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Effects of composition on low temperature sinterable Ba–Nd–Sm–Ti–O microwave dielectric materials

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Abstract

This work investigated the effects of MgO and ZnO additives on the microwave properties of $BRT_{114}=[(BaO{\cdot}R_2O_3{\cdot}4TiO_2){\cdot}0.06(2Bi_2O_3{\cdot}3TiO_2)]$ materials. Incorporation of small amount of ZnO (≦1 wt.%) markedly lowered the temperature coefficient of resonant frequency (τ_f), to around $\tau_f \fallingdotseq 1$ ppm/°C, slightly increased the density and dielectric constant (ε_r) of the materials, but degraded the $Q\times f$ factor . Doping 2.5 mol% of MgO, in addition to ZnO, further improved the τ_f -value for the BRT_{114} materials. The dielectric constant and the $Q\times f$ factor of the materials degrade pronouncedly when doped with too abundant ZnO. Microstructure and EDX analyses indicated that the main factor for degrading the microwave properties is the induction on formation of secondary phases. Moreover, sol–gel and fused Ba–B–Si glass reacted with BRT_{114} in quite a different way. Fused glass wets BRT_{114} materials more easily than the sol–gel derived glass, resulting in composite materials with higher density and larger dielectric constant. Precalcining the glass-dielectrics mixture, greatly improved the wetting ability of the glass and markedly increased the microwave properties of the glass/dielectric composite, i.e. LTCC materials.

Keywords: Fused glass; Glass/dielectric composite; LTCC materials; Sol–gel derived glass

1. Introduction

$BaO–R_2O_3–TiO_2$ series materials, where R is the rare earth element, possess superior microwave dielectric properties, such as high dielectric constant and high quality factor and low temperature coefficient of resonant frequency.[1–5] These materials have great potential for microwave device applications and have been extensively investigated. Processing of $BaO–Nd_2O_3–TiO_2$ series materials is very complicated due to the complex crystal structure of the materials, which easily induces the formation of intermediate phase. Iso-valent ions incorporation such as Sm_2O_3,- which form solid solution with the $BaO–R_2O_3–TiO_2$ materials, was observed to markedly modify the microwave dielectric properties of the materials.[3–5] The alivalent ions addition, such as Bi_2O_3, can also pronouncedly alter the material's properties.[6–8] The explanation on the corresponding mechanism is, however, still quite controversial. The investigation on the effect of additives, which modify the microstructure of the $BaO–R_2O_3–TiO_2$ series materials, is thus even more difficult.[9–11]

On the other hand, the trends for miniaturization of the microwave devices requires the development of low temperature cofirable ceramic (LTCC) materials. To lower the sintering temperature of the microwave dielectric materials to a level cofirable with Ag electrode materials, glass materials with low softening temperature were usually mixed with the microwave dielectric materials to form glass-ceramics composites.[12,13]

In this paper we develop a LTCC material consisting of $BaO–R_2O_3–TiO_2$ microwave dielectric materials and glass additives to result in high dielectric constant glass-ceramic composite materials. For the first, we improved the microwave dielectric properties of the $BaO{\cdot}(R_2O_3)_{1.08}{\cdot}(TiO_2)_{4.24}{\cdot}0.06(2Bi_2O_3{\cdot}3TiO_2)$ with $R=Nd_{0.72}Sm_{0.28}$, which were reported to possess the best microwave dielectric properties,[3–7] through the addition of MgO or ZnO species, among the $BaO–R_2O_3–TiO_2$ series materials. The MgO and ZnO additives were chosen because these dopants markedly improved the dielectric properties of other series of dielectric materials.[14,15] Then we used the $BaO–B_2O_3–SiO_2$ glass to reduce the sintering temperature necessary for densifying the materials.

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2. Experimental methods

The $BaO{\cdot}(R_2O_3)_{1.08}{\cdot}(TiO_2)_{4.24}{\cdot}0.06(2Bi_2O_3{\cdot}3TiO_2)$ with $R = Nd_{0.72}Sm_{0.28}$, designated as $(BRT)_{114}$, were prepared by conventional mixed oxide process. High purity materials, including $BaCO_3$ (Kali, 99.8%), TiO_2 (rutile, Bayor, 99.7%), $Nd_2(CO_3)_3$ (Rhodia, 99%), and Sm_2O_3 (Rhodia, 99.5%), with the nominal composition $BaO{\cdot}(R_2O_3)_{1.08}{\cdot}(TiO_2)_{4.24}{\cdot}0.06(2Bi_2O_3{\cdot}3TiO_2)$ where $R = Nd_{(0.72)}Sm_{(0.28)}$ were mixed and then calcined at 1170C for 2 h, followed by pulverization, pressing, and then sintering at 1330 °C for 2.5 h. In the first series of $(BRT)_{114}$, only ZnO with 0–3 wt.% was added. Whereas in the second series of $(BRT)_{114}$, 2.5 mol% MgO was doped in addition to the ZnO of the same proportion. In the preparation of LTCC materials, BRT_{114} (with median particle size of 1.0 μm) was mixed with sol-gel derived or fused $BaO–B_2O_3–SiO_2$ (51:45:4 wt.%) glass with median particle size of 1.5∼2 μm with different proportion (9–37.5wt.%). The glass–ceramic mixture were granulated, pelletized (500 kg/cm^2), and then sintered at 850–1000 °C for 2.5 h. These samples are designated as one-step processed ones. To facilitate the comparison, some of the glass–ceramic mixture was calcined at 700 °C for 2 h, followed by pulverization, granulation, pelletization and sintering process (designated as two-step process). The density of the sintered BRT_{114} materials was measured by the Archimedes method. The crystal structure and microstructure of the samples were examined using X-ray diffraction method (XRD, Simens D5000 diffractometer) and scanning electron microscopy (SEM, Hitach 2500-S with Kevex EDX). The microwave dielectric properties of the materials were measured by a cavity method using a HP 8722ES network analyzer.

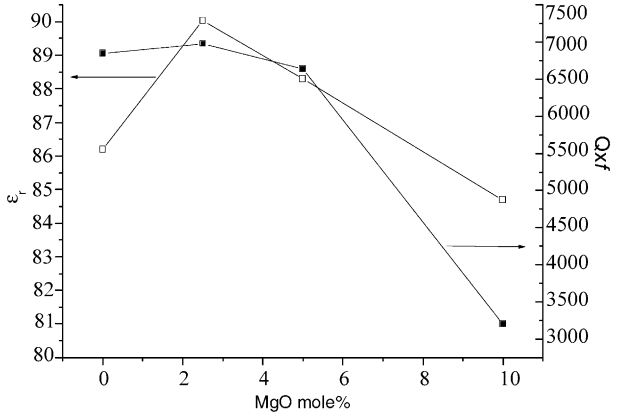

Fig. 1. Dielectric constant (ε_r) and Q×f versus MgO doping content for $(Ba_{1-x}Mg_x)O{\cdot}1.08(Nd_{0.72}Sm_{0.28})_2O_3{\cdot}4.24TiO_2{\cdot}0.6(Bi_2O_{3\cdot3}TiO_2)$, BRT114 materials.

3. Results and discussion

3.1. BRT_{114} dielectric ceramics

Incorporation of 2.5 mol% MgO into BRT_{114} materials markedly improved the sinterability of the materials, the sintered density increased from 92% T.D.(5.52 g/cm^3) to 96.5% T.D. (5.75 g/cm^3), when sintered at 1330 °C for 2.5 h [Fig. 2(a)]. SEM microstructure is not markedly changed due to the incorporation of a small proportion of MgO, but the number of pores seems greatly be depressed. (not shown). Addition of MgO beyond 2.5 mol% induced the formation of secondary phases, which monotonically degraded both the ε_r- and $Q{\times}f$-values (Fig. 1). Presumably, the Mg^{2+}-species can form solid solution when their concentration is smaller than 2.5 mol%.

For the BRT_{114} specimens including only ZnO additives [solid squares in Fig. 2(a)], the density of the samples increased markedly from 92% T.D. (5.52 g/cm^3) to 97% T.D (5.8 g/cm^3), when doped with 1 wt.% ZnO. The density decreased monotonously with further

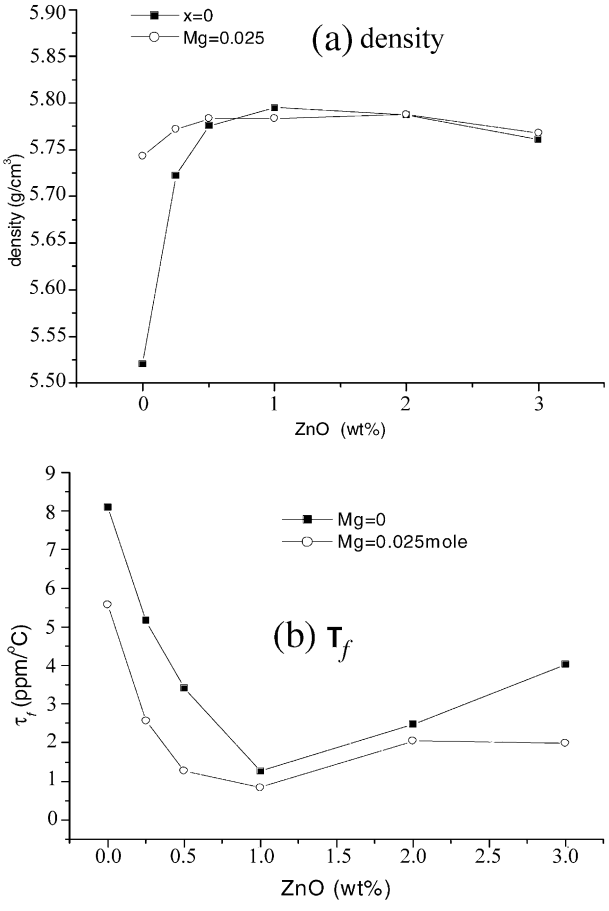

Fig. 2. The variation of microwave properties with amount of ZnO added into BRT_{114}: (a) density, and (b) temperature coefficient of resonant frequency, τ_f.

increase in ZnO-dopants larger than 1 *wt*.%. Similar behavior was observed for samples containing 2.5 mol% MgO [open circles, in Fig. 2(a)], that is, the density of MgO-doped BRT_{114} first increases with the ZnO content, reaches a maximum value of 96.8%T.D. (5.78 g/cm^3), and then decreases with further increase of ZnO addition.

Fig. 2(b) indicates the beneficial effect of MgO or ZnO addition on lowering the temperature coefficient of resonance frequency (τ_f) of BRT_{114} materials, a characteristic of concerned for the microwave device applications. For the materials containing no MgO additives, the value of τ_f reduces monotonously from 8 to 1.2 ppm/°C when the content of ZnO increases from 0 to 1.0 wt.% [solid squares in Fig. 2(b)]. The effect of ZnO addition on improving τ_f characteristic of BRT_{114} is even more pronounced when the specimen contains 2.5 mol% of MgO [open circles, in Fig. 2(b)]. A τ_f-value smaller than 0.8 ppm/°C was reached for the BRT_{114} co-doped with 2.5 mol% MgO, and 1 wt.% of ZnO. The τ_f-value increased again for materials containing more than 1 wt.% ZnO, regardless of whether the samples contain MgO species or not. Incorporation of a small proportion of ZnO (≦1 *wt*.%) to BRT_{114} materials, insignificantly alters their dielectric constant ($\varepsilon_r = 86$ to 89), but moderately reduces the $Q \times f$-value of the materials from $Q \times f = 7000$ to $Q \times f = 5000$ (not shown).

To understand how the addition of dopants affects the related microwave dielectric properties of BRT_{114} materials, the SEM microstruture was examined and is shown in Fig. 3, which reveals the secondary phases of equi-axis geometry emerged for the samples containing more than 1 wt.% of ZnO [Fig. 3(a) and (b)]. The other kind of secondary phase, stripe-shaped, emerged for those containing 2 *wt*.% of ZnO [Fig. 3(c)]. The EDX analyses reveal that the equi-axised phases contain low Sm Nd and are rich in Ti, but deficient in Zn element, whereas the stripe-shaped phase [cf. Fig. 3(c)] is a ZnO-rich intermediate compound. Apparently, the presence of these secondary phases is the main factor degrading the dielectric constant and $Q \times f$-value of the over-doped materials.

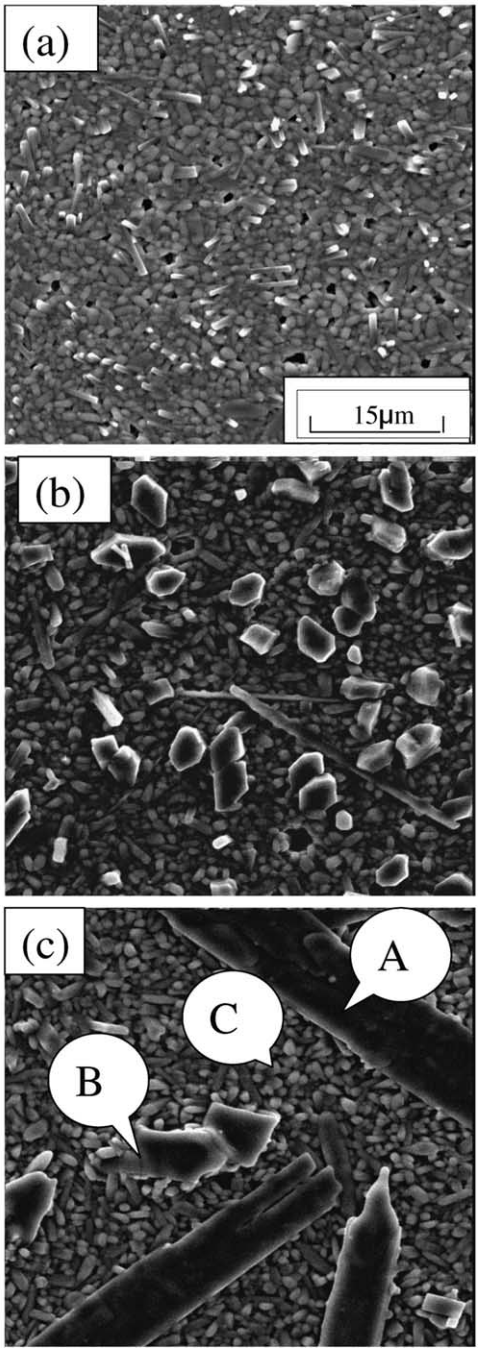

Fig. 3. The SEM micrographs for BRT_{114} with (a) 0.25 *wt*%, (b) 1 *wt*%, (c) 2 *wt*%, of ZnO additives.

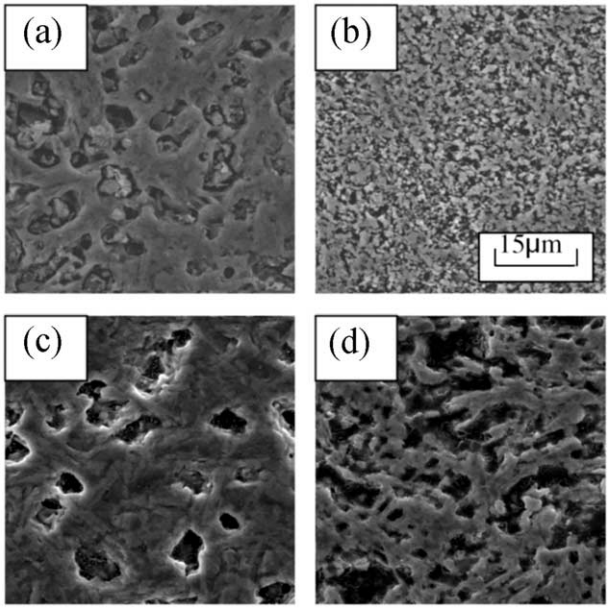

Fig. 4. The comparison of thermal etched SEM micrograph of samples, added with 33wt%, prepared by one-step process with (a) fused glass and (b) sol–gel derived glass; and by two-step process with (c) fused glass and (d) sol–gel derived glass.

3.2. Low temperature cofirable composite

To study the feasibility of using the composite of Ba–B–Si glass and BRT_{114} dielectrics as LTCC materials, pellets of these composite materials were prepared and their characteristic were investigated. It is observed that the nature of glass, sol–gel derived or fused, and the processing route for composite materials markedly influences the microwave properties and density of the materials even for materials containing same composition of glass and dielectrics.

Generally, sol–gel derived glass possesses much more inferior reactivity than the fused-glass, such that the corresponding composites show a markedly lower density and lower dielectric constant. Fig. 4(a) and (b) reveals that the feature size is smaller in sol–gel glass/dielectrics composite materials, inferring that the wettability of sol–gel derived glass is inferior to that of fused glass. Precalcining the glass/dielectric mixture profoundly improved the sinterability of the composite materials. The two-step processing increased the sintered density of fused glass/BRT_{114} Composite materials from 3.76 to 4.04 g/cm^3, when sintered at 950 °C, resulting in higher dielectric constant, ε_r increases from 12.4 to 13.4. In contrast, for the composite materials prepared from sol–gel derived glass, the precalcination insignificantly improved the characteristics of the samples. SEM micrographs shown in Fig. 4(c) and (d) indicate that the two-step process method increases the wettability of the glass pronouncedly, no matter whether the glass are fused or sol–gel derived.

4. Conclusions

This work investigated the effects of MgO and ZnO additives on the microwave properties and microstructure of $BRT_{114}=[(BaO{\cdot}Re_2O_3{\cdot}4TiO_2){\cdot}0.06(2Bi_2O_3{\cdot}3TiO_2)]$. Incorporation of small amount of ZnO pronouncedly improved the temperature coefficient of resonant frequency (τ_f), markedly increased the density and dielectric constant (ε_r), but degraded the $Q\times f$ factor for the BRT_{114} materials, no matter whether the materials contain MgO or not. Microstructure and EDX analyses indicated that the secondary phases, equi-axis or strip-like shape, were induced for materials containing too high concentration of ZnO.

Moreover, sol–gel derived and fused Ba–B–Si glass react with BRT_{114} in a different way, which results in marked characteristics for LTCC materials consisting of Ba–B–Si glass and BRT_{114} microwave dielectrics.

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