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Anti-reduction 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

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Abstract

The anti-reduction of Ti^{4+} ions in $Ba_{4.2}Sm_{9.2}Ti_{18}O_{54}$ (BST) ceramics at high sintering temperature over 1300 °C was investigated. MgO, Al_2O_3 and MnO_2 were added separately to suppress the reduction of Ti^{4+} ions so as to improve the microwave dielectric properties of BST ceramics. The microstructure of BST ceramics was analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). X-ray photoelectron spectroscopy (XPS) was used to study the electroconductivity of BST ceramics and valency changes of Ti ions. The results showed that MgO or Al_2O_3, when acting as an acceptor, could effectively suppress the reduction of Ti^{4+} ions and significantly improve the $Q \times f$ values of BST ceramics at the cost of dielectric constant. Meanwhile, MnO_2 as an oxidant had also improved the $Q \times f$ values but with no decrease in dielectric constant. Excellent microwave dielectric properties were achieved in $Ba_{4.2}Sm_{9.2}Ti_{18}O_{54}$ ceramics doped with 0.2 wt.% Al_2O_3 sintered at 1340 °C for 3 h: $\varepsilon_r = 76.9$, $Q \times f = 10{,}120$ GHz and $\tau_f = -22.7$ ppm/°C.

Keywords: A. Sintering; C. Dielectric properties; D. Perovskite; Ceramics; Crystal structure

1. Introduction

The rapid progress of modern mobile phones and satellite communication systems has created a high demand for the miniaturization of microwave devices. Ceramics with high ε_r, high $Q \times f$ values and near-zero τ_f have been extensively used for miniaturizing the dimensions of the resonators and filters [1].

$Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = La, Pr, Nd, Sm) solid solution systems are recognized as an important series of high permittivity microwave dielectric ceramics with dielectric constant ranging from 80 to 130 [2,3]. $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ system, as a member in this family, exhibits $\varepsilon_r \approx 80$, $Q \times f \approx 8000$ GHz and $\tau_f \approx -8$ ppm/°C at $x = 0.6$ [4]. Researches on this solid solution are commonly focused on these aspects: (a) control the τ_f value to near zero [5–7]; (b) substitution of A or B site in tungsten bronze structure [8–10]; (c) low temperature sintering [11–13]. Nevertheless, little attention has been attached to the improvement on $Q \times f$ values, which is of vital importance to microwave devices.

As reported by Templeton and Pullar [14,15], titanium dioxide ceramics tend to deoxidize at high temperature above 1300 °C or with deficient oxygen supply during sintering. The deoxidized reaction undergoes as below:

$$TiO_2 \rightarrow TiO_{2-x} + x/2O_2 \uparrow \quad (1)$$

Oxygen vacancies appear and tend to catch electrons to form *F*-color centers. A dark hole appears in central part of the sample when these electrons are emitted by combining with Ti^{4+} ions near-by to form $[Ti^{4+}e^-]$, which drastically increases the dielectric loss of TiO_2 ceramics. Similar dark holes have also been found in BST ceramics, with an undesirable impact on microwave dielectric properties. Templeton and Wang [14] reported that improved $Q \times f$ values were attained by adding a divalent or trivalent acceptor ion that has approximately equal radius to that of Ti^{4+} into TiO_2 ceramic. Whether this is also true for BST ceramics or not still needs to be demonstrated. Doping with a transition metal oxide, functioning as an oxidant, such as MnO_2 for instance [15], can also prevent the

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reduction of Ti^{4+} as shown below:

$$Mn^{4+} + Ti^{3+} \rightarrow Mn^{3+} + Ti^{4+} \quad (2)$$

$$Mn^{3+} + Ti^{3++} \rightarrow Mn^{2+} + Ti^{4+} \quad (3)$$

In the present study, MgO, Al_2O_3, MnO_2 are added to $Ba_{4.2}Sm_{9.2}Ti_{18}O_{54}$ ceramics and the mechanism of anti-reduction of Ti^{4+} by acceptor-doping has been investigated.

2. Experimental procedure

$Ba_{4.2}Sm_{9.2}Ti_{18}O_{54}$ ceramics were prepared by conventional solid-state reaction method. The raw materials—$BaCO_3$ (99.9%), Sm_2O_3 (99.9%), and TiO_2 (99.9%) powders were weighed according to the desired stoichiometry of $Ba_{4.2}Sm_{9.2}Ti_{18}O_{54}$. The powders were ground in deionized water for 24 h with ZrO_2 balls. The mixture was dried at 120 °C, and then calcined at 1150 °C in air for 3 h [16]. The calcined powders were mixed with 0.2 wt.% MgO (99.9%), Al_2O_3 (99.9%) and MnO_2 (99.5%) separately. Afterwards the mixtures were milled for 24 h, dried at 120 °C and granulated with polyvinyl alcohol (PVA). The granules were preformed and then sintered at 1300–1380 °C in air for 3 h with a heating rate of 5 °C/min.

The crystalline phase was identified using 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 BST ceramics was examined by a Hitachi S-4800 field emission scanning electron microscope. An ESCAlab250 X-ray photoelectron spectroscopy was used to observe the variation of electroconductivity and valency in center and edge of sintered BST samples. The method developed by Hakki and Coleman [17] was used to measure the microwave dielectric properties of the polished pellets. The measurement frequencies range from 3 to 4 GHz. All the microwave measurements were used in the TE_{011} mode of an Agilent E8363A PNA series network analyzer. τ_f was tested in the temperature range from 20 to 80 °C and can be calculated by noting the change in resonant frequency as:

$$\tau_f = \frac{f_2 - f_1}{60 f_1} \quad (4)$$

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

3. Results and discussion

3.1. Crystalline phase

Fig. 1a shows the X-ray diffraction patterns of $Ba_{4.2}Sm_{9.2}Ti_{18}O_{54}$ ceramics doped with none, MgO, Al_2O_3 and MnO_2 sintered at 1340 °C for 3 h. Only a single $BaSm_2Ti_4O_{12}$ phase is identified for a small amount of addition. However, it is found in Fig. 1b that diffraction peaks of BST ceramics doped with Al_2O_3 shift slightly toward higher 2θ degree values, while those doped with MgO or MnO_2 are exactly the opposite. It can be deduced, according to Bragg's law, that doping with Al_2O_3 has decreased the lattice parameters, but MgO or MnO_2 have

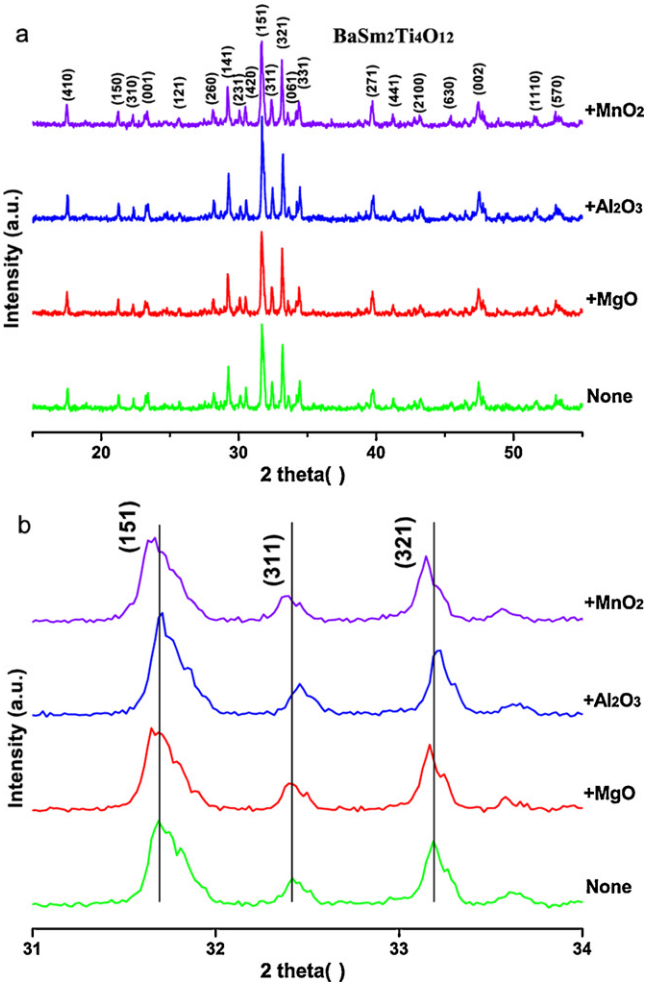

Fig. 1. Whole (a) and partial (b) X-ray diffraction patterns of $Ba_{4.2}Sm_{9.2}Ti_{18}O_{54}$ ceramics doped with none, MgO, Al_2O_3 and MnO_2 sintered at 1340 °C for 3 h.

expanded the lattice structure. The lattice parameters and volumes of BST ceramics shown in Table 1 are in accordance with what we deduced. We can infer from Table 2 that the lattice structure contracts only if the substitution of Ti^{4+} by Al^{3+} happens.

3.2. Density

Fig. 2 shows the density of $Ba_{4.2}Sm_{9.2}Ti_{18}O_{54}$ ceramics doped with none, MgO, Al_2O_3 and MnO_2 sintered at different temperatures for 3 h. The density of undoped BST ceramics increases with the increasing of the sintering temperature, and

Table 1
Lattice parameters of $Ba_{4.2}Sm_{9.2}Ti_{18}O_{54}$ ceramics doped with none, MgO, Al_2O_3 and MnO_2.

Sample	a/Å	b/Å	c/Å	V/Å^3
Undoped	22.295	22.322	22.280	22.317
+MgO	12.139	12.148	12.138	12.163
+Al_2O_3	3.828	3.830	3.826	3.832
+MnO_2	1036.10	1038.52	1034.62	1040.22