Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of the European Ceramic Society 25 (2005) 3451–3457
www.elsevier.com/locate/jeurceramsoc

Microwave frequency dielectric properties of hexagonal perovskites in the $Ba_5Ta_4O_{15}$–$BaTiO_3$ system

A.N. Baranov, Young-Jei Oh*

Materials Science and Technology Division, Korea Institute of Science and Technology, Seoul 136-791, South Korea

Received 9 September 2003; received in revised form 16 August 2004; accepted 27 August 2004
Available online 28 October 2004

Abstract

The dielectric properties of the hexagonal perovskites $Ba_8Ta_{4+0.8x}Ti_{3-x}O_{24}$ ($x = 0$, 0.4, and 0.8), $Ba_{10}Ta_{8-0.8x}Ti_xO_{30}$ ($x = 0.6$, 0.9, and 1.2) and $Ba_5Sr_2Ta_4ZrO_{21}$ were studied at microwave frequencies. XRD analysis did not reveal the presence of impurity phases in the obtained samples and the lattice parameters of solid solutions were linearly dependent on composition. These systems show a relatively high permittivity ($27 < \varepsilon < 44$) with a low dielectric loss ($10{,}000 < Q \times f < 31{,}000$ GHz). Solid solutions $Ba_{10}Ta_{8-0.8x}Ti_xO_{30}$ with disordered face-sharing octahedra show higher $Q \times f$ values compared to ordered $Ba_8Ta_{4+0.8x}Ti_{3-x}O_{24}$ compounds. Filling of empty vacancy layers by multicharged cations in the $Ba_5(Ta, Ti)_{4+\delta}O_{15}$ system ($0 < \delta < 1$) along with $Ba_5Sr_2Ta_4ZrO_{21}$ intergrowth leads to decrease a quality factor. The effect of increasing Ti content in the pseudobinary $Ba_5Ta_4O_{15}$–$BaTiO_3$ system on microwave dielectric properties is discussed.

Keywords: Dielectric properties; Perovskites; Tantalates; $Ba_5Ta_4O_{15}$; $BaTiO_3$

1. Introduction

Development of microwave ceramics with a high dielectric constant (ε_r) and good thermal stability together with small dielectric losses in wide temperature and frequency ranges is a key problem in the application of such materials to microwave technology. A combined study of both the crystal structure and the electrophysical properties of new compounds and solid solutions is necessary for the development of new ceramic materials. The dielectric properties of oxides based on the cubic perovskite structure depended on chemical composition, crystal structure and methods of synthesis.[1] The highest Q values have been obtained in ceramics based on ABO_3 perovskite structure where Ta^{5+} cations occupy 2/3 of the B-positions with 1/3 of the positions occupied by Mg^{2+} or Zn^{2+} cation.[1,2] It has been recognized that Q could be enhanced by inducing cation ordering through prolonged sintering at high temperatures.[1,3]

However, there are few reports of the dielectric properties of B-site deficient hexagonal perovskites $AB_{1-x}O_3$ containing mixed cubic/hexagonal stacking sequences. These oxides crystallize as hexagonal perovskites and their crystal structure corresponds to close-packed stacking of AO_3 layers. Stacking sequences can be described using c and h notation where c means cubic stacking with different neighboring layers and h means hexagonal stacking with alike neighboring layers. Accordingly, two types of octahedra are present in these structures—face-sharing octahedra (FSO) and corner-sharing octahedra (CSO). The stability of such cation deficient structures strongly depends on the size and the formal charge of the B-site cations. The need for electroneutrality leads to the appearance of vacancies on the B-sites. For the $A_nB_{n-1}O_{3n}$ homologous series the vacancies are usually ordered between hh layers and structure can be described as alternation of completely filled B-cation layers separated by vacancy layers. This octahedral framework is known for its great ability to accommodate various structural modifications. This possibility is combined with the phenomenal range of catalytic, electronic and magnetic properties.

* Corresponding author. Tel.: +82 2 958 5553; fax: +82 2 958 6720.
E-mail address: youngjei@kist.re.kr (Y.-J. Oh).

0955-2219/$ – see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2004.09.010

The microwave dielectric properties of $A_5B_4O_{15}$ ceramics (A = Ba, Sr, Mg, Zn, Ca; B = Nb, Ta) have been determined.[4,5] The best $Q \times f$ values among these hexagonal compounds were obtained for $Ba_5Ta_4O_{15}$ and $Ba_5Nb_4O_{15}$.[6] Increase of $Q \times f$ values at substitution of A-site Ba^{2+} cations with Sr^{2+} in $(Ba_{5-x}Sr_x)Nb_4O_{15}$ has been studied.[7] It has been shown that the Ti-based $La_4Ba_2Ti_5O_{18}$ perovskite with similar hexagonal structure have a low dielectric loss ($Q \times f = 31{,}839$) and high permittivity ($\varepsilon_r = 46$).[8] Recently it was reported about high ($Q \times f = 62{,}000$) value of $Ba_8ZnTa_6O_{24}$ hexagonal perovskite.[9] This compound is isostructural to the $Ba_8ZnTa_6O_{24}$ hexagonal perovskite with eight-layer $(cchc)_2$ close-packed arrangement of BaO_3 layers.[10]

In the $Ba_5Ta_4O_{15}$–$BaTiO_3$ system two types of solid solution—$Ba_8Ta_{4+0.8x}Ti_{3-x}O_{24}$ and $Ba_{10}Ta_{8-0.8x}Ti_xO_{30}$ have been detected. These solid solutions have two types of FSO with different occupancies of the vacancy layer by Ta atoms, Ti atoms and vacancies, which result in formation of a superstructure. In the $Ba_{10}Ta_{8-0.8x}Ti_xO_{30}$ structures FSO also occur in a disordered fashion and in the $Ba_8Ta_{4+0.8x}Ti_{3-x}O_{24}$ structure in an ordered fashion.[11] Compounds in the $Ba_5Ta_4O_{15}$–$BaZrO_3$ system also form intergrowth structures with alternating $Ba_5Ta_4O_{15}$-type and $BaZrO_3$-type structural blocks.[12] These $Ba_5Ta_4O_{15}$–$BaTiO_3$ (BTT) systems are of interest as model systems for the study of microwave dielectric properties of B-site substituted hexagonal perovskites with varying types of order.

In this paper microwave dielectric properties of $Ba_8Ta_{4+0.8x}Ti_{3-x}O_{24}$ ($x = 0$, 0.4, and 0.8) and $Ba_{10}Ta_{8-0.8x}Ti_xO_{30}$ ($x = 0.6$, 0.9, and 1.2) solid solutions of hexagonal perovskites and $Ba_5Sr_2Ta_4ZrO_{21}$ composition, were investigated. The influence of substitution of Ta^{5+} by Ti^{4+} in the $Ba_5Ta_4O_{15}$ "parent" compound in the pseudobinary $Ba_5Ta_4O_{15}$–$BaTiO_3$ system on microwave dielectric properties is discussed.

2. Experimental procedures

All studied samples were prepared by a solid-state synthesis technique using $BaCO_3$, Ta_2O_5 and TiO_2 as initial reagents. Stoichiometric amounts of the powders were ball milled using zirconia balls in plastic containers for 24 h in deionized water. The pelletized samples were preheated to 1000 °C for 40 h. The calcined tablets were crushed, ball milled again, mixed with 2 drops of 5 wt.% solution of polyvinylalcohol (PVA) as binder, and uniaxially pressed in cylindrical disks with 10 mm diameter and 7 mm height under pressure of 200 MPa. The samples were fired 40 h at 1400 °C on air with two intermediate exposures during heating for 1 and 2 h at 350 and 1000 °C, respectively, for removing the binder and traces of barium carbonates. The sintered samples were well polished and their bulk density was measured using Archimedes method. The morphology of the samples was examined by scanning electron microscopy (FE-SEM; Hitachi S-4200 SEM). The decomposition of the precursor powders was studied by thermal gravimetric analysis (TGA) on air in platinum crucible using thermogravimetric analyzer (Universal V1.8M TA Instruments). The crystal structure and phase purity of the samples were studied by X-ray diffraction techniques. X-ray powder diffraction (XRD) data of the synthesized samples were collected by a Rigaku RINT DMAX 2500 diffractometer (Cu Kα radiation). All peaks for the composition #1–3 match with $Ba_8Ta_4Ti_3O_{24}$ compound (S.G. $P6_3/mmc$ (194); JCPDS card 44-0264) and for composition #4–6 with $Ba_{10}Ta_{7.04}Ti_{1.2}O_{30}$ compound (S.G. $P6_3/mmc$ (194); JCPDS card 44-0561). The lattice parameters of the samples were calculated by the least-square fitting method (Table 1). Specimens were examined using a PHILLIPS CM30 TEM operated at 200 kV. Thin foils for TEM were prepared by the conventional technique of slicing the annealed samples using a diamond saw, ultrasonic cutting to discs of 3 mm in diameter, mechanical polishing using SiC grits, dimple grinding (Gatan Dimple grinder) and

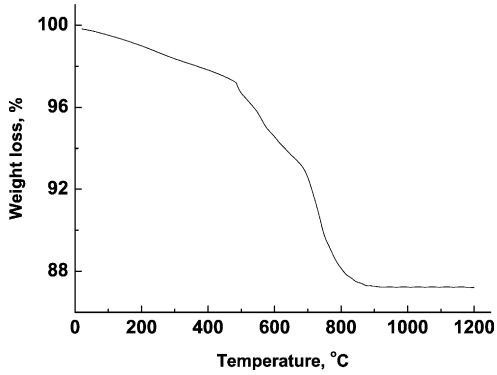

Fig. 1. TGA curve of the ball-milled precursor—mixture of $BaCO_3$, Ta_2O_5 and TiO_2 with 5% PVA binder (composition #1).

Table 1
Lattice parameters of BTT samples calculated from XRD diffractograms

Sample no.	Composition	x	a (Å)	c (Å)	a (Å) (Ref. 11)	c (Å) (Ref. 11)
1	$Ba_8Ta_{4+0.8x}Ti_{3-x}O_{24}$	0	5.7882	18.833	5.7913(1)	18.8710(7)
2		0.4	5.7942	18.879		
3		0.8	5.8033	18.898	5.8038(9)	18.912(5)
4	$Ba_{10}Ta_{8-0.8x}Ti_xO_{30}$	1.2	5.7965	23.767	5.7966(1)	23.7482(7)
5		0.9	5.8008	23.802		
6		0.6	5.8027	23.817	5.8056(5)	23.860(3)