Ba$_3$ZnTa$_{2-x}$Nb$_x$O$_9$ and Ba$_3$MgTa$_{2-x}$Nb$_x$O$_9$ $(0 \leq x \leq 1)$: synthesis, structure and dielectric properties

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(Refereed)
Received 22 October 2001; accepted 23 August 2002

Abstract

Oxides belonging to the families Ba$_3$ZnTa$_{2-x}$Nb$_x$O$_9$ and Ba$_3$MgTa$_{2-x}$Nb$_x$O$_9$ were synthesized by the solid state reaction route. Sintering temperatures of 1300°C led to oxides with disordered (cubic) perovskite structure. However, on sintering at 1425°C hexagonally ordered structures were obtained for Ba$_3$MgTa$_{2-x}$Nb$_x$O$_9$ over the entire range $(0 \leq x \leq 1)$ of composition, while for Ba$_3$ZnTa$_{2-x}$Nb$_x$O$_9$ the ordered structure exists in a limited range $(0 < x < 0.5)$. The dielectric constant is close to 30 for the Ba$_3$ZnTa$_{2-x}$Nb$_x$O$_9$ family of oxides while the Mg analogues have lower dielectric constant of $\approx 18$ in the range 50 Hz to 500 kHz. At microwave frequencies (5-7 GHz) dielectric constant increases with increase in niobium concentration (22-26) for Ba$_3$ZnTa$_{2-x}$Nb$_x$O$_9$; for Ba$_3$MgTa$_{2-x}$Nb$_x$O$_9$ it varies between 12 and 14. The "Zn" compounds have much higher quality factors and lower temperature coefficient of resonant frequency compared to the "Mg" analogues.

Keywords: A. Oxides; B. Chemical synthesis; C. X-ray diffraction; D. Dielectric properties
1. Introduction

In recent years, materials for dielectric resonators have received considerable attention due to their application in the area of microwave communication. They permit miniaturization of microwave devices such as duplex filters, down converters and voltage controlled oscillators. Perovskite-related oxides of the type $A(B_{1/3}B_2^{2/3})O_3$ or $A_3BB_2O_9$ have been found to have appropriate dielectric properties for some of the applications at microwave frequencies. These oxides crystallize in the disordered (cubic) structure or in the ordered triple perovskite (hexagonal) structure. The above series of oxides were first synthesized by Roy [1] and Galasso et al. [2] and some of these oxides were later found to show extremely low dielectric loss at microwave frequencies [3]. $Ba_3ZnTa_2O_9$ (BZT) and $Ba_3MgTa_2O_9$ (BMT) have disordered structures at lower temperature and transform to the ordered (hexagonal) structure at around 1400°C for BZT and 1600°C for BMT [3-6]. The niobium analogue, $Ba_3ZnNb_2O_9$ was earlier reported to have the disordered perovskite structure [7]. It is now known that with proper annealing (1400°C for 12 h) a fully ordered 1:2 perovskite structure can be obtained [8]. Higher temperature annealing or quenching lead to disordered structures [8,9]. The tantalates like $Ba_3ZnTa_2O_9$ or $Ba_3MgTa_2O_9$ are currently being used in devices [3,4].

We have been interested in the structure and properties of the solid solutions between $Ba_3ZnTa_2O_9-Ba_3ZnNb_2O_9$ and $Ba_3MgTa_2O_9-Ba_3MgNb_2O_9$. In an earlier study [10] we have reported the dielectric properties of $Ba_3ZnTa_{2-x}Nb_xO_9$, and $Ba_3Mg-Ta_{2-x}Nb_xO_9$ sintered at 1300°C. The dielectric properties were reported in a limited range of low frequencies (40 Hz to 100 kHz). In this paper, we report the synthesis, detailed structural characteristics and dielectric properties of the above families of oxides sintered at 1425°C. The dielectric properties have been studied both in the low frequency region (50 Hz to 500 kHz) as well as at microwave frequencies (GHz region).

2. Experimental

The starting materials were $BaCO_3$ (CDH, India, 99.5%), $MgO$ (CDH, India, 97%), $ZnO$ (CDH, India, 99.5%), $Nb_2O_5$ (CDH, India, 99.5%) and $Ta_2O_5$ (Aldrich, 99%). Stoichiometric quantities were weighed, ground and calcined at 1000°C for 30 h with couple of intermittent grindings and were then further heated at 1200°C for 12 h. The calcined powders were mixed with polyvinylalcohol (PVA) and sintered at 1425°C for 4 h. The $BaMg_{1/3}Ta_{2-x}Nb_xO_9$ samples were further sintered at 1425°C for 4 more hours. These pellets were polished and used for high frequency (GHz) measurements.

Powder X-ray diffraction (PXRD) studies were carried out using a Bruker D8 Advance diffractometer, with Ni-filtered Cu Ka radiation. Lattice parameters were calculated by a least square fit to the observed $d$-values. The grain size of the samples were obtained on fractured surfaces of the sintered pellets by means of a Cambridge Stereoscan 360 scanning electron microscope. The density of the sintered disks were measured by the Archimedes method.
The dielectric constant and dielectric loss at low frequencies (50 Hz to 500 kHz) were measured using an HP 4284L LCR meter on well sintered disks (1425°C) coated with aluminum.

For measurements at microwave frequencies (5-10 GHz) the technique of Sree-moolanadhan et al. [11] is followed. The disks used for microwave dielectric property measurements had an aspect ratio (DIL) of ~1.2, which is in the permitted range reported by Kobayashi and Katoh [12]. To measure the dielectric constant ‘ε’ the cylindrical resonator was sandwiched between two gold plated brass disks and the microwave energy coupled using electric-field probes as described by Courtney [13]. Using a Hewlett-Packard (HP) 8510B network analyzer and accessories, the TE₀₁₁ resonant frequency (f₀) of the dielectric resonator was identified and the dielectric constant (ε), calculated with a HP 9000, 300 series instrumentation computer from the following formula developed by Hakki and Coleman [14]

\[ \varepsilon = 1 + \left( \frac{\lambda_0}{\pi D} \right)^2 \left( \alpha_1^2 + \beta_1^2 \right) \]  

(1)

In this equation JSJ is obtained from/₀ and the sample dimensions; ω is given by the mode chart of Hakki and Coleman [14]. The unloaded quality factor Q of the resonator was measured using the 'stripline method' proposed by Khanna and Garault [15]. A 50 Q copper stripline was etched on an RT/Duroid substrate (a commercial low loss PTFE substrate) and housed in a brass enclosure. The cylindrical DR (dielectric resonator) sample was placed symmetrically near the stripline and adjusted to get maximum coupling. From the HP 8510B network analyzer, the lowest transmission coefficient S₂₁ was selected and S₂₁ was calculated using the formula:

\[ S_{21u} = S_{21} \left( \frac{2}{1 + S_{21}^2} \right)^{1/2} \]  

(2)

The width of the resonance curve corresponding to S₂₁ was taken as Δf. From the frequency of resonance 'f₀' and Δf, the value of the unloaded Q—factor was calculated. This method of Q measurement is of great practical use since it gives the Q of a DR sample in an actual working environment [16]. For measuring the iy (temperature coefficient of resonant frequency), the DR sample was heated inside an aluminum cavity from 25 to 80°C. The shift in resonant frequency with temperature is plotted. From the slope obtained from the plot the temperature coefficient of resonant frequency is calculated using the relation

\[ \tau_f = f_0^{-1} \left( \frac{\Delta f}{\Delta T} \right) \]  

(3)

3. Results and discussion

The PXRD patterns of oxides of the type Ba₃ZnTa₂₋ₓNbₓO₉ (0 ≤ x ≤ 1) could be indexed in a cubic cell for all the compositions sintered at 1000°C. The cubic structure
persists even after sintering at 1300°C. The lattice parameter 'a' calculated from the indexed powder patterns was ~4.1 Å. No impurity peaks were present in the powder diffraction patterns. Our studies corroborate with earlier reports [7,8] carried out on the end members Ba$_3$ZnTa$_2$O$_9$ and Ba$_3$ZnNb$_2$O$_9$. Sintering further at 1425°C, we observe the presence of additional reflections in the powder XRD pattern. All the reflections could be indexed on the basis of a hexagonal cell. The hexagonally ordered structure persists till $x = 0.5$ in the Ba$_3$ZnTa$_{2-x}$Nb$_x$O$_9$ family (Fig. 1). It is to be noted

Fig. 1. Powder XRD patterns for oxides of the Ba$_3$ZnTa$_{2-x}$Nb$_x$O$_9$ system sintered at 1425°C.
Table 1
Details of the compositions and structural parameters of the phases in the Ba$_3$ZnTa$_{2-x}$Nb$_x$O$_9$ (0.1 < $x$ < 1) system

<table>
<thead>
<tr>
<th>Composition</th>
<th>$a_{\text{cubic}}$ (Å)$^a$</th>
<th>$a_{\text{cubic/fhhex}}$ (Å)$^b$</th>
<th>$c_{\text{hex}}$ (Å)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba$<em>3$ZnTa$</em>{1.9}$Nb$_{0.1}$O$_9$</td>
<td>4.080 (1)</td>
<td>5.777 (2)</td>
<td>7.077 (2)</td>
</tr>
<tr>
<td>Ba$<em>3$ZnTa$</em>{1.7}$Nb$_{0.3}$O$_9$</td>
<td>4.086 (1)</td>
<td>5.774 (2)</td>
<td>7.084 (1)</td>
</tr>
<tr>
<td>Ba$<em>3$ZnTa$</em>{1.5}$Nb$_{0.5}$O$_9$</td>
<td>4.086 (1)</td>
<td>5.769 (4)</td>
<td>7.079 (3)</td>
</tr>
<tr>
<td>Ba$<em>3$ZnTa$</em>{1.25}$Nb$_{0.75}$O$_9$</td>
<td>4.091 (1)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ba$_3$ZnTa$_3$O$_9$</td>
<td>4.085 (1)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ After 1300°C heating.

$^b$ After 1425°C sintered.

$^c$ Same as after 1300°C heating.

that pure Ba$_3$ZnTa$_2$O$_9$ gets hexagonally ordered [3,6] beyond 1400°C. The intensity of the superstructure (1 0 0) reflection ($d$ = ~ 5.8 Å) decreases with increasing niobium concentration. There is hardly any change in the lattice parameter with composition (Table 1) which is to be expected since both the Nb and Ta ions have the same ionic radii (0.64) [17]. Ba$_3$ZnTa$_{2-x}$Nb$_x$O$_9$ samples sintered at 1425°C in this study was found to have bulk density above 96% of the theoretical value for all compositions.

Oxides belonging to the Ba$_3$MgTa$_{2-x}$Nb$_x$O$_9$ (0 < $x$ < 1) family show the presence of a cubic phase for the materials synthesized at 1000°C. A small amount (5%) of Ba$_3$Ta$_4$O$_{15}$ impurity phase is observed in these samples. Sintering further at 1300°C does not lead to any phase transformation and all the reflections after sintering were satisfactorily indexed on a cubic cell (Table 2). The lattice parameter ‘a’ was found to be in the range of 4.09-4.1 Å. On further sintering these samples at 1425°C leads to the hexagonal structure for all the oxides throughout the solid solution range studied (Fig. 2). The amount of impurity phase (Ba$_3$Ta$_4$O$_{15}$) was found to be around 5% for all the compositions. In Table 2, we show the hexagonal lattice parameters obtained for the above ordered phases.

Scanning electron micrographs for the Ba$_3$ZnTa$_{2-x}$Nb$_x$O$_9$ samples sintered at 1300°C for 12 h show grain size diameter in the range 1-2 µm. The SEM studies of disks sintered at 1425°C (Fig. 3) show grains of around 2-3 µm in diameter.

Table 2
Details of the compositions and structural parameters in the Ba$_3$MgTa$_{2-x}$Nb$_x$O$_9$ (0.1 < $x$ < 1) system

<table>
<thead>
<tr>
<th>Composition</th>
<th>$a_{\text{cubic}}$ (Å)$^a$</th>
<th>$a_{\text{hex}}$ (Å)$^b$</th>
<th>$c_{\text{hex}}$ (Å)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba$<em>3$MgTa$</em>{1.9}$Nb$_{0.1}$O$_9$</td>
<td>4.093 (1)</td>
<td>5.737 (3)</td>
<td>7.062 (3)</td>
</tr>
<tr>
<td>Ba$<em>3$MgTa$</em>{1.7}$Nb$_{0.3}$O$_9$</td>
<td>4.086 (1)</td>
<td>5.729 (4)</td>
<td>7.048 (4)</td>
</tr>
<tr>
<td>Ba$<em>3$MgTa$</em>{1.5}$Nb$_{0.5}$O$_9$</td>
<td>4.086 (1)</td>
<td>5.748 (3)</td>
<td>7.059 (4)</td>
</tr>
<tr>
<td>Ba$<em>3$MgTa$</em>{1.25}$Nb$_{0.75}$O$_9$</td>
<td>4.086 (3)</td>
<td>5.738 (3)</td>
<td>7.049 (4)</td>
</tr>
<tr>
<td>Ba$_3$MgTa$_3$O$_9$</td>
<td>4.096 (1)</td>
<td>5.738 (3)</td>
<td>7.062 (3)</td>
</tr>
</tbody>
</table>

$^a$ After 1300°C heating.

$^b$ After 1425°C sintered.
density of the sintered disks (1425°C) was found to be around 95% of the theoretical density.

The Ba$_3$MgTa$_{2-x}$Nb$_x$O$_9$ oxides after 1000°C heat treatment had a grain size of less than 0.5 μm. SEM micrographs of Ba$_3$MgTa$_{1.5}$Nb$_{0.5}$O$_9$ sintered at 1000 and 1300 and 1425°C have been found to be very similar. Thus, the grain size does not increase appreciably on raising the temperature from 1000 to 1425°C. These grains in the sintered disks (at 1425°C) are densely packed. Fig. 4 shows the scanning electron micrograph of the oxides sintered at 1425°C for $x = 0.1, 0.5$ and $1.0$ compositions.

The dielectric properties of the oxides of the Ba$_3$ZnTa$_{2-x}$Nb$_x$O$_9$ family were investigated in the frequency range of 50 Hz to 500 kHz. The dielectric constant for all the compositions of Ba$_3$ZnTa$_{2-x}$Nb$_x$O$_9$ ($x = 0.1-1.0$) decreases with increase in frequency (Fig. 5). The dielectric constant varies between 26 and 30 and the dielectric loss was less than 0.08 at 500 kHz for all the above compositions. The dielectric constant shows strong dispersion at low frequencies (below 10 kHz) for the $x = 0.1$ and $0.25$ compositions. The dielectric constant ($\varepsilon$) at microwave frequency (~5.5 GHz) increases from 22 to 26 with increase in concentration of Nb. It may be noted that $\varepsilon$ for Ba$_3$ZnTa$_2$O$_9$ is around 30 in the 10-12 GHz range of frequency.
We have studied the variation of the resonant frequency ($f_0$) as a function of temperature (Fig. 6). The temperature coefficient of resonant frequency ($T_0$) for the above oxides show a very low value of around +10 ppm/°C (Table 3). These materials have very low dielectric loss, low revalues and reasonable dielectric constant (~25) and may be useful for microwave applications.

The dielectric properties measured as a function of frequency for members of the Ba$_3$MgTa$_2$–xNb$_x$O$_9$ family are shown in Fig. 7. These samples were sintered at 1425°C for 12 h. The dielectric constant ($e$) decreases with increase in frequency for all the oxides studied and has a value of 15-20 at 500 kHz. The dielectric loss ($D$) was found to be less than 0.15 for all the compositions at 500 kHz. The dielectric constant shows strong dispersion below 1 kHz for most of the compositions.
Fig. 4. Scanning electron micrographs of sintered disks (1425°C) of oxides of $\text{Ba}_3\text{MgTa}_{2-x}\text{Nb}_x\text{O}_9$
(a) $x = 0.1$; (b) $x = 0.50$; (c) $x = 1.0$. 
The dielectric properties of the above oxides (sintered at 1425°C) were also measured at microwave frequencies (~6-7 GHz). The dielectric constant (ε) varies between 12 and 14 for the different oxides (Table 4). Ba₃MgTa₂O₉ sintered at 1550-1600°C, has a dielectric constant of around 30 at 11-12 GHz [6]. Although the oxides synthesized by us show an ordered hexagonal structure after sintering at 1425°C,
Fig. 6. Variation of the resonant frequency ($f_0$) in the GHz region with temperature for $\text{Ba}_3\text{ZnTa}_{2-x}\text{Nb}_x\text{O}_9$ system.

Table 3
Dielectric properties for $\text{Ba}_3\text{ZnTa}_{2-x}\text{Nb}_x\text{O}_9$ at GHz frequencies

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\varepsilon$</th>
<th>$D$</th>
<th>$f_{ix}/\alpha$</th>
<th>$if$ (ppm/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ba}<em>3\text{ZnTa}</em>{1.8}\text{Nb}_{0.2}\text{O}_9$</td>
<td>22.42</td>
<td>0.00061</td>
<td>1640 x 5.6587</td>
<td>+ 11.3</td>
</tr>
<tr>
<td>$\text{Ba}<em>3\text{ZnTa}</em>{1.75}\text{Nb}_{0.25}\text{O}_9$</td>
<td>23.36</td>
<td>0.00042</td>
<td>2365 x 5.7682</td>
<td>+ 13.2</td>
</tr>
<tr>
<td>$\text{Ba}<em>3\text{ZnTa}</em>{1.5}\text{Nb}_{0.5}\text{O}_9$</td>
<td>25.57</td>
<td>0.00067</td>
<td>1482 x 5.5031</td>
<td>+ 9.69</td>
</tr>
<tr>
<td>$\text{Ba}<em>3\text{ZnTa}</em>{1.25}\text{Nb}_{0.75}\text{O}_9$</td>
<td>26.51</td>
<td>0.00079</td>
<td>1255 x 5.4703</td>
<td>+ 9.73</td>
</tr>
<tr>
<td>$\text{Ba}_3\text{ZnTaNbO}_9$</td>
<td>26.45</td>
<td>0.0010</td>
<td>983 x 5.4710</td>
<td>+ 7.78</td>
</tr>
</tbody>
</table>
Fig. 7. Variation of the dielectric constant ($\varepsilon$) and dielectric loss ($D$) with logarithm of frequency for Ba$_3$MgTa$_{2-x}$Nb$_x$O$_9$ system. Filled diamonds represent the dielectric constant while filled squares represent dielectric loss.
Table 4
Dielectric properties for Ba₃MgTa₂₋ₓNbₓO₉ at GHz frequencies

<table>
<thead>
<tr>
<th>Composition</th>
<th>e</th>
<th>D</th>
<th>Q × f₀</th>
<th>if (ppm/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba₃MgTa₄.1Nb₀.109</td>
<td>12.44</td>
<td>0.0021</td>
<td>461 x 7.3872</td>
<td>+20.50</td>
</tr>
<tr>
<td>Ba₃MgTa₄.25Nb₀.2509</td>
<td>12.43</td>
<td>0.0028</td>
<td>351 x 5.8675</td>
<td>+21.46</td>
</tr>
<tr>
<td>Ba₃MgTa₄.5Nb₀.509</td>
<td>13.94</td>
<td>0.0018</td>
<td>544 x 6.9721</td>
<td>-22.52</td>
</tr>
<tr>
<td>Ba₃MgTa₅Nb₀.7509</td>
<td>11.78</td>
<td>0.0027</td>
<td>365 x 7.3750</td>
<td>+20.31</td>
</tr>
<tr>
<td>Ba₃MgTaNbO₉</td>
<td>13.94</td>
<td>0.0018</td>
<td>544 x 6.9721</td>
<td>+16.9</td>
</tr>
</tbody>
</table>

The dielectric constant is considerably lower compared to the oxides sintered at 1600°C [6]. The quality factor (Q) at 6-7 GHz is low (400-550) as compared to samples of Ba₃ZnTa₂₋ₓNbₓO₉ phases where the quality factor is close to 1500 (Tables 3 and 4). The variation of the resonant frequency with temperature is shown in Fig. 8. We note

![Fig. 8. Variation of the resonant frequency (f₀) in the GHz region with temperature for Ba₃MgTa₂₋ₓNbₓO₉ system.](image-url)
that the temperature coefficient of resonant frequency (iy) is positive and decreases with increasing niobium content (Table 4). However, at \( x = 0.5 \) the upvalue becomes negative. The reason for this anomaly is not clear to us at present. The possibility of having positive and negative values of iy in slightly different compositions may be used to obtain near zero iy values. However, the above materials have much lower dielectric constant compared to \( \text{Ba}_3\text{ZnTa}_{2-x}\text{Nb}_x\text{O}_9 \) as found in our study. From the SEM studies on the oxides of the \( \text{Ba}_3\text{MgTa}_{2-x}\text{Nb}_x\text{O}_9 \) family we observed small grains of around 0.5 \( \mu \text{m} \) even in disks sintered at 1425°C. In addition, the bulk density obtained by us (95%) may not include the surface porosity and hence the actual density may be lower. We believe that higher sintering temperatures may be needed to obtain larger grains and higher density which would improve the dielectric properties. Thus, we see that the sintering condition and grain size influence the dielectric properties dramatically even though the ordered structure is present in these oxides.

4. Conclusions

Various members of the \( \text{Ba}_3\text{ZnTa}_{2-x}\text{Nb}_x\text{O}_9 \) and \( \text{Ba}_3\text{MgTa}_{2-x}\text{Nb}_x\text{O}_9 \) family of oxides have been synthesized by the conventional solid state method. PXRD studies show that sintering at 1425°C leads to hexagonal ordering for all the compounds in the \( \text{Ba}_3\text{MgTa}_{2-x}\text{Nb}_x\text{O}_9 \) system. Members of \( \text{Ba}_3\text{ZnTa}_{2-x}\text{Nb}_x\text{O}_9 \) show ordering up to \( x = 0.5 \). The dielectric constant at GHz frequency for \( \text{Ba}_3\text{ZnTa}_{2-x}\text{Nb}_x\text{O}_9 \) varies from 22 to 26 and temperature coefficient of resonant frequency (iy) was around +7 to +11 ppm/°C. The oxides belonging to the \( \text{Ba}_3\text{MgTa}_{2-x}\text{Nb}_x\text{O}_9 \) family show a dielectric constant of 12 and the iy varies from +17 to +22 ppm/°C for different compositions studied. The \( x = 0.5 \) composition shows a negative iy of —22.5 ppm/°C.

Acknowledgments

AKG thanks BRNS (DAE) Govt. of India for financial assistance.

References