Transactions of the Materials Research Society of Japan. Vol. 20

Temperature and Pressure Dependencies of Microwave Dielectric Properties of a System $(Ba_{1-x}Ca_x)(Mg_{1/3}Ta_{2/3})O_3$

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Well sintered ceramics of the nominal title composition were prepared to measure microwave dielectric properties. They were characterized to have two solubility limits at x=0.25 and x=0.9. ε_r increased markedly from 25 of $Ba(Mg_{1/3}Ta_{2/3})O_3$ to 35.5 to take a peak at the first solubility limit. The temperature coefficients of resonance frequency exhibited a similar composition dependence with that of ε_r. However, $f \cdot Q$ showed a different dependence from those of ε_r and TCf. The pressure dependencies of capacities of $Ba(Mg_{1/3}Ta_{2/3})O_3$ were measured smaller than those of rutile and $SrTiO_3$.

1. INTRODUCTION

Paraelectric properties of perovskite oxides change by partial substitutions of there A-site ions by another ions. Are there simple rules for the substitutions to predict changes in paraelectric properties — relative permittivity, dielectric loss, and those changes with temperature? This inquiry is a motivation of the foregoing [1] and this studies by setting aside examining those absolute values of mother compounds. This is an interim report to accumulate data to discuss that simple rule.

2. EXPERIMENTAL

The nominal composition of the system studied was $(Ba_{1-x}Ca_x)(Mg_{1/3}Ta_{2/3})O_3$. Guaranteed grade reagents were used to prepare specimens according to a normal ceramic processing. A micro pulverizer (Fritsch, P-5), setting 80 ml pots made of partially stabilized zirconia, was used before and after calcinations. The shaped powder was CIPed under 196 MPa. Disks about 8 mm in diameter with length 1 mm or 4 mm were made by sintering in air at 1600℃ for 5 h followed by cooling at 270℃/h rate. Specimens were characterized by XRD(Rigaku, RINT2500 VHF) with Cu$K\alpha$ radiation, TEM

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(JEM, 2000EX), SEM, and density by an Archimedes method. Silicon was added as an internal standard to correct from 15 to 20 diffraction angles which were used to calculate lattice constants.

The two faces of a disk were carefully polished to be parallel by using a cylinder tool. The microwave dielectric properties were measured by means of the Hakki-Coleman [2] and Kobayashi [3] method on the TE_{011} mode at about 10 GHz. A network analyzer (HP, 8722C) system was used to calculate by a program SU2-RODTE01 Ver.2 [3]. More than three disks with a length of 4 mm were measured at temperatures from 20 to 80 ℃. A piston/cylinder high pressure apparatus (Sugino Machine, HPV-150C4) filled with a silicone oil was used to measure capacities up to 1.5 GPa at 20 and 80℃. A disk, 1 mm in thickness, with two electroded faces by Pt-sputtering was covered by a silicone putty. The two lead wires, which were attached to the electrodes, passed through holes of the high pressure plunger; further they were connected to a capacitance bridge (Andeen-Hagerline, 2500A) which operated at 1 kHz.

3. RESULTS

3.1. Characterization

In this system two main phases appeared in XRD; one was $Ba(Mg_{1/3}Ta_{2/3})O_3$ and its Ca containing solid solutions (abbreviated as BCMT), and the other was $Ca(Mg_{1/3}Ta_{2/3})O_3$ and its Ba containing solid solutions (abbreviated as CBMT). The latter phase is not listed in JCPDS, however, we are expecting the prepared specimen is monophase and will be identified with $Ca(Mg_{1/3}Ta_{2/3})O_3$.

Lattice parameters change with x as Fig. 1, suggesting that x=0.3 is a limit of this substitution. However, trace diffractions of CBMT were detected in the specimen with x of 0.25. In the opposite compositional end, BCMT was first detected in CBMT at x=0.9. No sign of superstructures were seen in electron diffraction patterns with x of 0.16. It was concluded from this results that specimens of $x \leq 0.25$ contained very small amounts of an impurity phase. A note in proof was as follow: the peak intensity of a strong line (d=289 pm) of the impurity was 2.6% of that of the 101 line (d=409 pm) of BCMT. Relative densities of disks were 97±1% except that for x=0.0 with 95%.

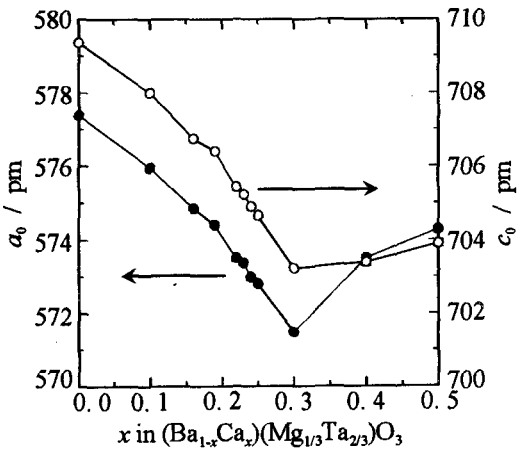

Figure 1. Lattice constants and their estimated standard deviations of hexagonal BCMT.

3.2. Dielectric Property

Dielectric properties measured at microwave frequencies are shown in Figs. 2 and 3. The writing on abscissa of figures represents the nominal composition, that is, not necessarily shows compositions of phases. The relative permittivity (ε_r) of BMT of this study is well compared with reported [4,5]. The value increases significantly taking a peak, 35.5, and further, ε_r decreases with x almost linearly. The x parameter at the peak coincide with the single phase limit of BCMT. That is ε_r of BCMT increases with a Ca content to take the maximum at the solubility limit.

The temperature coefficient of resonance frequency (TCf) was calculated using two data at 20 and 80℃. The two features in Fig. 2 are markedly resembling, which suggests that is a certain parameter which can replace x, abscissa of the figure. Although, at present, we know no practical character of the suggested parameter.

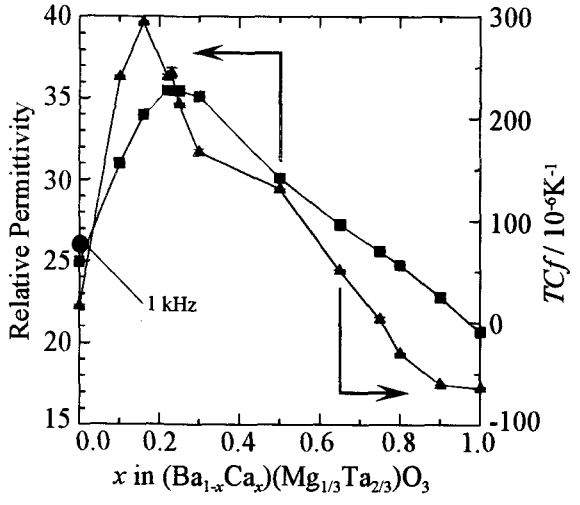

Figure 2. Relative permittivity and temperature coefficient of resonance frequency vs. composition. Standard deviations on more than three disks are shown. The solid circle is a data measured at 1 kHz.

The f•Q value of BMT in Fig.3 is about one half of the reported [5], which may be caused by insufficient annealing this of experiment. f•Q decreases sharply with x on both compositional ends to have a central plateau. It is evident by comparing the two figures that the other replacing abscissa parameter in Fig. 2, suggested above, can not work as a parameter of Fig. 3.

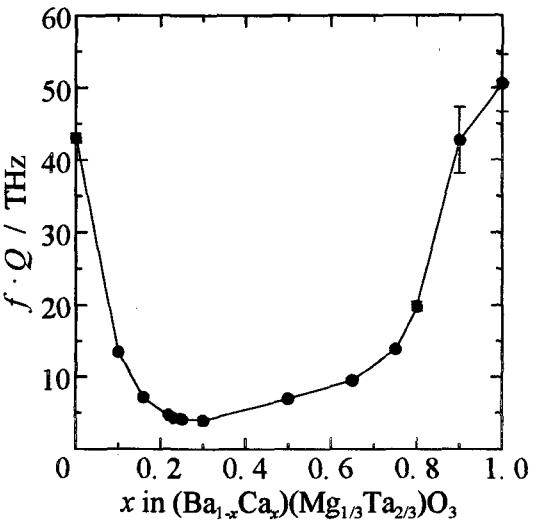

Figure 3. f•Q and its standard deviation vs. nominal composition.

3.3. Effect of Pressure

Pressure dependencies of capacities were measured at 1 kHz for $Ba(Mg_{1/3}Ta_{2/3})O_3$. Normalized results are compared in Fig. 4 with those of $SrTiO_3$ [6] and rutile [7]. The effect of pressure on the size of the disk was calibrated

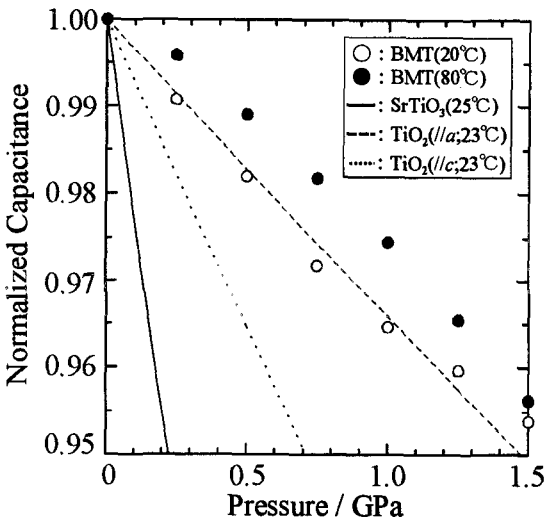

Figure 4. Normalized capacitance vs. pressure of $Ba(Mg_{1/3}Ta_{2/3})O_3$ at 20 and 80℃. Those data are cited for rutile and $SrTiO_3$.

using a volume compressibility of rutile [7], however, plots in that revised figure — the ordinate of it was $\varepsilon_r(P_p)/\varepsilon_r(P_0)$ — deviated negligibly from the plots in Fig. 4.

The slope of the plots at 80℃ is smaller than that of 20℃. The stronger dependence on pressure at lower temperatures are also reported for rutile and PbF_2 [8]. It is notable that the pressure dependence of capacities of BMT is smaller significantly than that of rutile, and smaller by far than that of $SrTiO_3$.

4. DISCUSSION

The increase in ε_r with x of this study is sharp by far than that reported for $(Ba_{1-x}Sr_x)(Mg_{1/3}Ta_{2/3})O_3$ [4]. This new observation coincides perfectly with the foregoing [1]. That is, the increases in ε_r's by the A-site substitutions of paraelectric perovskites are of the order of $(Ba_{1-x}Ca_x)$ » $(Ba_{1-x}Sr_x)$ › $(Sr_{1-x}Ca_x)$. Further, all the discussion of the references 1 is valid.

Acknowledgment: This work is supported by a grant-in-aid for Developmental Scientific Research of MESC of Japan with a contract No. 07555200, and by a grant of Japan Private School Promotion Foundation for the development of characteristic education. Dr. Takemoto is acknowledged for his various help.

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