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Phase development in $Ba(Mg_{1/3}Ta_{2/3})O_3$ via conventional and B-site precursor routes

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Abstract

Phase-formation stages in $Ba(Mg_{1/3}Ta_{2/3})O_3$, prepared by conventional and B-site precursor methods, were investigated and the results are compared. Appropriate powder mixtures were heat-treated at selected temperatures and characterized by X-ray diffraction (XRD) in order to examine the phase development. In the conventional route, monophasic perovskite, finally resulted at high temperatures, had several preliminary intermediate phases, whereas in the B-site precursor method the perovskite formed directly from the reactants. The perovskite formation using B-site precursors was completed at significantly lower temperatures.

Keywords: A. Powders: solid-state reaction; B. X-ray methods; Ceramics; Perovskite oxides

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1. Introduction

Complex perovskite $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) is the barium-analog of a relaxor lead magnesium tantalate $Pb(Mg_{1/3}Ta_{2/3})O_3$ (PMT). BMT has been used for telecommunication resonator/filter components, which operate in microwave-frequency range. This is due to the excellent properties of the high dielectric loss quality as well as the small temperature coefficient of resonant frequency [1–3]. The cations of Mg and Ta in BMT developed a long-range structural ordering of 1:2 ratio in the octahedral lattice sites [3–7]. In addition, the degree of ordering increased with increasing annealing time [3,6,8–10].

The opinion about reaction routes of BMT during heat treatment in that the single-phase perovskite formed directly from $BaCO_3$, MgO, and Ta_2O_5 without any intermediate phases are somewhat controversial [9]. The opposite inhibition of the perovskite formation by the development of intermediate phases was also reported [11,12], even though it started from the same species of reactants. Therefore, the formation stages of perovskite BMT were investigated in the present study in order to clarify the argument regarding phase development. A two-step B-site precursor method was additionally attempted to allow for comparisons between the two different synthesis routes, especially in terms of perovskite formation.

The B-site precursor method [13,14], also called the columbite process [15,16], has been widely adopted in $A(B',B'')O_3$ compositions to enhance perovskite-formation yields. In this method, the constituent components of $B'O$ and $B''O$ reacted separately to form B-site precursor complexes. This was followed by further reactions of the product with the A-site component for perovskite development. Chances of formation of the parasitic pyrochlore phase(s) could, therefore, be effectively suppressed by bypassing the direct reaction route between AO and $B''O$, especially when the A and B'' cations are Pb and Ta/Nb, respectively. Successful results have been reported so far in many compositions, including $Pb(Mg_{1/3}Ta_{2/3})O_3$ [17,18] and $Pb(Mg_{1/3}Nb_{2/3})O_3$ [14–16,19,20].

2. Experimental

Starting materials were $BaCO_3$, MgO, and Ta_2O_5, each with a chemical purity ~99.9% level. During powder preparation, stoichiometric amounts of constituent chemicals were used without any addition of excess amount, which was frequently practiced in the cases of the Pb-based relaxor compositions [15,16,21–24].

Reaction routes of the conventional (one-step calcination of the constituent components) and the B-site precursor methods

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are as follows:

$$BaCO_3 + \tfrac{1}{3}MgO + \tfrac{1}{3}Ta_2O_5 \rightarrow Ba(Mg_{1/3}Ta_{2/3})O_3 + CO_2 \text{ (Process I)} \quad (1)$$

and

$$BaCO_3 + \tfrac{1}{3}MgTa_2O_6 \rightarrow Ba(Mg_{1/3}Ta_{2/3})O_3 + CO_2 \text{ (Process II).} \quad (2)$$

Powder mixtures of the three constituent components in proportionate amounts of Process I, Eq. (1), were wet-milled for 12 h using ZrO_2 media under alcohol in polyethylene containers in order to achieve intimate mixing. After drying for 24 h, the milled powders were heated to selected temperatures (heating rate = 300 °C/h), where they were kept for 2 h, followed by natural cooling. The investigated temperature range was 800–1300 °C in 50 °C increments. The reaction products were then examined by powder XRD in order to identify the formed phases. Similar studies were also carried out for Process II, Eq. (2), in the same temperature range. The B-site precursor $MgTa_2O_6$ powders were prepared separately from equimolar mixtures of MgO and Ta_2O_5 by calcination for 2 h at 1250 °C [17,18].

3. Results and discussion

XRD results of Processes I and II (conventional and B-site precursor routes, respectively) are presented in Figs. 1(a) and 2(a), respectively, as a function of heat treatment temperatures. Relative fractions of the phases were determined semi-quantitatively by comparing the integrated intensity levels of the major X-ray peaks and the results are plotted in Figs. 1(b) and 2(b). The results in Process I were found complicated, where $BaCO_3$ and MgO seemed to compete strongly for a chemical reaction with Ta_2O_5, thus resulting in coexistence of the starting materials as well as the newly developed phases of $Ba_5Ta_4O_{15}$ (B_5T_2, ICDD No. 72–631), $Ba_4Ta_2O_9$ (B_4T, ICDD No. 49-904), $MgTa_2O_6$ (MT, ICDD No. 32-631), and perovskite BMT (ICDD Nos. 82-371/87-1733) at 800 °C. With increasing temperatures, MT and the two species of the starting materials disappeared immediately, whereas B_5T_2 and B_4T reached a maximum intensity at 900 and 950 °C, respectively, followed by gradual disappearances. Phase fractions of the perovskite then increased rapidly with a further slow increasing with temperature and reached full extents at ≥1200 °C. Such step forming of several intermediate phases before the completion of the perovskite at high temperature is similar to reported literature [11,12]. Meanwhile, the direct formation of perovskite BMT from raw materials (i.e., without any intermediate phases) in an identical conventional route has

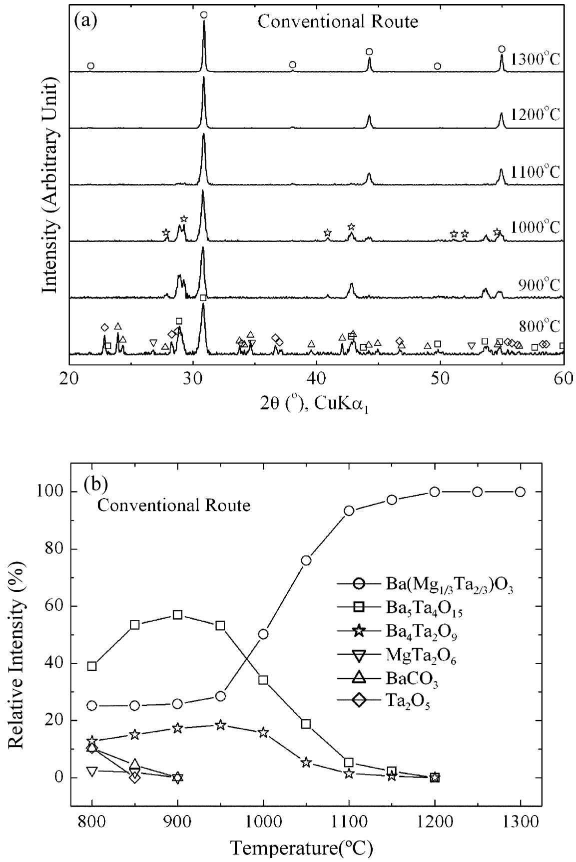

Fig. 1. X-ray diffraction patterns (a) and relative fractions of the developed phases (b) in $BaCO_3$ + 1/3MgO + 1/3Ta_2O_5 (Process I). (a): (△) $BaCO_3$; (◇) Ta_2O_5; (▽) $MgTa_2O_6$; (□) $Ba_5Ta_4O_{15}$; (☆) $Ba_4Ta_2O_9$; (○) $Ba(Mg_{1/3}Ta_{2/3})O_3$.

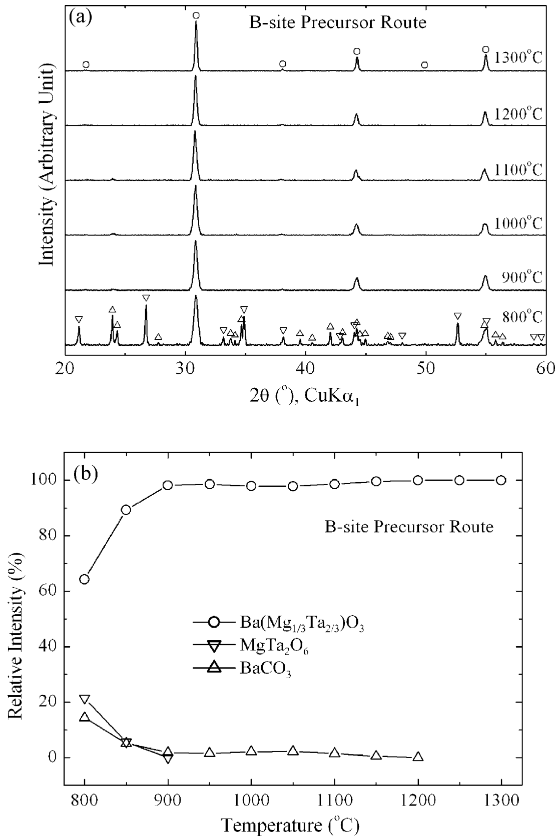

Fig. 2. X-ray diffraction patterns (a) and relative fractions of the developed phases (b) in $BaCO_3$ + 1/3$MgTa_2O_6$ (Process II). (a): (△) $BaCO_3$; (▽) $MgTa_2O_6$; (○) $Ba(Mg_{1/3}Ta_{2/3})O_3$.

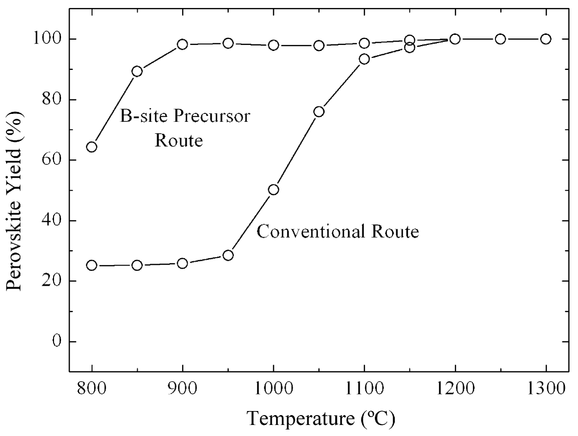

Fig. 3. Comparison of perovskite fractions prepared using two processes.

also been reported [9]. This is somewhat doubtful, because at least one B_5T_2 phase can be identified by X-ray.

By contrast, the results of Process II were less complex and the perovskite phase was developed directly from $BaCO_3$ and B-site precursor $MgTa_2O_6$, which is similar to the direct formation of perovskite PMT from PbO and $MgTa_2O_6$ [25]. Formation of the perovskite was almost completed (perovskite fraction >98%) as low as 900 °C. Meanwhile, the X-ray peaks of $BaCO_3$ in Process II survived up to relatively high temperatures, higher than in Process I. The reason of it is not clear.

The results of phase development in the present study are quite similar to those of previous reports in that, the formation of intermediate phases inhibited perovskite development up to 1400 °C (Process I [11,12]), whereas a utilization of the alternate route (Process II) produced nearly phase-pure perovskite after heat treatment at 1000 °C [12]. Moreover, the major intermediate phases were identical to those reported in the literature [12], but the species were slightly different in another [11]. However, in the present study, the perovskite formation temperatures were lower by 200 and 100 °C in the two processes. The 1:2 structural ordering between Mg and Ta in the octahedral lattice sites could not be observed in Figs. 1(a) and 2(a). This seems to be related with too short time of heat treatment (2 h), as longer time is needed to develop the ordering.

Temperature-dependent fractions of the perovskite in the two processes are replotted in Fig. 3. The final results are basically identical, regardless of the presence of intermediate stages. The observed difference is that the formation temperature was significantly lower in Process II, as much as 300 °C. Hence, in the present study, we also supported the effectiveness of the B-site precursor method over the conventional one-step calcination in the preparation of complex-perovskite powders.

4. Summary

In conventional route, the development of perovskite $Ba(Mg_{1/3}Ta_{2/3})O_3$ was completed by several intermediate phases of $MgTa_2O_6$ as well as $Ba_5Ta_4O_{15}$ and $Ba_4Ta_2O_9$. In contrast, by B-site precursor route, the perovskite development was directly from the raw materials of $BaCO_3$ and $MgTa_2O_6$ without any observed intermediate phases. In addition, phase formation in the B-site precursor route was completed at 900 °C, which is significantly lower than corresponding temperatures of 1200 °C in the conventional route.

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