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Effect of nonstoichiometry on the microstructure and microwave dielectric properties of $Ba(Mg_{1/2}W_{1/2})O_3$ ceramics

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Abstract

Effects of nonstoichiometry on crystal structure and the microstructure of double perovskite $Ba(Mg_{1/2}W_{1/2})O_3$ ceramics have been investigated by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and Raman spectrometry in this paper. The microwave dielectric properties of the ceramics were studied with a network analyzer at the frequency of about 8–11 GHz. The results show that small deviation from stoichiometric composition has little influence on the crystal structure such as B-site 1:1 ordering degree. Evaporation of BaO was confirmed during the sintering of BMW ceramics, which in turn produce more $BaWO_4$ phase. Ba-deficiency or W-excess in BMW could improve the sinterability and $Q\times f$ value, while Ba-excess or W-deficiency could suppress the formation of $BaWO_4$ at the expense of increase in sintering temperature and decrease in $Q\times f$ value. Mg nonstoichiometry has little effect on the variation of $BaWO_4$ content and $Q\times f$ value. Maximum $Q\times f$ value of about 140,000 GHz could be obtained for the Ba-deficient or W-excessive samples after sintering at 1500 °C/2 h or 1550 °C/2 h, respectively. All Mg-nonstoichiometric compositions exhibit high $Q\times f$ value of about 120,000 GHz after sintering at 1550 °C/2 h. All well-densified samples have dielectric permittivity of about 19–20 and τ_f value varied within the range of $-21\sim-28$ ppm/°C.

Keywords: Double perovskite; Nonstoichiometry; Structure stability; Micowave dielectric properties

1. Introduction

It is well known that high cation ordering leads to large $Q\times f$ values of complex perovskite ceramics. $Ba(Mg_{1/2}W_{1/2})O_3$ (BMW) exhibits the double perovskite structure, in which the B site cations are 1:1 ordered due to their large difference in size and charge. In view of the high ordering degree, BMW is a promising candidate for high-Q dielectric ceramic, which has attracted many attentions [1–5]. Khalyavin et al. have studied the microstructure and microwave dielectric properties of $Ba(Me_{1/2}W_{1/2})O_3$ (Me = Mg, Ni, Zn) [2]. It was found that $Ba(Mg_{1/2}W_{1/2})O_3$ (BMW) double perovskite has dielectric properties of $\varepsilon_r=15$–17.6, $Q\times f=45{,}200-57{,}300$ GHz, $\tau_f=-25$ ppm/°C. $BaWO_4$ impurity phase appears at temperature > 1200 °C. Above its melting point of about 1475 °C [6], liquid phase is formed and remains at triple grained boundary junction as a sintering additive. Microwave dielectric properties of $\varepsilon_r=8.1$, $Q\times f=57{,}500$ (GHz), $\tau_f=-78$ ppm/°C has been reported for $BaWO_4$ by Yoon et al. [7]. Bian et al. [4] investigated the microwave dielectric properties of $A_{1-3x/2}Lax(Mg_{1/2}W_{1/2})O_3$ (A = Ba, Sr, Ca; $0.0\le x\le 0.05$), and found that small amount of La-substitution for A site cation could suppress the formation of AWO4 at high temperature. Small level of La-substitution for Ba ($x=0.02$) substantially improves the $Q\times f$ value to more than 100,000 GHz, however increases the sintering temperature to about 1600 °C simultaneously due to the lack of $BaWO_4$ liquid phase. In our previous paper [5], we studied the structure stability and microwave dielectric properties of Ca-doped BMW ($Ba_2Mg_{1-x}Ca_xWO_6$). The structure instability and decomposition of Ba_2MgWO_6 at high temperature are suggested to be caused by the large lattice strain energy due to the under-bonded Mg–O and over-bonded Ba–O bonds. This view is supposed be generalized to the instability of other complex perovskites such as $Ba(Zn_{1/2}W_{1/2})O_3$, $Ba(Zn_{1/3}Nb_{2/3})O_3$ and $Ba(Mg_{1/3}Ta_{2/3})O_3$, in which barium

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tungstate, barium niobate and barium tantalate could be easily formed at high temperature, respectively. Small amount of Ca-doping is also useful to the suppression of $BaWO_4$ formation due to the increase in Mg/Ca–O bond strength and decrease in Ba–O bond strength. However it still cannot completely suppress the decomposition of $Ba_2Mg_{1-x}Ca_xWO_6$ at the sintering temperature above 1400 °C. Excellent combined microwave dielectric properties with $\varepsilon_r=20.8$, $Q\times f=120{,}729$ GHz, and $\tau_f=0$ ppm/°C could be obtained by small level of Ca-doping ($x=0.1$). However the remained amorphous MgO and BaO, which accompanied with the appearnce of $BaWO_4$ in BMW ceramic, considerably decrease the $Q\times f$ value when the sample was stored under ambient conditions for a long time due to the hygroscopy of MgO and BaO in the air humidity [5]. Complete suppression of the decomposition of BMW during sintering is therefore of crucial importance for practical application.

The decomposition of Ba_2ZnWO_6 at high temperature is confirmed to be caused by the sublimation of ZnO due to its high partial pressure in air [8]. However, in the case of Ba_2MgWO_6, the vaporization of BaO rather than MgO should be expected due to its comparatively high vapor pressure at high temperature [9]. The possible vaporization of BaO would in turn facilitate the decomposition of Ba_2MgWO_6 and shift the bulk composition chemistries toward the WO_3-richer portion of the system, which would produce more secondary phases including $BaWO_4$ and MgO according to the mass balance equation. Therefore excessive BaO content is supposed to hinder the appearance of $BaWO_4$. For many barium based complex preovskites such as $Ba(Mg_{1/3}Ta_{2/3})O_3$, $BaZn_{1/3}Nb_{2/3}O_3$, it is has been reported that small deviations from its stoichiometric composition have pronounced effects on the phase constituent, sinterability, B-site cations ordering and microwave dielectric properties [10–13]. On the whole, small amount of A-site or B′-site deficiency around the stoichiometric composition usually improves the sinterability and ordering degree of B site cations, hence considerably increases the microwave quality factor. But over deficiency of A-site cation would result in the appearance of impurity phases such as barium niobates or barium tantalates, which leads to the decrease in $Q\times f$ value. Opposite effect is observed for the A-site or B′-site excessive compositions.

In this paper, therefore, we have investigated the effect of A, B′ and B″ site cation nonstoichiometry on the phase composition, microstructure and microwave dielectric properties of BMW.

2. Experimental

The samples of $Ba_{1+x}(MgW)_{1/2}O_3$ ($x=-0.015$, -0.010, -0.005, 0, 0.005, 0.010 and 0.015), $Ba(Mg_{1+y}W)_{1/2}O_3$ ($y=-0.02$, -0.01, 0, 0.01 and 0.02) and $Ba(MgW_{1+z})_{1/2}O_3$ ($z=-0.02$, -0.01, 0, 0.01 and 0.02) were prepared by a conventional solid-state reaction process from $BaCO_3$ (99.7%), MgO(99.7%), and WO_3(99.5%) starting materials. The starting materials were weighed according to the above formula and ball milled in ethanol with zirconia milling media for 24 h, then dried and calcined at 1200 °C for 2 h in

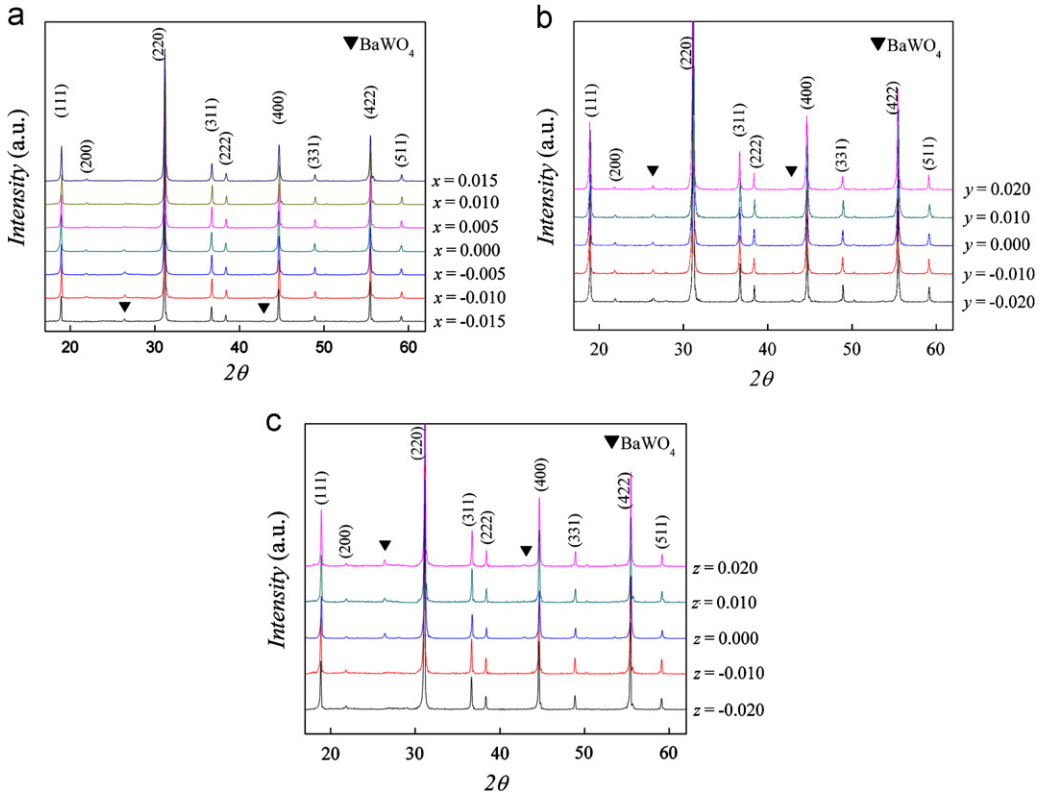

Fig. 1. Powder XRD patterns for (a) $Ba_{1+x}(MgW)_{1/2}O_3$, (b) $Ba(Mg_{1+y}W)_{1/2}O_3$ and (c) $Ba(MgW_{1+z})_{1/2}O_3$ sintered at 1500 °C/2 h.