MECHANICAL PROPERTIES OF $CA_XMG_{1-X}NB_2O_6$ FOR LTCC (X=0,0.2,0.4,0.6,0.8,1)

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Abstract

A series of $Ca_xMg_{1-x}Nb_2O_6$ *(x=0,0.2,0.4,0.6,0.8,1)* columbites has been prepared using sol-gel technique. The samples were sintered at 900^0C for 6 hours. Structural characterization of the prepared samples has been done using X-ray diffraction (XRD) method. Microstructure has been studied using SEM. To study their applicability in low temperature cofired ceramic (LTCC) technology, elastic properties have been characterized for mechanical compatibility. Elastic behaviour was investigated at 300 K, employing ultrasonic pulse transmission technique at 1 MHz. The values of elastic moduli and acoustic Debye temperature (μD) were computed from longitudinal and shear velocities. The measured values were corrected to zero porosity using Hasselman and Fulrath's formula. The elastic constants of the samples, estimated using Modi's heterogeneous metal-mixture rule, were also reported. The variation of elastic moduli was interpreted in terms of strength of interatomic bonding.

Keywords: Columbite, sol-gel, elastic modulii, Debye temperature, LTCC.

I. INTRODUCTION

Low Temperature Cofired Ceramics (LTCC) is a new emerging technology enabling the miniaturization of electronic circuits. LTCC offers significant benefits over conventional PCBs (Printed circuit Board) 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°C to 1000°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°C to 1050°C restricts their use in those technologies where the firing temperature is $>$ 1100°C. Hence the low firing temperature of 900°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. $Ca_xMg_{1-x}Nb_2O_6$ *(x=0,0.2,0.4,0.6,0.8,1)* 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. Microstructure plays major role in determining the mechanical properties. 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 Hasselman and Fulrath's formula [3] and compared with model given by Modi et al. [4].

II. EXPERIMENTAL METHOD

The starting materials used for preparation of powders $Ca_xMg_{1-x}Nb_2O_6$ using sol–gel method for the present study were calcium nitrate [$Ca(NO_3)_2 \cdot 6H_2O$] (FINAR), magnesium nitrate [$Mg(NO_3)_2 \cdot 6H_2O$] (FINAR), niobium chloride ($NbCl_5$) (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, $Nb(OC_2H_5)_5$, was synthesized from niobium chloride and ethanol, (C_2H_5OH), according to the general reaction (1) [5-7]:

$$NbCl_5 + 5C_2H_5OH \longrightarrow Nb(OC_2H_5)_5 + 5HCl) \quad (1)$$

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 2/3rd of its original volume. Then it was dried at 120°C for 10 h, and then the $Ca_xMg_{1-x}Nb_2O_6$ *(x=0,0.2,0.4,0.6,0.8,1)* powders were obtained after calcinations at 700°C for 4h in air. Above mentioned powders were grinded and pressed into pellets. Then the samples were sintered at 900°C for 6 hrs.

The structural phase formation of the sintered samples was studied by XRD using Rigaku X-ray Diffractometer for 2θ 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 amplifed output signal was displayed on a 100 MHz digital storage oscilloscope (Tektronix model No. 2221). The difference in time *T* between two overlapping received pulse trains was noted using a timer. The velocity of sound was measured using the equation $V = t/T$, where t is the thickness of the sample. The overall accuracy of these measurements is $\pm$ 10 ms^{-1}.

The density of these synthesized samples have been measured using Archemedes principle.

III. RESULTS AND DISCUSSION

A 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 ANb_2O_6 (A = Ca, Mg). These peaks were matched with JCPDS file no. ($CaNb_2O_6$: 71-2406, Pbcn; $MgNb_2O_6$: 88-0708, Pbcn;) giving orthorhombic structure. The 2θ value shifts to the larger end for smaller lattice parameters [9].

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

$$D = \frac{k \times \lambda}{\beta \times \cos(\theta)} \quad (2)$$

Where

k = constant = 0.89

λ = wavelength of X-ray = 0.1542 nm

β = half peak width

θ = 1/2 of 2θ

The average crystallite size of the prepared samples were tabulated in Table I. The values are of 40-50 nm which were in good agreement with the earlier reported values. Bulk density and porosity were provided in Table I.

Table 1: Average Crystallite Size, Density & Porosity

Sample	Avg. crystalline size (nm)	Density (gm/cc)	C
$CaNb_2O_6$	44	3.655	0.2
$Ca_{0.8}Mg_{0.2}Nb_2O_6$	39	2.954	0.15
$Ca_{0.6}Mg_{0.4}Nb_2O_6$	44	3.205	0.14
$Ca_{0.4}Mg_{0.6}Nb_2O_6$	44	3.359	0.13
$Ca_{0.2}Mg_{0.8}Nb_2O_6$	50	3.641	0.12
$MgNb_2O_6$	50	3.759	0.16

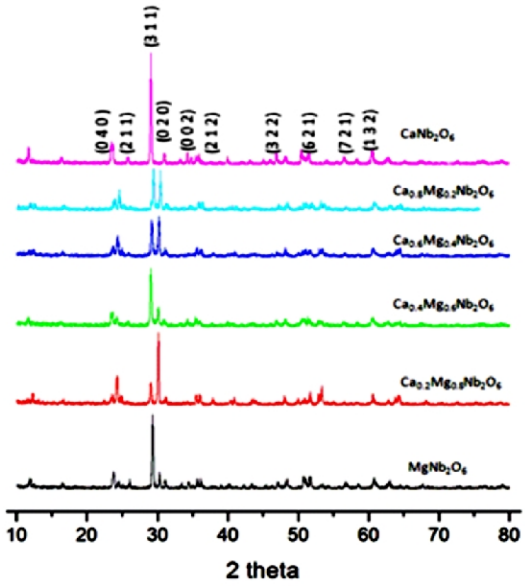

Fig. 1. XRD pattern of $Ca_XMg_{1-X}Nb_2O_6$

B. *Microscopy Characterization*

The microstructure plays a major contributing role in controlling mechanical properties of the composition. Hence microstructure has been studied by Scanning Electron Microscopy (SEM). The pictures have shown in figure 2.

From the figures it can be seen that the compositions are of single phases and the grain sizes are of nanocrystalline order and grain sizes increases with magnesium content but the variation is not much and it is due to the difference in ionic radius or covalency.

C. *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].

$$\text{longitudinal modulus, } L = \rho v_L^2 \tag{3}$$

$$\text{shear modulus, } G = \rho v_s^2 \tag{4}$$

$$\text{bulk modulus, } B = L - \frac{4}{3} G \tag{5}$$

$$\text{Poisson's ratio, } \sigma = \frac{3B - 2G}{6B + 2G} \tag{6}$$

$$\text{Young's modulus, } E = (1 + \sigma)\, 2G \tag{7}$$

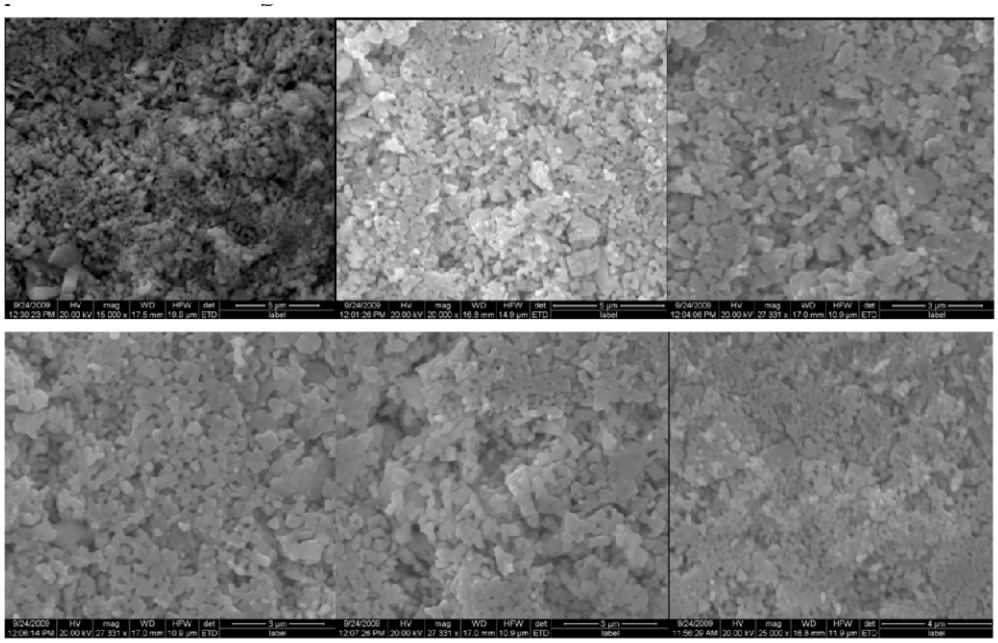

Fig. 2 SEM pictures of $Ca_XMg_{1-X}Nb_2O_6$

The acoustic Debye temperature ($_D$), 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 $_D$ were determined using the following Anderson formula [11].

$$\theta_D = \frac{h}{K_B}\left(\frac{3\rho N_A q}{4\pi M}\right)^{1/3} v_m \quad (8)$$

where h is the Planck constant, K_B is the Boltzmann constant, ρ 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

$$v_m = \left[\frac{1}{3}\left(\frac{1}{v_L^3} + \frac{3}{v_S^3}\right)\right]^{-1/3} \quad (9)$$

The measured values of elastic constants are summarized in Table II. As the materials under the present investigation are porous (C 0.1-0.2), the measured elastic moduli were corrected to zero porosity using the following Hasselmanand Fulrath (HF) formulae [3].

$$\frac{1}{E_0} = \frac{1}{E}\left[1 - \frac{3C(1-\sigma)(9+5\sigma)}{2(7-5\sigma)}\right] \quad (10)$$

$$\frac{1}{G_0} = \frac{1}{G}\left[1 - \frac{15C(1-\sigma)}{7-5\sigma}\right] \quad (11)$$

$$B_0 = \frac{E_0 G_0}{3(3G_0 - E_0)} \quad (12)$$

$$\sigma_0 = \frac{E_0}{2G_0} - 1 \quad (13)$$

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

$$K^* = \frac{1}{n}\sum_n c_n K_n \quad (14)$$

where K^* is either elastic modulus or acoustic Debye temperature of the composition to be estimated, nl 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 III with porosity corrected values.

The variation in elastic parameters with Ca content can be interpreted in terms strength of inter atomic bonding [14]. When smaller Mg^{2+} ions (0.72 A) are replaced by larger Ca^{2+} (1.00 A) ions [1], the length of inter atomic bonding increases and results in

Table 2: Measured Elastic Moduli & Debye Temperature

Sample	v_L	v_S	v_m	L	G	B	E	σ	θ_D (K)
	(m/s)			(GPa)					
1. $CaNb_2O_6$	3692	1973	2047	49.82	14.23	30.84	37	0.2	157
2. $Ca_{0.8}Mg_{0.2}Nb_2O_6$	3989	1968	2053	47	11.44	19.07	28.6	0.25	146
3. $Ca_{0.6}Mg_{0.4}Nb_2O_6$	3838	1956	2036	47.2	12.26	20.43	30.65	0.25	149
4. $Ca_{0.4}Mg_{0.6}Nb_2O_6$	3813	2004	2082	48.8	13.49	22.5	33.73	0.25	155
5. $Ca_{0.2}Mg_{0.8}Nb_2O_6$	3687	1962	2037	49.5	13.99	23.34	34.98	0.25	157
6. $MgNb_2O_6$	3829	2199.8	2267	55.11	18.2	37.29	46.96	0.29	176

Table 3: Porosity Corrected & Modeled Elastic Moduli

Sample	G_0	B_0	E_0	σ_0	G^*	B^*	E^*	σ^*
	(GPa)				(GPa)			
1	23.4	57.23	61.78	0.32	27.8	119	76.7	0.37
2	16.2	28.33	40.82	0.26	21.3	90.65	58.75	0.28
3	16.9	29.58	42.59	0.26	21.8	92.05	60	0.27
4	18.1	31.6	45.6	0.26	22.3	93.45	61.25	0.27
5	18.3	32.04	46.12	0.26	22.8	94.85	62.5	0.27
6	26.5	60.9	69.43	0.31	31	128.3	85	0.36

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 II and III) and lie in the theoretical range from – 1 to 0.5.

The increasing Ca concentration results in the decrease in the acoustic Debye temperature (Table II), which suggests the enhancement in lattice vibrations with Ca substitution [4].

D. Thermo mechanical Properties

Thermal properties like thermal conductivity and thermal coefficient of expansion influence the mechanical properties. So thermal conductivity (K) and thermal coefficient of expansion (á) have been measured for this series. Other mechanical properties like yield strength (Sy), tensile strength (St), and thermal shock resistance (Tsr) can be calculated using following formulae.

$$Sy = G/2\pi \quad (15)$$

$$St = 0.05 * E \quad (16)$$

$$Tsr = K*St/(E * \alpha) \quad (17)$$

These values are given in table 1V.

Table 4: Thermomechanical Properties

Sample	K (W/m. K)	α (ppm/ $^{\circ}C$)	Sy (GPa)	St (GPa)	Tsr ($x10^6W$)
1	2.5	2.97	2.265	1.85	0.04
2	1.2	2.2	1.821	1.43	0.027
3	1.3	2.3	1.95	1.53	0.028
4	1.4	2.8	2.147	1.69	0.025
5	1.5	3	2.227	1.75	0.025
6	3	4.3	2.897	2.35	0.035

IV. CONCLUSION

The values of elastic moduli of $Ca_xMg_{1-x}Nb_2O_6$ *(x=0,0.2,0.4,0.6,0.8,1)* columbites at room temperature were reported and porosity corrections were also presented. The observed decrease in the elastic constants with Ca substitution suggests the weakening of the inter atomic bonding with the increase in Ca content. The decrease in acoustic Debye temperature suggests the enhancement of lattice vibrations with Ca substitution. Mechanical properties viz. tensile and yield strength along with thermal shock resistance have been measured too.

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