Phase evolution and microwave dielectric properties of (Bi$_{1-x}$Ln$_x$)$_2$MoO$_6$ (Ln = Nd and La, x ≤ 0.3) ceramics

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1. Introduction

The development of high-speed and high-frequency digital devices, which are capable of transferring large amounts of information in a short time, is one of the main strategic drivers of the consumer electronics market. Meanwhile, demands for miniaturization and performance enhancement of microwave devices have increased with the development of the modern communication system. Thus, there have been increasing investigations on microwave dielectric materials to miniaturize the microwave resonator because the size of the device is inversely proportional to $\varepsilon_r^{1/2}$ [4].

A great number of excellent microwave dielectric materials were developed, such as Sr$_2$CaAl$_2$SiO$_7$ [5], ZnO-Nb$_2$O$_5$ [6], Bi (Nb, Ta, Sb)O$_4$ [7-9], Li$_2$O-Nb$_2$O$_5$-TiO$_2$ [10], (Zr, Sn)TiO$_4$ [11], BaO-TiO$_2$-Nb$_2$O$_5$ [12], and the (A$_1$A$_2$)(B$_1$B$_2$)O$_5$ complex perovskite system [13]. While most of them need high sintering temperatures above 1200 °C. Nowadays, investigations on new compounds with intrinsically lower sintering temperatures have attracted much more attention [14-17]. In the Bi$_2$O$_3$-MoO$_3$ system, six compounds with pure phase were reported and all of them were glass-free low-firing microwave dielectric materials. [18] The Bi$_2$MoO$_6$ ceramic with a monoclinic structure was reported to possess a low sintering temperature (750 °C), a high Qf value (16,700 GHz), and a negative TCF value (~114 ppm/°C). TCF value could be tailored to near zero by ceramic composites, such as Bi$_2$MoO$_6$-TiO$_2$ composites, and a temperature stable low-firing microwave dielectric material was obtained in our previous work [19]. Substitution is another good way to modify TCF values of microwave dielectrics [20-23]. Rare earth cations, such as La$^{3+}$ and Nd$^{3+}$, have the same chemical valence and similar ionic radii to Bi$^{3+}$, so solid solutions

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[2,3] while a large dielectric constant ($\varepsilon_r$) is also required for the microwave dielectric material to miniaturize the microwave resonator because the size of the device is inversely proportional to $\varepsilon_r^{1/2}$ [4].

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might be formed in the (Bi\(_1-x\)Ln\(_x\))\(_2\)MoO\(_6\) (Ln=Nd and La) system. According to literatures’ reports, both Nd\(_2\)MoO\(_6\) and La\(_2\)MoO\(_6\) can crystallize as tetragonal crystal structure with a \(I\bar{4}_{1}/a\cd\) space group [24,25]. The La\(_2\)MoO\(_6\) is a kind of optical materials which can be activated with the trivalent rare earth ions [26], and the Nd\(_2\)MoO\(_6\) ceramic, which can be densified well at 1350 °C, is a microwave dielectric material with a permittivity (\(\varepsilon_r\)) of 13.8, a Q value of 66,400 GHz, and a TCF value of –53 ppm/°C [27]. In the present work, (Bi\(_1-x\)Ln\(_x\))\(_2\)MoO\(_6\) (Ln=Nd and La, \(x < 0.3\)) ceramics were prepared by conventional solid state reaction method, and sintering behavior, phase evolution, microstructure and microwave dielectric properties were investigated in detail.

2. Experimental procedure

Proportionate amounts of reagent-grade Bi\(_2\)O\(_3\) (> 99%, Shu-Du Powders Co. Ltd., Chengdu, China), La\(_2\)O\(_3\) (> 99.99%, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China), Nd\(_2\)O\(_3\) (> 99.99%, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China), and MoO\(_3\) (> 99%, Fuchen Chemical Reagents, Tianjin, China) were prepared according to the stoichiometric compound formulation of (Bi\(_1-x\)Ln\(_x\))\(_2\)MoO\(_6\) (Ln=Nd and La, \(x=0.0, 0.1, 0.2, \) and 0.3). Powders were mixed and milled for 4.5 h using a planetary mill (Nanjing Machine Factory, Nanjing, China). The mixtures were dried and calcined at 550–650 °C for 5 h. The calcined powders were ball milled again for 5 h, and then the dried powders were pressed into cylinders (10 mm in diameter and 4–5 mm in height) in a steel die with 5 wt% PVA binder addition under a uniaxial pressure of 20 MPa. Samples were sintered at temperatures from 830 to 1030 °C for 2 h.

Densities of the sintered specimens were measured by Archimedes method. To examine phase structure, sintered ceramics were crushed into powders. Room temperature X-ray diffraction (XRD) measurement was performed by using a XRD with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometer, Tokyo, Japan). The XRD measurement was performed by using a solid state reaction method with a network analyzer (HP 8720 Network Analyzer, Hewlett-Packard) and a temperature chamber (Delta Design, Poway, CA). The room temperature X-ray diffraction patterns were obtained in (Bi\(_1-x\)Ln\(_x\))\(_2\)MoO\(_6\) ceramics. Almost all the diffraction peaks of the samples (except (Bi\(_0.7\)Nd\(_0.3\))\(_2\)MoO\(_6\)) can be indexed on a monoclinic cell, which was similar with parent Bi\(_2\)MoO\(_6\). It indicates that solid solutions, which crystallized as single monoclinic phase structure with space group P2\(_1\)/c, were obtained in (Bi\(_1-x\)Ln\(_x\))\(_2\)MoO\(_6\) (\(x \leq 0.3\)) and (Bi\(_1-x\)Nd\(_x\))\(_2\)MoO\(_6\) (\(x \leq 0.2\)) ceramics. The diffraction peaks (080) and (002) separated from each other with the substitution of Bi\(^{3+}\) by Nd\(^{3+}\) and/or La\(^{3+}\), because the cell parameters varied with substitution. In the (Bi\(_0.7\)Nd\(_{0.3}\))\(_2\)MoO\(_6\) ceramics, a small amount of tetragonal Nd\(_2\)MoO\(_6\) phase with space group \(I\bar{4}_{1}/a\cd\) was detected besides the Bi\(_2\)MoO\(_6\) solid solution phase. As we know, both pure Nd\(_2\)MoO\(_6\) and La\(_2\)MoO\(_6\) crystallize as tetragonal crystal structure with \(I\bar{4}_{1}/a\cd\) phase structure. In the range of (Bi\(_1-x\)Nd\(_x\))\(_2\)MoO\(_6\) ceramics, almost all the diffraction peaks of (Bi\(_1-x\)Nd\(_x\))\(_2\)MoO\(_6\) (\(x \leq 0.3\)) ceramics can be indexed as a single monoclinic phase structure with space group P2\(_1\)/c.

3. Results and discussion

Fig. 1 presents X-ray diffraction patterns of the (Bi\(_1-x\)Nd\(_x\))\(_2\)MoO\(_6\) and (Bi\(_1-x\)La\(_x\))\(_2\)MoO\(_6\) ceramics. Almost all the diffraction peaks of the samples (except (Bi\(_0.7\)Nd\(_0.3\))\(_2\)MoO\(_6\)) can be indexed on a monoclinic cell, which was similar with parent Bi\(_2\)MoO\(_6\). It indicates that solid solutions, which crystallized as single monoclinic phase structure with space group P2\(_1\)/c, were obtained in (Bi\(_1-x\)Ln\(_x\))\(_2\)MoO\(_6\) ceramics. Almost all the diffraction peaks of the samples (except (Bi\(_0.7\)Nd\(_0.3\))\(_2\)MoO\(_6\)) can be indexed on a monoclinic cell, which was similar with parent Bi\(_2\)MoO\(_6\). It indicates that solid solutions, which crystallized as single monoclinic phase structure with space group P2\(_1\)/c, were obtained in (Bi\(_1-x\)Ln\(_x\))\(_2\)MoO\(_6\) ceramics. Almost all the diffraction peaks of the samples (except (Bi\(_0.7\)Nd\(_0.3\))\(_2\)MoO\(_6\)) can be indexed on a monoclinic cell, which was similar with parent Bi\(_2\)MoO\(_6\). It indicates that solid solutions, which crystallized as single monoclinic phase structure with space group P2\(_1\)/c, were obtained in (Bi\(_1-x\)Ln\(_x\))\(_2\)MoO\(_6\) ceramics. Almost all the diffraction peaks of the samples (except (Bi\(_0.7\)Nd\(_0.3\))\(_2\)MoO\(_6\)) can be indexed on a monoclinic cell, which was similar with parent Bi\(_2\)MoO\(_6\). It indicates that solid solutions, which crystallized as single monoclinic phase structure with space group P2\(_1\)/c, were obtained in (Bi\(_1-x\)Ln\(_x\))\(_2\)MoO\(_6\) ceramics. Almost all the

\[
T \text{CF} = \frac{T_r - T_0}{T_r \times (T - T_0)} \times 10^6 \text{ppm/°C},
\]

where \(T_r\) and \(T_0\) are the TE01 resonant frequencies at temperature T and T0 (room temperature), respectively.

![Fig. 1. X-ray diffraction patterns of (a) (Bi\(_1-x\)Nd\(_x\))\(_2\)MoO\(_6\) and (b) (Bi\(_1-x\)La\(_x\))\(_2\)MoO\(_6\) ceramics.](image-url)
temperatures could not be too high to densify \((\text{Bi}_{1-x}\text{Ln}_x)\text{MoO}_6\) \((\text{Ln}=\text{Nd and La})\) ceramics.

Fig. 3 presents SEM images of as-fired surfaces of the \((\text{Bi}_{1-x}\text{Ln}_x)\text{MoO}_6\) and \((\text{Bi}_{1-x}\text{La}_x)\text{MoO}_6\) ceramics. All the ceramics had been well densified with little pores inside. The gains were uniform and there was no secondary phase grains in all \((\text{Bi}_{1-x}\text{La}_x)\text{MoO}_6\) \((x \leq 0.3)\) ceramics and \((\text{Bi}_{0.9}\text{Nd}_{0.1})\text{MoO}_6\) ceramic. In the \((\text{Bi}_{0.8}\text{Nd}_{0.2})\text{MoO}_6\) and \((\text{Bi}_{0.7}\text{Nd}_{0.3})\text{MoO}_6\) ceramics, a small amount of secondary phase grains with octahedral shape were detected in the grain boundaries, which might be tetragonal \(\text{Nd}_2\text{MoO}_6\) grains according to the XRD results above. It means that the secondary phase appeared in \((\text{Bi}_{0.8}\text{Nd}_{0.2})\text{MoO}_6\) ceramic, but the amount was too small to be detected by XRD experimental. On the other hand, the secondary phase grains gathered to the surface of the sample, so they can only be observed on the surface from SEM image.

Microwave dielectric properties of \((\text{Bi}_{1-x}\text{Nd}_x)\text{MoO}_6\) and \((\text{Bi}_{1-x}\text{La}_x)\text{MoO}_6\) ceramics were shown in Fig. 4. Permittivity decreased gradually with the substitution for \(\text{Bi}^{3+}\) by \(\text{Nd}^{3+}\) and/or \(\text{La}^{3+}\) because of their smaller dielectric polarizabilities of \(\text{Nd}^{3+}\) \((5.01 \text{ Å}^3)\) and \(\text{La}^{3+}\) \((6.07 \text{ Å}^3)\) than \(\text{Bi}^{3+}\) \((6.12 \text{ Å}^3)\) [29]. Permittivity decreased from 31.5 of pure \(\text{Bi}_2\text{MoO}_6\) ceramic to 22.6 at \(x=0.3\) for \((\text{Bi}_{1-x}\text{Nd}_x)\text{MoO}_6\) ceramics and to 20.7 at \(x=0.3\) for \((\text{Bi}_{1-x}\text{La}_x)\text{MoO}_6\) ceramics, respectively. Permittivity of the \((\text{Bi}_{1-x}\text{Nd}_x)\text{MoO}_6\) ceramic was a little larger than that of \((\text{Bi}_{1-x}\text{La}_x)\text{MoO}_6\) ceramic with the same \(x\) value, which might be attributed to the influence of the secondary phase \(\text{Nd}_2\text{MoO}_6\).

It is shown in Fig. 4(b) that Qf value first increased remarkably...
and then decreased slightly with the increase of substitution amount. Maximum Qf values were achieved at x=0.2, and the maximum Qf values were 30,200 GHz in (Bi0.8Nd0.2)2MoO6 ceramics and 32,900 GHz in (Bi0.8La0.2)2MoO6 ceramics, respectively. TCF value of (Bi1–xNd2)2MoO6 (Ln=Nd and La) ceramics shifted towards zero with the substitution of Bi3+ by Nd3+ and/or La3+, as shown in Fig. 4(c). When x=0.3, the TCF values of (Bi1–xNd2)2MoO6 and (Bi1–xLa2)2MoO6 ceramics were −70 and −85 ppm/°C, respectively. It means that both temperature stability and Qf value can be improved by appropriate substitution of Bi3+ by Nd3+ and/or La3+ in Bi2MoO6 system. Table 1 presents the sintering temperatures and microwave dielectric properties of several typical microwave dielectrics.

Table 1: Sintering Temperatures and Microwave Dielectric Properties of Several Typical Microwave Dielectrics

<table>
<thead>
<tr>
<th>Sample</th>
<th>S.T. (°C)</th>
<th>Permittivity</th>
<th>Qf value (GHz)</th>
<th>TCF (ppm/°C)</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>SnAl2O4</td>
<td>1650</td>
<td>20.4</td>
<td>65,000</td>
<td>−74</td>
<td>[31]</td>
</tr>
<tr>
<td>LaAl2O4 + 0.25 wt% CuO</td>
<td>1460</td>
<td>20.7</td>
<td>48,000</td>
<td>−80</td>
<td>[33]</td>
</tr>
<tr>
<td>BiTe2O6</td>
<td>650</td>
<td>21</td>
<td>50,300</td>
<td>−51</td>
<td>[32]</td>
</tr>
<tr>
<td>NdAl2O3</td>
<td>1650</td>
<td>22.3</td>
<td>58,000</td>
<td>−33</td>
<td>[31]</td>
</tr>
<tr>
<td>LiNb2O6</td>
<td>1075</td>
<td>24</td>
<td>58,000</td>
<td>−96</td>
<td>[30]</td>
</tr>
<tr>
<td>(Bi0.8La0.2)2MoO6</td>
<td>930</td>
<td>23.6</td>
<td>32,900</td>
<td>−96</td>
<td>This work</td>
</tr>
<tr>
<td>(Bi0.8Nd0.2)2MoO6</td>
<td>930</td>
<td>24.2</td>
<td>30,200</td>
<td>−91</td>
<td>This work</td>
</tr>
<tr>
<td>Li2ZnTi3O8</td>
<td>1075</td>
<td>25.6</td>
<td>72,000</td>
<td>−11.2</td>
<td>[34,35]</td>
</tr>
<tr>
<td>Li2MgTi3O8</td>
<td>1075</td>
<td>27.2</td>
<td>42,000</td>
<td>+3.2</td>
<td>[34,35]</td>
</tr>
</tbody>
</table>

S.T.: Sintering Temperature.

4. Conclusions

Microwave dielectric ceramics, (Bi1–xNd2)2MoO6 and (Bi1–xLa2)2MoO6 were prepared by conventional solid state reaction method. Solid solutions with monoclinic structure were obtained for (Bi1–xLa2)2MoO6 ceramics when x ≤ 0.3. While in the (Bi1–xNd2)2MoO6 ceramics, tetragonal Nd2MoO6 phase with space group I41/acd appeared when x ≥ 0.2 besides the Bi2MoO6 solid solution phase. With the increase of substitution amount, sintering temperature of the (Bi1–xNd2)2MoO6 and (Bi1–xLa2)2MoO6 ceramics increased from 850 °C to about 970 °C, and permittivity decreased from 31.5 to 22.6 and 20.7, respectively. Both temperature stability and Qf value were improved. Maximum Qf values were 30,200 GHz in (Bi0.8Nd0.2)2MoO6 ceramics and 32,900 GHz in (Bi0.8La0.2)2MoO6 ceramics, respectively. TCF value of (Bi1–xNd2)2MoO6 ceramics shifted towards zero with the substitution of Bi3+ by Nd3+ and/or La3+. When x=0.3, TCF values of (Bi1–xNd2)2MoO6 and (Bi1–xLa2)2MoO6 ceramics were −70 and −85 ppm/°C, respectively.

Acknowledgments

This work was supported the Young Star Project of Science and Technology of Shaanxi Province (2015JXXJ-39) and the State Key Laboratory of New Ceramic and Fine Processing Tsinghua University (grant number KF201507).

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