Processing and Characterization of Microwave Dielectric Ceramics and Thin Films-Nd$_2$(Ti$_{2/3}$Al$_{1/3}$)$_3$O$_{9-δ}$ and (Ba$_{0.7}$Sr$_{0.3}$)TiO$_3$

Hong-Wen Wang

Department of Chemistry,
Chung-Yuan Christian University,
Chung-Li, 320, Taiwan, R.O.C.
E-mail: hongwen@cycu.edu.tw

Abstract

Reactive powders of stoichiometry Nd$_2$(Ti$_{2/3}$Al$_{1/3}$)$_3$O$_{9-δ}$ and thin films of (Ba$_{0.7}$Sr$_{0.3}$)TiO$_3$ have been prepared by the conventional mixed-oxide method and the metal-organic deposition method, respectively. The corresponded phases after calcination and sintering are investigated by XRD diffraction. Single phase of Nd$_2$(Ti$_{2/3}$Al$_{1/3}$)$_3$O$_{9-δ}$ could be only obtained by sintering over 1400°C for 4 h. (Ba$_{0.7}$Sr$_{0.3}$)TiO$_3$ thin film well crystallizes at as low as 570°C after Au-doping by MOD method. Nd$_2$(Ti$_{2/3}$Al$_{1/3}$)$_3$O$_{9-δ}$ possesses excellent temperature stability of frequency. Substitution of Nd by Ca, Sr, or Pb can also readily form the single phase (Nd,X)$_2$Ti$_3$O$_{9-δ}$, but inferior microwave properties are observed. The leakage current of BST thin films are found to be reduced by doping Au or codoping Mg/La or Mg/Nb. Mg/La and Mg/Nb reduces leakage current even more when annealing is performed at high temperatures.

Key Words: Nd$_2$(Ti$_{2/3}$Al$_{1/3}$)$_3$O$_{9-δ}$, (Ba$_{0.7}$Sr$_{0.3}$)TiO$_3$, Microwave Dielectric Ceramic, Thin Film

1. Introduction

Ceramic materials used for dielectric resonator [1-5] or phase shifter [6,7] in microwave communication systems have become indispensable components in modern world. This is due to the dielectric ceramic’s capability to reduce the size of microwave components and flexibility of tunable properties.

The characteristics necessary for a bulk materials used in dielectric resonator are high dielectric constant ($\varepsilon_r$), high quality factor (Q) and near zero temperature coefficients of resonant frequency ($\tau_f$). Since 1970’s, several materials, including Ba$_2$Ti$_9$O$_{20}$ [1], MgTiO$_3$-CaTiO$_3$ [2], (Zr,Sn)TiO$_4$ [3], BaO-PbO-Nd$_2$O$_3$-TiO$_2$ [3], Ba(Zr,Zn,Ta)O$_3$ [4], have been developed for microwave use. Ceramic materials in the bulk form with $\varepsilon_r$ values from 20 to 90 in the range of microwave frequency are readily available.

The requirements of thin films for tunable microwave device include [8]: (1) a low loss tangent, tan $\delta < 0.01$; (2) a large variation in the dielectric constant with applied d.c. bias, ~50% tenability; (3) for impedance matching purposes, the dielectric constant $\varepsilon_r$ must be less than 500; and (4) the film must possess low leakage current $J$ (A/cm$^2$) characteristics. It turns out that (Ba$_{1-x}$Sr$_x$)TiO$_3$ thin film is a promising materials for tunable microwave devices. The tenability of this material arises because it is possible to change its dielectric constant with application of an electric field.

Interest in Nd-Ti-O dielectric materials arose as a result of the observation that they possess good temperature stability and low dielectric loss at microwave frequencies and makes them good candidate materials for resonator applications [3,9]. There are several stable compounds in the Nd-Ti-O
system, namely, such as Nd$_2$TiO$_5$, Nd$_2$Ti$_2$O$_7$, Nd$_3$TiO$_{2.5}$. However, there is one meta-stable phase Nd$_2$Ti$_3$O$_{9.5}$ which is rarely reported and not found in the Nd-Ti-O phase diagram. This phase was firstly reported by Leonov [10] in 1966 and only recently synthesized as A$_2$Nd$_2$Ti$_3$O$_{10}$ (A=Na, K, H) using acid exchange by Richard [11]. It was found that Nd$_2$Ti$_3$O$_{9.8}$ is a layered orthorhombic perovskite and contains a high concentration of oxygen vacancies.

The synthesis of Nd$_2$Ti$_3$O$_{9.8}$ phase could not be achieved by the conventional mixed-oxide method [12-14] and is rarely reported. In this study, we report that substitution Nd or Ti by other dopants leads to the formation of single phase Nd$_2$Ti$_3$O$_{9.8}$ materials by using conventional mixed-oxide method. The crystallization of BST thin film is enhanced by the addition of Au and the leakage current of the films is reduced by the dopant (Au) or codopants (Mg/La, Mg/Nb) using standard metallo-organic deposition (MOD) method.

2. Experimental

The starting materials for Nd$_2$(Ti$_{2/3}$Al$_{1/3}$)$_3$O$_{9.8}$ were Nd$_2$O$_3$, TiO$_2$, and Al$_2$O$_3$, and for (Nd$_{2/3}$X$_{1/3}$)$_2$Ti$_3$O$_{9.8}$ are Nd$_2$O$_3$, TiO$_2$, with X = CaO, PbO, and SrCO$_3$. The mixture was ball-mixing for 12 h and calcined at 1100 °C for 4 h. The calcined powder was milled for 12 h and sintered at 1200~1450 °C for 4 hours in atmosphere. All the resulting phases of the precursors after calcinations and sintering were examined using XRD. The sintered samples were pulverized before the examination by X-ray diffraction. The microwave properties of bulk materials were measured by established post-resonant method [15].

The starting materials for (BaSr)TiO$_3$ thin film were barium acetate Ba(CH$_3$COO)$_2$, strontium acetate Sr(CH$_3$COO)$_2$, titanium n-butoxide Ti(C$_4$H$_9$O)$_4$, glacial acetic acid (CH$_3$COOH) and 2-methoxyethanol (C$_3$H$_8$O$_2$) were used as solvents. The stock solutions of desired compositions were prepared by established MOD method [16]. Then, a mixed solution with various specified quantities of Au solution was added to the above-mentioned solution for Au-doped BST films [17]. For the study of Mg/La, and Mg/Nb co-doped BST films, the solution of various molar concentrations of La, or Nb, with fixed 5 mol% Mg were added to the BST solution [16]. The filtered solutions were deposited on platinized Si wafer (Pt/Ti/SiO$_2$/Si) by two-step spin-coating (1000 rpm, 10 s, and 6000 rpm, 30 s). The wet coatings were pyrolyzed at 550~800 °C for 10 min. The deposition-pyrolyzing process was repeated in order to achieve the desired thickness.

The final films were annealed at corresponding temperatures for 1 h. The phase development was investigated using X-ray diffraction. The leakage current was measured by a Hewlett-Packard precision semiconductor parameter analyzer HP4156 at 1V~5V.

3. Results and Discussion

3.1 Nd$_2$(Ti$_{2/3}$Al$_{1/3}$)$_3$O$_{9.8}$ Ceramics

Figure 1(a) shows that the result of calcined powder for Nd$_2$(Ti$_{2/3}$Al$_{1/3}$)$_3$O$_{9.8}$, which is identical to Nd$_2$Ti$_2$O$_7$ phases. The calcined powder for (Nd$_{2/3}$X$_{1/3}$)$_2$Ti$_3$O$_{9.8}$ with X= Sr, Ca, and Pb, however, are clear peaks of Nd$_2$Ti$_3$O$_{9.8}$ phase (JCPDS file No. 200774) with very minor Nd$_4$Ti$_9$O$_{24}$ phases as shown in Figure 2(b)~(d). These powders were sintered at 1200~1450 °C for 4 h. Within this temperature range, we obtained almost single phase Nd$_2$Ti$_3$O$_{9.8}$, as shown in Figure 2(a)~(d). Single phase Nd$_2$(Ti$_{2/3}$Al$_{1/3}$)$_3$O$_{9.8}$ can only be obtained at a temperature over 1400 °C for 4 h. Below 1400 °C, however, the phase of Nd$_2$(Ti$_{2/3}$Al$_{1/3}$)$_3$O$_{9.8}$ become diminished and Nd$_2$Ti$_2$O$_7$ is the major phase.

![Figure 1](image-url)

**Figure 1. Phases after calcination for**

(a) Nd$_2$(Ti$_{2/3}$Al$_{1/3}$)$_3$O$_{9.8}$; (b) (Nd$_{2/3}$Sr$_{1/3}$)$_2$Ti$_3$O$_{9.8}$; (c) (Nd$_{2/3}$Ca$_{1/3}$)$_2$Ti$_3$O$_{9.8}$; (d) (Nd$_{2/3}$Pb$_{1/3}$)$_2$Ti$_3$O$_{9.8}$; A=Nd$_2$Ti$_2$O$_7$, B=Nd$_4$Ti$_9$O$_{24}$, C=Nd$_2$Ti$_3$O$_{9.8}$
Processing and Characterization of Microwave Dielectric Ceramics and Thin Films—Nd\(_2\)(Ti\(_{2/3}\)Al\(_{1/3}\))\(_3\)O\(_9\)-\(\delta\) and (Ba\(_{0.7}\)Sr\(_{0.3}\))TiO\(_3\)

Figure 2. Phases after sintering for
(a) Nd\(_2\)(Ti\(_{2/3}\)Al\(_{1/3}\))\(_3\)O\(_9\)-\(\delta\); (b) Nd\(_2\)(Sr\(_{1/3}\))\(_2\)Ti\(_3\)O\(_9\)-\(\delta\); (c) Nd\(_2\)(Ca\(_{1/3}\))\(_2\)Ti\(_3\)O\(_9\)-\(\delta\); (d) Nd\(_2\)(Pb\(_{1/3}\))\(_2\)Ti\(_3\)O\(_9\)-\(\delta\); B=Nd\(_4\)Ti\(_9\)O\(_{24}\), C=Nd\(_2\)Ti\(_3\)O\(_9\)-\(\delta\)

Table 1 shows the microwave properties of these materials, it is obvious that Nd\(_2\)(Ti\(_{2/3}\)Al\(_{1/3}\))\(_3\)O\(_9\)-\(\delta\) possesses good temperature stability and deserved a more detail study.

Table 1. The microwave properties of studied bulk materials, Fr = resonant frequency

<table>
<thead>
<tr>
<th>Materials</th>
<th>Temp/Time</th>
<th>(\varepsilon_r) (Fr)</th>
<th>Q</th>
<th>(\tau_f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd(<em>2)(Ti(</em>{2/3})Al(_{1/3}))(_3)O(_9)-(\delta)</td>
<td>1450°C/10h</td>
<td>36.5 (6.6GHz)</td>
<td>1800</td>
<td>-3.3 ppm</td>
</tr>
<tr>
<td>(Nd(<em>{2/3})Sr(</em>{1/3}))(_2)Ti(_3)O(_9)-(\delta)</td>
<td>1300°C/4h</td>
<td>90 (4.1GHz)</td>
<td>970</td>
<td>199 ppm</td>
</tr>
<tr>
<td>(Nd(<em>{2/3})Ca(</em>{1/3}))(_2)Ti(_3)O(_9)-(\delta)</td>
<td>1300°C/10h</td>
<td>93.5 (4.1GHz)</td>
<td>245</td>
<td>136 ppm</td>
</tr>
<tr>
<td>(Nd(<em>{2/3})Pb(</em>{1/3}))(_2)Ti(_3)O(_9)-(\delta)</td>
<td>1300°C/4h</td>
<td>59.6 (5.5GHz)</td>
<td>541</td>
<td>288 ppm</td>
</tr>
</tbody>
</table>

3.2 (Ba\(_{0.7}\)Sr\(_{0.3}\))TiO\(_3\) Thin Film

Figure 3 shows the XRD results for the four different BST samples. In the sample with no gold (sample A), only a small broad peak is observed, at 2\(\theta\approx\)31.8°, which can be assigned to the (110) plane of cubic (Ba\(_{0.7}\)Sr\(_{0.3}\))TiO\(_3\). On the other hand, for the sample with the 0.5mol% gold (C =1 mol%, and D =5 mol%) to the BST film, the peaks intensity for the (100), (110) and (200) planes increases. From the above results, it could be concluded that adding gold to the BST films enhances crystallization in these films. It is also clear that as low as 0.5mol% Au dopant leads crystallization of BST phase at 570 °C, which is much lower than the normal 700 °C for undoped BST films.

Figure 4(a) and 4(b) show the leakage current of Mg-La- and Mg-Nb-codoped specimens. There is a minimum leakage current when the donor concentration is 10 mol%, at which it is obvious that at 10 mol% of donor, the amount of all the positive charges equal to the amount of negative charges, i.e., neutrality compensation occurs:

\[ \text{[Mg}^{n+}\text{]} = \text{[La}^{n+}\text{]} \]  
\[ 2 \text{[Mg}^{n+}\text{]} = \text{[Nb}^{n+}\text{]} \]

Before the compensation of charges occurs, the leakage current also decreases with increasing donor concentration and shifts to a lower value when the annealing temperature increases. Above 10 mol% donor concentration, however, the leakage current again increases. It is believed that beyond the concentration of compensation (10 mol% of donor), more donors contribute more conducting electrons and thus results in an increase of leakage current. It is proposed that the potential barrier of the codoped materials is enhanced by defect dipoles: Mg\(_{\text{II}^+}\) — 2 La\(_{\text{II}}\)\(^*\), or Mg\(_{\text{II}^+}\) — 2 Nb\(_{\text{II}}\)\(^*\), which form an insulating layer around grain boundaries and are responsible for the lower leakage current at higher annealing temperature.
Figure 4. Leakage current for the BST thin films with (a) Au, annealed at 700 °C; (b) 5 mol% Mg/La; (c) 5 mol% Mg/Nb codopant. The leakage current reduces as the dopant concentration increases.

Acknowledgment

The financial support of grant number NSC 89-2113-M-033-016 from National Science Council, Taiwan, R.O.C. is greatly appreciated.

References


Manuscript Received: Apr. 19, 2002
and Accepted: May 24, 2002