Study of elastic moduli of low temperature sintered $\text{Ni}_{0.5}\text{A}_{0.5}\text{Nb}_2\text{O}_6$ for LTCC ($A = \text{Ca, Mg, Cu}$)

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Abstract

$\text{Ni}_{0.5}\text{A}_{0.5}\text{Nb}_2\text{O}_6$ ($A = \text{Ca, Mg, Cu}$) columbites have been prepared using sol–gel technique sintered at 900 $^\circ$C for 6 h as per the firing temperature of LTCC. Structural characterization has been done using X-ray diffraction method and morphology by FESEM. Elastic properties have been characterized for mechanical compatibility toward the application in LTCC technology. Elastic moduli and acoustic Debye temperature were computed employing ultrasonic pulse transmission technique by measuring longitudinal and shear velocities. Porosity correction has been done using Hasselman and Fulrath’s formula and estimation using Modi’s heterogeneous metal-mixture rule. The variation of elastic moduli was interpreted in terms of strength of interatomic bonding.

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1. Introduction

Low temperature cofired ceramics (LTCC) is a new emerging technology enabling the miniaturization of electronic circuits. LTCC offers significant benefits over conventional printed circuit board (PCB) for use in RF and high density fast digital applications that could require hermeticity with good thermal, dielectric and mechanical properties. Unlike the other technologies, the low firing temperature of 900–1000 $^\circ$C in LTCC allows conducting metals of high electrical conductivity like silver, gold and copper to be used for conducting lines. Their low melting point which ranges from 950 $^\circ$C to 1050 $^\circ$C restricts their use in those technologies where the firing temperature is $>1100$ $^\circ$C. Hence the low firing temperature of 900 $^\circ$C in LTCC permits the use of these good conductors and hence reduces the overall transmission loss of the signal in the substrate of the electronic circuits. This characteristic also helps in achieving less delay of the signal propagation as well as less power consumption.

The materials available in the market for LTCC substrate are glass and ceramic composites. Although the addition of glass reduces the sintering temperature and enhances the properties of the composite for its use in LTCC substrate, it also reacts with the conductor and deteriorates certain properties as well as the compatibility. Hence, in the present investigation the glass free ceramics materials were studied to satisfy the requirement of LTCC substrate.

In the era of finding a suitable substrate material for LTCC technology, niobates have been reported for providing compatible results with lower cost as well as availability. Their
properties are already reviewed extensively [1] but at a higher sintering temperature.

In this present work, a series of single phase columbites viz. \( \text{NiO}_x\text{A}_{0.5}\text{NbO}_6 \) (\( A = \text{Ca}, \text{Mg}, \text{Cu} \)) has been prepared using sol–gel technique at a sintering temperature of 900 °C. Structural characterization of these samples has been done using XRD. Densities of the samples were measured using Archimedes principle. The determination of the elastic constants of these materials will provide ample information regarding mechanical strength, fracture toughness, and thermal shock resistance. This study is done employing ultrasonic pulse-transmission (UPT) technique at room temperature [2]. The measured values were corrected to zero porosity using Has- selman and Fulrath’s formula [3] and compared with model given by Modi et al. [4].

### 2. Experimental

The starting materials used for preparation of powders \( \text{NiO}_x\text{A}_{0.5}\text{NbO}_6 \) (\( A = \text{Ca}, \text{Mg}, \text{Cu} \)) using sol–gel method for the present study were calcium nitrate \( [\text{Ni(NO}_3]_2\cdot6\text{H}_2\text{O} \) (FINAR), magnesium nitrate \( [\text{A(NO}_3]_2\cdot6\text{H}_2\text{O} \) (FINAR), niobium chloride \( \text{NbCl}_5 \) (Sigma–Aldrich), ethylene glycol (EG) (FINAR) and citric acid anhydrous (CA) (FINAR), with purities of over 99.9%. First, the stoichiometric amount of calcium nitrate, magnesium nitrate and niobium ethoxide were dissolved in distilled water. Niobium ethoxide, \( \text{Nb}[(\text{OC}_2\text{H}_5)_5] \), was synthesized from niobium chloride and ethanol \( (\text{C}_2\text{H}_5\text{OH}) \), according to the general reaction (1) [5–7]:

\[
\text{NbCl}_5 + 5\text{C}_2\text{H}_5\text{OH} \rightarrow \text{Nb}[(\text{OC}_2\text{H}_5)_5] + 5\text{HCl}
\] (1)

A sufficient amount of citric acid was added as a chelating agent to form a solution. Citric acid to the total metal ions in the molar ratio of 3:2 was used for this purpose. The pH was adjusted to 7 and EG is also added as a stabilizing agent. The precursor containing A and Nb was stirred and heated till the volume of the solution was 2/3 of its original volume. Then it was dried at 120 °C for 10 h, and then the \( \text{NiO}_x\text{A}_{0.5}\text{NbO}_6 \) (\( A = \text{Ca}, \text{Mg}, \text{Cu} \)) powders were obtained after calcinations at 700 °C for 4 h in air. Above mentioned powders were ground and pressed into pellets. Then the samples were sintered at 900 °C for 6 h.

The structural phase formation of the sintered samples was studied by XRD using Rigaku X-ray Diffractometer for 2\( \theta \) values from 10° to 60° at a slow rate. The ultrasonic measurements were carried out by the UPT technique at room temperature (300 K) [8]. Longitudinal and shear velocities have been measured using X- and Y-cut quartz transducers, respectively, with a fundamental frequency of 1 MHz. The rf pulses generated by the pulse oscillator were applied to the transmitting transducer, which converts them into acoustic pulses. These acoustic pulses, after propagating through the test sample, were converted back into electrical signals by the receiving transducers. The amplified output signal was displayed on a 100 MHz digital storage oscilloscope (Tektronix model No. 2221). The difference in time \( \Delta T \) between two overlapping received pulse trains was noted using a timer. The velocity of sound was measured using the equation \( V = \frac{t}{\Delta T} \), where \( t \) is the thickness of the sample. The overall accuracy of these measurements is ±10 ms−1.

The density of these synthesized samples has been measured using Archimedes principle.

### 3. Results and discussion

#### 3.1. XRD

The XRD patterns of sintered powder samples were shown in Fig. 1. It can be seen that all the diffraction peaks of main crystal phase can be indexed in accordance with orthorhombic phase of ANbO\(_6\) (\( A = \text{Ca}, \text{Mg}, \text{Cu}, \text{Ni} \)). These peaks were matched with JCPDS file no. (CaNbO\(_6\)): 71-2406, Pbcn; MgNbO\(_6\): 88-0708, Pbcn; CuNbO\(_6\): 39-0562, Pcan; NiNbO\(_6\): 73-1519, Pbcn) giving orthorhombic structure. The 2\( \theta \) value shifts to the larger end for smaller lattice parameters [9].

Average crystallite sizes of the samples are calculated using the formula given below.

\[
D = \frac{k \times \lambda}{\beta \times \cos(\theta)}
\] (2)

where \( k = \text{constant} = 0.90; \lambda = \text{wavelength of X-ray} = 0.1542 \text{nm}; \beta = \text{half peak width; and} \theta = 1/2 \text{ of } 2\theta \).

The average crystallite sizes of the prepared samples were tabulated in Table 1. The values are of 40–60 nm.

Bulk density measured was provided in Table 1. Bulk density for Cu is more followed by Ni, Mg and Ca. The variation with doping observed is uniform with the doping. Copper niobate forms at a lower temperature as compared to that of magnesium followed by nickel and then calcium. Hence doping may provide easier sinterability and better density. Same time due to difference in structural symmetry, the proper formation is hindered which may lead to lower density. These values are lower compared to the earlier reported due to the present low sintering temperature, i.e. 900 °C but are optimum from LTCC substrate point of view.

#### 3.2. FESEM

For morphology analysis, FESEM has been carried over these four samples. It is shown in Fig. 2. One can observe that the grain growth varies with different compositions. It may be due to their ease of sinterability such as for Mg doping as compared to Ca doping at lower temperature where the better grain growth has been observed. Better density in case...
of copper doping as compared to others has been observed. The doping sometimes acts as hindrance in grain growth due to different structural orientations of the pure compositions. Hence doped composition presents a lesser grain size as compared to the original pure compositions. The grain size is well matched with that of measured from XRD results.

3.3. Elastic properties

The values of elastic constants were calculated using the longitudinal ($v_L$) and shear ($v_S$) velocities obtained from UPT and employing the following formulae [10]:

\[
\text{Longitudinal modulus, } L = \rho v_L^2,
\]

(3)

\[
\text{Shear modulus, } G = \rho v_S^2.
\]

(4)

\[
\text{Bulk modulus, } B = L^{-4/3} G
\]

(5)

\[
\text{Poisson's ratio, } \sigma = \frac{3B - 2G}{2B + 2G}
\]

(6)

\[
\text{Young's modulus, } E = (1 + \sigma)2G
\]

(7)

The acoustic Debye temperature ($\theta_D$), at which nearly all modes of vibrations in a solid are excited, plays an important role in the study of a large number of solid-state problems involving lattice vibrations. Hence, the values of $\theta_D$ were determined using the following Anderson formula [11]:

\[
\theta_D = \frac{h}{K_B} \left( \frac{3\rho N_A q}{4\pi M} \right)^{1/3} v_m
\]

(8)

where $h$ is the Planck constant, $K_B$ is the Boltzmann constant, $\rho$ is the bulk density of the sample, $N_A$ is the Avogadro number, $q$ is the number of atoms in the unit formula (in the present case $q = 4$), $M$ is the molecular weight and $v_m$ is the mean sound velocity.

$v_m$ is given by the following formula using Debye's rule:

\[
v_m = \left[ \frac{1}{3} \left( \frac{1}{v_L^3} + \frac{2}{v_S^3} \right) \right]^{-1/3}
\]

(9)

The measured values of elastic constants are summarized in Table 2. As the materials under the present investigation are porous ($C \approx 0.1–0.2$), the measured elastic moduli were

![Fig. 1 – XRD patterns of Ni$_{0.5}$A$_{0.5}$Nb$_2$O$_6$ (A = Ca, Mg, Cu).](image)
corrected to zero porosity using the following Hasselman and Fulrath (HF) formulae [3]:

\[
\frac{1}{E_0} = \frac{1}{E} \left[ 1 - \frac{3(1 - \sigma)(9 + 5\sigma)}{2(7 - 5\sigma)} \right]
\]  

(10)

\[
\frac{1}{G_0} = \frac{1}{G} \left[ 1 - \frac{15(1 - \sigma)}{7 - 5\sigma} \right]
\]  

(11)

Recently, Modi et al. [4] have developed a model, known as Modi heterogeneous metal-mixture rule (MMMR) to estimate the elastic constants. According to this model, the value of elastic constant or acoustic Debye temperature can be calculated by using the following formula:

\[
B_0 = \frac{E_0G_0}{3(3G_0 - E_0)}
\]  

(12)

\[
K^* = \frac{1}{n} \sum_{\pi} c_n K_n
\]  

(14)

**Table 2** – Measured elastic moduli and Debye temperature of Ni\(_{0.5}A_{0.5}\)Nb\(_2\)O\(_6\) (A = Ca, Mg, Cu).

<table>
<thead>
<tr>
<th>Sample</th>
<th>(v_L) (m s(^{-1}))</th>
<th>(v_S)</th>
<th>(v_m)</th>
<th>(L)</th>
<th>(G)</th>
<th>(B)</th>
<th>(E) (GPa)</th>
<th>(\sigma)</th>
<th>(\theta_0) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CaNb(_2)O(_6)</td>
<td>3692</td>
<td>1973</td>
<td>2047</td>
<td>49.82</td>
<td>14.23</td>
<td>30.8</td>
<td>34.15</td>
<td>0.2</td>
<td>157</td>
</tr>
<tr>
<td>2. Ca(<em>{0.5})Ni(</em>{0.5})Nb(_2)O(_6)</td>
<td>3789</td>
<td>2173</td>
<td>2240</td>
<td>53.4</td>
<td>17.56</td>
<td>29.9</td>
<td>43.9</td>
<td>0.25</td>
<td>169.5</td>
</tr>
<tr>
<td>3. NiNb(_2)O(_6)</td>
<td>3929</td>
<td>2371</td>
<td>2431</td>
<td>61.1</td>
<td>22.2</td>
<td>31.7</td>
<td>54.17</td>
<td>0.22</td>
<td>186</td>
</tr>
<tr>
<td>4. Mg(<em>{0.5})Ni(</em>{0.5})Nb(_2)O(_6)</td>
<td>3873</td>
<td>2339</td>
<td>2398</td>
<td>57.3</td>
<td>20.9</td>
<td>29.4</td>
<td>50.58</td>
<td>0.21</td>
<td>184.6</td>
</tr>
<tr>
<td>5. MgNb(_2)O(_6)</td>
<td>3829</td>
<td>2199.8</td>
<td>2267</td>
<td>55.11</td>
<td>18.21</td>
<td>30.84</td>
<td>45.5</td>
<td>0.25</td>
<td>176</td>
</tr>
<tr>
<td>6. Cu(<em>{0.5})Ni(</em>{0.5})Nb(_2)O(_6)</td>
<td>3986</td>
<td>2462</td>
<td>2517.5</td>
<td>63.7</td>
<td>24.3</td>
<td>31.3</td>
<td>58.32</td>
<td>0.2</td>
<td>193.2</td>
</tr>
<tr>
<td>7. CuNb(_2)O(_6)</td>
<td>3970</td>
<td>2478</td>
<td>2531</td>
<td>67</td>
<td>26.1</td>
<td>32.3</td>
<td>61.6</td>
<td>0.28</td>
<td>197.4</td>
</tr>
</tbody>
</table>
Table 3 – Porosity corrected and modeled elastic moduli of Ni$_{0.5}$A$_{0.5}$Nb$_2$O$_6$ (A = Ca, Mg, Cu).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity fraction</th>
<th>$G_0$</th>
<th>$B_0$</th>
<th>$E_0$</th>
<th>$\sigma_0$</th>
<th>$G^*$</th>
<th>$B^*$</th>
<th>$E^*$</th>
<th>$\sigma^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>23.4</td>
<td>57.23</td>
<td>61.78</td>
<td>0.32</td>
<td>27.8</td>
<td>119</td>
<td>76.7</td>
<td>0.37</td>
</tr>
<tr>
<td>2</td>
<td>0.18</td>
<td>27.07</td>
<td>50.87</td>
<td>68.98</td>
<td>0.27</td>
<td>39.1</td>
<td>146.2</td>
<td>106.7</td>
<td>0.37</td>
</tr>
<tr>
<td>3</td>
<td>0.14</td>
<td>30.76</td>
<td>44.13</td>
<td>74.89</td>
<td>0.22</td>
<td>50.33</td>
<td>173.33</td>
<td>136.7</td>
<td>0.37</td>
</tr>
<tr>
<td>4</td>
<td>0.15</td>
<td>29.79</td>
<td>42.56</td>
<td>72.46</td>
<td>0.22</td>
<td>40.6</td>
<td>150.8</td>
<td>110.9</td>
<td>0.37</td>
</tr>
<tr>
<td>5</td>
<td>0.16</td>
<td>26.5</td>
<td>60.9</td>
<td>69.43</td>
<td>0.31</td>
<td>31</td>
<td>128.3</td>
<td>85</td>
<td>0.36</td>
</tr>
<tr>
<td>6</td>
<td>0.13</td>
<td>26.21</td>
<td>67.99</td>
<td>69.66</td>
<td>0.33</td>
<td>36.17</td>
<td>144.15</td>
<td>98.85</td>
<td>0.37</td>
</tr>
<tr>
<td>7</td>
<td>0.12</td>
<td>34.43</td>
<td>41.87</td>
<td>81.07</td>
<td>0.28</td>
<td>41.33</td>
<td>160</td>
<td>112.7</td>
<td>0.38</td>
</tr>
</tbody>
</table>

where $K^*$ is either elastic modulus or acoustic Debye temperature of the composition to be estimated, $n$ is the total number of metal cations in the unit chemical formula, $c$ is the concentration of the $n^{th}$ cation in the formula unit, while $K$ is the corresponding modulus or acoustic Debye temperature of the metallic element. The elastic moduli and the Debye temperature values of the metallic elements are taken from the literature [12,13] to estimate $K^*$. These modeled values are provided in Table 3 with porosity corrected values.

The variation in elastic parameters can be interpreted in terms of strength of inter-atomic bonding [14]. When smaller ions are replaced by larger ions [1], the length of inter-atomic bonding increases and results in the decrease in strength of inter atomic bonding, which in turn decreases the elastic moduli.

From the above results, it can be observed that both measured and corrected values of elastic moduli change in the same manner and it confirms the quality of the test samples. The measured and corrected values of Poisson’s ratio are found to be in good agreement (Tables 2 and 3) and lie in the theoretical range from –1 to 0.5.

The decrease in the acoustic Debye temperature (Table 2) suggests the enhancement in lattice vibrations with substitution [4].

4. Conclusion

The values of elastic moduli of Ni$_{0.5}$A$_{0.5}$Nb$_2$O$_6$ (A = Ca, Mg, Cu) columbites at room temperature were reported and porosity corrections were also presented. The observed decrease in the elastic constants with substitution suggests the weakening of the inter-atomic bonding. The decrease in acoustic Debye temperature suggests the enhancement of lattice vibrations. Moreover, the presented elastic properties of these samples are providing satisfactory results toward the application as LTCC substrate.

Conflicts of interest

The authors declare no conflicts of interest.

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References