also observed in the BaO–TiO_2–rare earth oxide system. Therefore, phase control is expected to be extremely difficult in such a system [3]. However, it is shown that this system is composed of two phases only. No peaks were observed except those for $BaTi_4O_9$ and $BaPr_2Ti_4O_{12}$.

The atomic percents of Pr, Ti, Ba and O on the surface of BPT00 and BPT20 samples, calculated from the corresponding photoelectron peak area sensitivity factor corrections are listed in Table 2. It can be seen that the oxygen content in deep layers increased, and the Ti and Pr content decreased with the addition of $BaTi_4O_9$ fibers.

Table 1
Composition of materials used for investigation

Material code	Composition
BPT00	($0.64BaTi_4O_9$–$0.36BaPr_2Ti_4O_{12}$)
BPT10	($0.64BaTi_4O_9$–$0.36BaPr_2Ti_4O_{12}$) + 10vol.% $BaTi_4O_9$ fibers
BPT20	($0.64BaTi_4O_9$–$0.36BaPr_2Ti_4O_{12}$) + 20vol.% $BaTi_4O_9$ fibers
BPT30	($0.64BaTi_4O_9$–$0.36BaPr_2Ti_4O_{12}$) + 30vol.% $BaTi_4O_9$ fibers
BPT40	($0.64BaTi_4O_9$–$0.36BaPr_2Ti_4O_{12}$) + 40vol.% $BaTi_4O_9$ fibers

Table 2
Composition of BPT00 and BPT20 samples according to XPS analysis (at %)

Samples	Ti	O	Ba	Pr
BPT00	27.16	58.56	10.11	4.17
BPT20	26.90	61.86	8.13	3.11

The high-resolution XPS spectra of the Ti2p taken at the depth of BPT00 and BPT20 samples after being sputtering for 600 s were shown in Fig. 2. The Ti2p region can be decomposed into several contributions

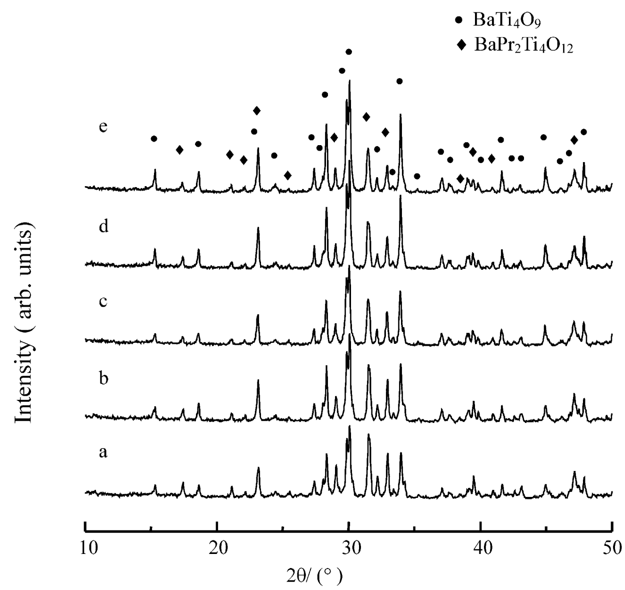

Fig. 1. X-ray diffraction patterns of the $BaTi_4O_9$(f)/$0.64BaTi_4O_9$–$0.36BaPr_2Ti_4O_{12}$ composites. (a) BPT00, (b) BPT10, (c) BPT20, (d) BPT30, (e) BPT40.

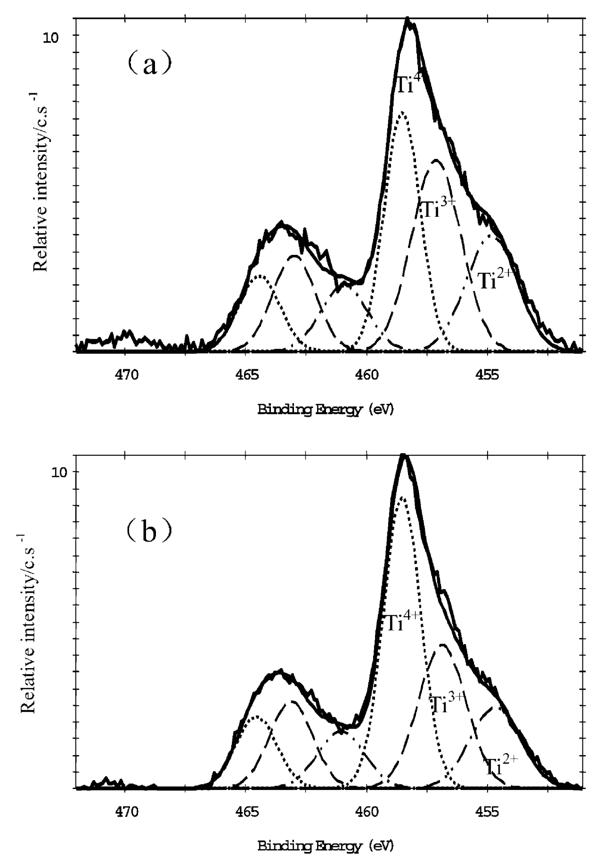

Fig. 2. XPS spectra of the Ti2p region for surface of the samples (a) BPT00 and (b) BPT20.

corresponding to different oxidation states of titanium. Each contribution consists of a doublet between $2p_{3/2}$ and $2p_{1/2}$ peaks. For the BPT00 sample, the Ti2p region can be decomposed into three contributions corresponding to +4, +3, +2 oxidation states of titanium. Two peaks situated at $Eb(Ti2p_{3/2})=458.48$ eV and $Eb(Ti2p_{1/2})=464.43$ eV, with peak positions corresponding to the 4+ oxidation state of Ti. The doublet of Ti^{3+} situated at $Eb(Ti2p_{3/2})=457.11$ eV and $Eb(Ti2p_{1/2})=463.06$ eV. The two symmetric peaks of the doublet of Ti^{2+} have the following binding energies Eb(Ti2p3/2) = 454.81 eV and $Eb(Ti2p_{1/2})=460.75$ eV. The relative contribution of these three components to the spectrum, as determined by fitting, is 35.92% (Ti^{4+}), 39.28% (Ti^{3+}), 24.80%(Ti^{2+}), respectively.

As shown in Fig. 2(b), after addition of 20% $BaTi_4O_9$ fibers, it was found that the spectrum at depth contained the doublet of Ti^{4+} as major feature. The peaks of Ti^{4+}doublet has the binding energies of $Eb(Ti2p_{3/2})=458.56$ eV and $Eb(Ti2p_{1/2})=464.51$ eV. The peaks of Ti^{3+}doublet has the binding energies of $Eb(Ti2p_{3/2})=457.17$ eV and $Eb(Ti2p_{1/2})=463.12$ eV. The peaks of Ti^{2+}doublet has the binding energies of $Eb(Ti2p_{3/2})=454.66$ eV and $Eb(Ti2p_{1/2})=460.61$ eV. The relative contribution of Ti^{4+}, Ti^{3+} and Ti^{2+} states are drastically modified, becoming 49.71% (Ti^{4+}), 31.41% (Ti^{3+}), 18.88% (Ti^{2+}), respectively.

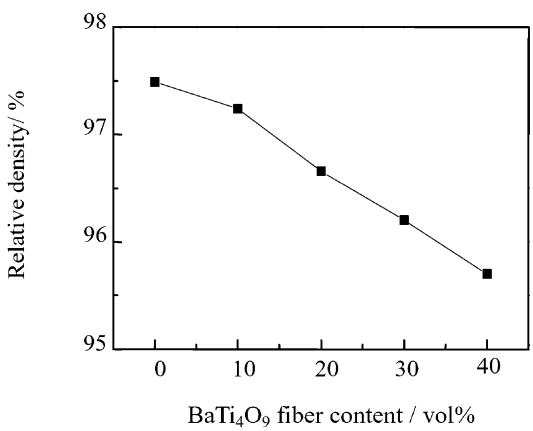

Fig. 3. Relative density of $BaTi_4O_9(f)/(0.64BaTi_4O_9-0.36BaPr_2Ti_4O_{12})$ composites as a function of $BaTi_4O_9$ fibers content.

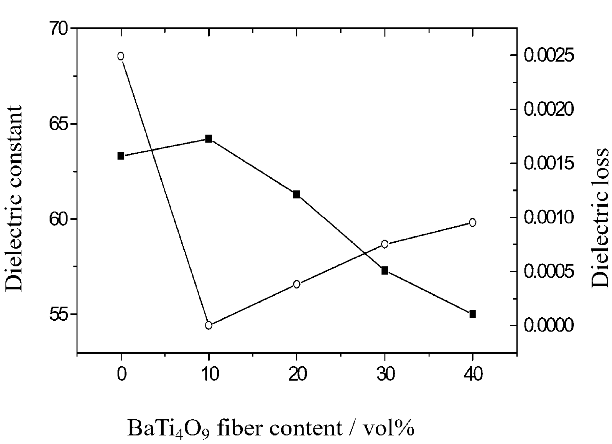

Fig. 4. Dielectric properties of $BaTi_4O_9(f)/(0.64BaTi_4O_9-0.36Ba$-$0.36BaPr_2Ti_4O_{12})$ composites as a function of $BaTi_4O_9$ fibers content at 1 MHz.

As generally observed in many titanates, high temperature sintering leads to the formation of Oxygen vacancies, which is accompanied by the formation of Ti^{3+} ions, due to the reduction caused by equilibrium with a low oxygen activity in air [5]. And the reduction of Ti^{4+} to Ti^{3+} gives rise to a severe degradation of dielectric properties [6]. However, the addition of $BaTi_4O_9$ fibers leads to the decrease of Ti^{3+} and Ti^{2+} and increase of the oxygen element, which greatly improve the dielectric properties of this system.

The variation of relative density of $BaTi_4O_9(f)/(0.64BaTi_4O_9+0.36BaPr_2Ti_4O_{12})$ composites sintered at 1300 °C with the addition of $BaTi_4O_9$ fibers is shown in Fig. 3. It is shown that the relative density decreases gradually with increasing $BaTi_4O_9$ fibers content.

Fig. 4 shows the variation of dielectric constant and dielectric loss of $BaTi_4O_9(f)/(0.64BaTi_4O_9+0.36$-$BaPr_2Ti_4O_{12})$ composites as function of $BaTi_4O_9$ fibers at 1 MHz. The dielectric constant for the BPT00 sample is 63, and that of this system decreases with the increasing of $BaTi_4O_9$ fibers except for BPT10 samples, which is due to the low ε_r value of $BaTi_4O_9$ fibers ($\varepsilon_r=39.9$ at 1 MHz). However, the values of dielectric constant of these system composites fail to fall on the calculated values deduced from the mixing relations of the two components.

On the other hand, the addition of $BaTi_4O_9$ fibers greatly decreases the dielectric loss, which is closely related to the relative density. As can be seen in Fig. 4, the normalized value of dielectric loss decreases with the increase of $BaTi_4O_9$ fibers content, and it reaches a minimum at 10%, and then increases gradually, which is due to the decreasing relative density. That is to say, the effect of $BaTi_4O_9$ fibers addition on dielectric loss is most significant in the BPT10 sample, which has $\varepsilon_r=64$, $tg\ \delta=1\times10^{-4}$ at 1 MHz.

4. Conclusions

$BaTi_4O_9(f)/(0.64BaTi_4O_9+0.36BaPr_2Ti_4O_{12})$ composites system is composed of two phases, i.e. $BaTi_4O_9$ and $BaPr_2Ti_4O_{12}$. The content of Ti^{3+} and Ti^{2+} decrease and that of oxygen element increases in the BPT system composites due to the addition of $BaTi_4O_9$ fibers, which make the dielectric properties of this system greatly improved. BPT10 sample, which has 10% $BaTi_4O_9$ fibers, has the best dielectric properties in this system, its $\varepsilon_r=64$, $tg\ \delta=1\times10^{-4}$ (at 1 MHz), which might be a potential candidate for microwave dielectric ceramics.

Acknowledgements

This work is partly supported by Grant-in-Aid for PhD to start their Scientific Research from Harbin Institute Technology, PR China.

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