Available online at www.sciencedirect.com
ScienceDirect
Materials Research Bulletin 43 (2008) 730–734
Materials Research Bulletin
www.elsevier.com/locate/matresbu

Crystallographic and dielectric properties of barium-substituted $Pb(Mg_{1/3}Ta_{2/3})O_3$ ceramics

Tai-Kwang Park, Jee-Su Kim, Nam-Kyoung Kim *

Department of Inorganic Materials Engineering, Kyungpook National University, Daegu 702-701, Republic of Korea

Received 17 January 2007; received in revised form 2 March 2007; accepted 26 March 2007
Available online 30 March 2007

Abstract

Ceramic powders of $(Ba,Pb)Pb(Mg_{1/3}Ta_{2/3})O_3$ were prepared via a B-site precursor route. Crystal symmetries and lattice parameters were determined. Monophasic perovskite was developed after the two-step reaction process, in which the lattice parameters showed linear changes in the entire composition range. Dielectric responses of the ceramics with compositional and frequency changes were investigated. The results were also compared with the $(Ba,Pb)(Zn_{1/3}Ta_{2/3})O_3$ data.

Keywords: A. Ceramics; A. Oxides; C. X-ray diffraction; B. Dielectric properties

1. Introduction

Lead magnesium tantalate $Pb(Mg_{1/3}Ta_{2/3})O_3$ (PMT) is one of the earliest-known ferroelectric compounds of complex-perovskite stoichiometry [1–4]. Maximum dielectric constant values of PMT are substantially high (≤9000, 1 kHz) at −98 to −77 °C. In addition, the dielectric constant peaks were rather broad and exhibited frequency-dependent relaxation. Lead magnesium niobate $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), a niobium-analog of PMT, is also a well-known complex perovskite [2,3,5,6]. Maximum dielectric constant values of PMN are even higher (≤20,000) at slightly below room temperature.

When compared with PMN, PMT has been studied much less so far, due probably to the lower dielectric constant values as well as to the dielectric maximum temperatures that are too low for commercial applications. As barium is capable of replacing lead in $Pb(Mg_{1/3}Nb_{2/3})O_3$ at all ratios [7] while maintaining a perovskite structure, a similar substitution to $Pb(Mg_{1/3}Ta_{2/3})O_3$ can also be expected. In the present study, therefore, effects of Ba substitution for Pb in PMT on phase development and dielectric responses were investigated.

Ceramic powders were prepared by a B-site precursor method [8,9], which is conceptually identical to (but more comprehensive than) the columbite process [10,11]. The method has been proven to be highly effective in the preparation of complex-perovskite $(Pb/Ba)(B',B'')O_3$ powders with minimal fractions of parasitic pyrochlore, especially when the B'' cations are Nb and/or Ta [9,12].

---

* Corresponding author. Tel.: +82 53 950 5636; fax: +82 53 950 5645.
E-mail address: nkkim@knu.ac.kr (N.-K. Kim).

0025-5408/$ – see front matter
doi:10.1016/j.materresbull.2007.03.026

2. Experimental

The pseudobinary yBa($Mg_{1/3}Ta_{2/3}$)O_3-(1−y)Pb($Mg_{1/3}Ta_{2/3}$)O_3 system under investigation can be written as a solid solution form of (Ba_yPb_{1-y})($Mg_{1/3}Ta_{2/3}$)O_3 (BPMT in short hereafter), where the values of y were selected from 0.0 to 1.0 at regular intervals of 0.2. The starting materials were high-purity chemicals of $BaCO_3$ (99.9%), PbO (99.5%), MgO (99.9%), and Ta_2O_5 (99.9%). Moisture contents of the raw materials and of the synthesized precursor powders were measured and introduced into the batch calculations in order to maintain the stoichiometries as close to the nominal values as possible.

B-site precursor powders of $MgTa_2O_6$ were prepared from constituent chemicals by wet-milling under alcohol (ZrO_2 media), drying, and calcining at 1200 °C for 2 h in air [13]. The resultant products were wet-milled, dried, and calcined one more time under identical conditions to promote phase formation. $BaCO_3$ and PbO were added to the precursor powders in appropriate proportions, i.e. without any excess amount. The mixed batches were wet-milled, dried, and calcined at 850 °C ($y = 0.0$–0.8) and 1250 °C ($y = 1.0$) for 2 h, followed by additional calcination at 900 °C for $y = 0.0$–0.8. The powders thus prepared were examined by X-ray diffraction (XRD) to identify the phases formed.

The BPMT powders, with polyvinyl alcohol added as binder (2 wt.% aqueous solution), were isostatically pressed into pellet form. The powder compacts were fired at 1300–1650 °C for 1 h in a multiple-enclosure inverted-crucible setup to suppress PbO loss. Sintered pellets were ground and polished to achieve parallel surfaces, over which gold was sputtered for electrical measurements. Weak-field low-frequency dielectric constant and loss values were measured upon cooling using an impedance analyzer (HP4194A).

3. Results and discussion

X-ray patterns of the prepared B-site precursor powders after the first and second calcination are compared with a reported profile of $MgTa_2O_6$ (trirutile structure, ICDD No. 32-631) in Fig. 1. $MgTa_2O_6$ was formed at first stage, but the formation was not complete. Hence, the second calcination stage was adopted, by which the positions as well as intensities of the peaks matched quite satisfactorily to those of the reported data, verifying that the synthesized powders for the next step were virtually monophasic $MgTa_2O_6$.

X-ray diffraction profiles of the BPMT powders (after calcination) are contrasted in Fig. 2(a). All of the patterns can be interpreted to be phase-pure perovskite with a (pseudo)cubic symmetry, except for a negligible fraction of coexisting pyrochlore phase at $y = 0.0$. Even though perovskite was still virtually the sole phase present after the sintering process, as shown in Fig. 2(b), three major differences were apparent: (1) narrower peaks with reduced widths, (2) disappearance of the parasitic pyrochlore at $y = 0.0$, and (3) developments of $Ba_{0.5}TaO_3$ (ICDD No. 17-793) and perovskite superlattice at $y = 0.8$. The first point of reduced peak widths indicates improved crystallinity, which resulted from exposure to higher temperatures during sintering. The second and third ones of pyrochlore

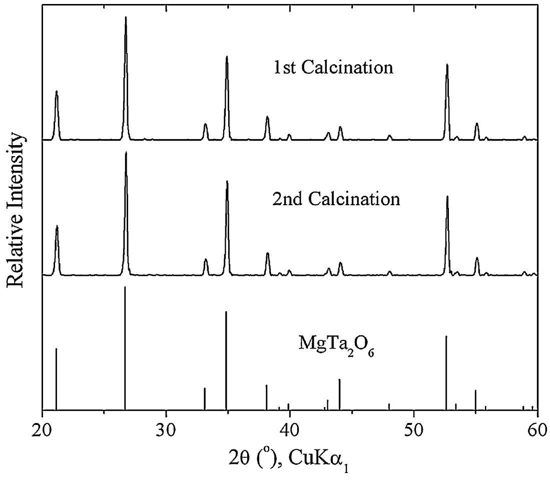

Fig. 1. X-ray diffraction results of the precursor powder after the first and second calcination with a reported profile of $MgTa_2O_6$.