Dielectric and Thermal Studies of ANb_2O_6 (A=Ca, Mg, Cu, Ni) for LTCC Application

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***Abstract*—A series of ANb_2O_6 (A=Ca, Mg, Cu, Ni) columbites and 50% Ni doped with $CaNb_2O_6$,$MgNb_2O_6$ and $CuNb_2O_6$ has been prepared using sol-gel technique. The samples were sintered at 9000C for 6 hours. Structural characterization of the prepared samples has been done using X-ray diffraction (XRD) method. To study their applicability in low temperature cofired ceramic (LTCC) technology, dielectric and thermal properties have been characterized. Microwave dielectric properties like dielectric constant and Qf values over Ku-band for all the compositions have been measured. Dielectric constant was found to fall between 4.8 to 10. Thermal properties like thermal conductivity and thermal coefficient of expansion (TCE) were measured over a temperature range from room temperature to 900 0C. Thermal conductivity was found to be of the order of 1-2 W/m 0K while TCE was of the order of 5-10 x 10-6/0C. TCE of some of the compositions have shown negative value at 900 0C.**

***Index Terms*— LTCC, sol-gel, dielectric constant, niobates, ku-band, thermal conductivity, thermal coefficient of expansion.**

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 require hermeticity with good thermal, dielectric and mechanical properties. Unlike the other technologies, the low firing temperature of 900^0C to 1000^0C 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 ^{0}C to 1050 ^{0}C restricts their use in those technologies where the firing temperature is > 1100 ^{0}C. Hence the low firing temperature of 900 ^{0}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. ANb_2O_6 (A=Ca,Mg,Cu,Ni) and 50% Ni doped with $CaNb_2O_6$,$MgNb_2O_6$ and $CuNb_2O_6$ has been prepared using sol-gel technique at a sintering temperature of 900 ^{0}C. Structural characterization of these samples has been done using XRD. Dielectric properties viz. ε_r and Qf values have been measured over Ku-band frequency using network analyser. Densities of the samples were measured using Archimedes principle. Thermal properties viz. thermal conductivity, specific heat and thermal expansion coefficient have been measured over a temperature range upto 900^0C. Thermal studies of these samples have not been reported earlier.

II. EXPERIMENTAL

The starting materials used for preparation of ANb_2O_6 (A=Ca,Mg,Cu,Ni) powders using sol–gel method for the present study were calcium nitrate $[A(NO_3)_2{\cdot}6H_2O]$(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) [2]-[4].

$$NbCl_5 + 5C_2H_5OH \rightarrow Nb(OC_2H_5)_5 + 5HCl. \qquad (1)$$

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 ^{0}C for 10 h, and then the ANB_2O_6 (A=Ca, Mg, Cu, Ni) powders were obtained after calcinations at 700 ^{0}c for 4h in air. above mentioned powders were grinded and pressed into pellets. then the samples were sintered at 900^0 c for 6hrs. The structural phase formation of the sintered samples was studied by xrd using rigaku x-ray diffractometer for 2θ values from 10^0 to 60^0 at a slow rate. Dielectric characterization which includes dielectric constant and

Manuscript received October 9, 2001; revised November 20, 2011.

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Qfactor of the samples has been done by Nicolson-Rose method using agilent PNA network analyser. Thermal Conductivity of the samples experiment has been carried out using Laser Flash Analysis technique (LFA 427 of Netzsch) and thermal coefficient of expansion of the samples has been measured using a Thermo-mechanical analyser (TMA), machine model: TMA Q400, TA Instruments, USA with a dilatometer kit.

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, Cu, Ni). These peaks were matched with JCPDS file no.($CaNb_2O_6$: 71-2406,Pbcn; $MgNb_2O_6$: 88-0708,Pbcn; $CuNb_2O_6$: 39-0562,Pcan; $NiNb_2O_6$:73-1519,Pbcn) giving orthorhombic structure. The 2θ value shifts to the larger end for smaller lattice parameters[5].

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

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

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 1. The values are of 40-50 nm which were in good agreement with the earlier reported values.

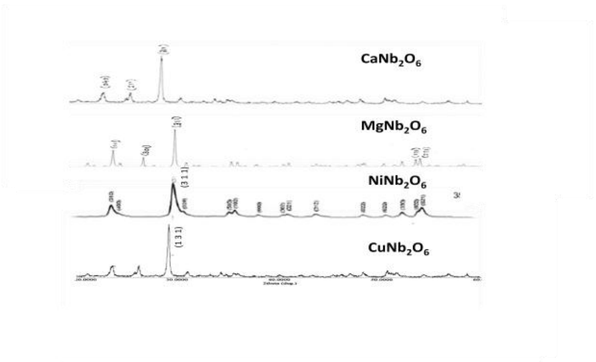

Fig. 1. XRD pattern of ANb_2O_6

TABLE I : AVERAGE CRYSTALLITE SIZE

Sample	Avg. crystallite size in nm
$CaNb_2O_6$	44
$MgNb_2O_6$	50
$NiNb_2O_6$	55
$CuNb_2O_6$	62

B. *Dielectric Studies*

The dielectric constant of a sample is defined as the root over of the ratio of velocity of electromagnetic signal in vacuum to velocity in the sample. The greater the dielectric constant of the material, the slower the wave propagation. So for the transmission of electromagnetic signal in the substrate for the electronic circuits, dielectric constant of the material used for the fabrication of that substrate should be low. On the other hand, greater value of the dielectric constant of the substrate used for the fabrication of the electronic circuit provides more miniaturization of the circuitry. LTCC provides not only the faster communication of the signal but also miniaturization to the total volume of the electronic package. Hence the optimised value for a material to be useful for LTCC substrate is chosen to be between 5 to10 [6], [7].

The measurement of the dielectric constant for all the samples was carried out by Nicolson-rose method i.e transmission-reflection cavity method using a PNA series of Agilent made network analyser over the frequency range from 14 GHz to 18 GHz. At higher frequencies, the dielectric constant is mainly due to lattice contribution. As the charge careers fail to respond to the applied external electric field, the electronic and ionic polarizations are poor at higher frequencies. The dielectric constant vs. frequency for all the basic samples along with Ni doped with $CaNb_2O_6$, $MgNb_2O_6$ and $CuNb_2O_6$ were shown in the figure 2. The decrease of ε was easily understood because of the reduced ionic radii[1]. Lower ionic radius provides less contribution towards ionic polarization and hence a lower value of dielectric constant [8]. The increase of ε in $CuNb_2O_6$ might be due to high density compared to the other samples in the respective series and hence with $Ni0_{.5}Cu_{0.5}Nb_2O_6$. Porous material consists of high concentration of air which may reduce the dielectric constant of the material. The measured dielectric constants of these present samples were less than the earlier reported ones [9]. This is due to the lower sintering temperature of 900 ^{0}C than that of the reported one. This was understood that as the 100% density could not been achieved at this lower temperature, the measured dielectric constant has been low [10].

For practical applications, the dielectric constant of the substrate should not vary much with frequency. From the results obtained over the Ku-band frequency, it shows that the variation of dielectric constant of these samples w.r.t frequency is of the order of $0.4x10^{-10}$ Hz^{-1} which is negligible. The error in this measurement is 0.2% as per the measurement technique standard.

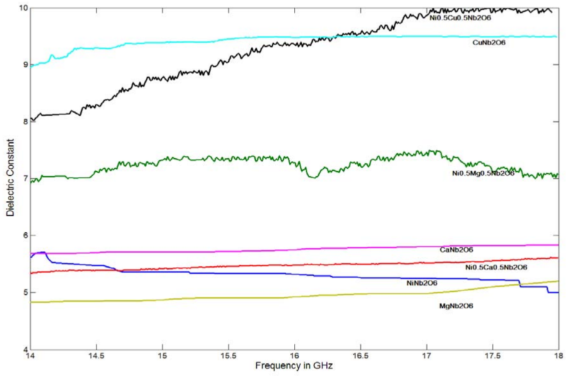

Fig. 2. Dielectric constant vs. frequency

The loss tangent values and Qf values [6] calculated were given in the table 2. The increase in loss tangent values may be due to space charge accumulation which due to dielectric dispersion process at higher frequency and unfilled outer electron shells[11]. Qf values have a linear relation with crystallite size as observed in the present case.

The measured Qf values of the present samples were less than that of the earlier reported values which is perhaps the reason of low sintering temperature of 900^0C[12]. As it is earlier discussed that lower sintering temperature provides a lesser density, the Qf values were found to be less [13].

C. *Thermal Studies*

Thermal studies are carried out to ensure the compatibility as well as thermal stability of these samples towards LTCC application.

1) *Thermal conductivity*

Thermal Conductivity explains about the amount of heat flow throughout the material. For better thermal stability, the heat flow should be high i.e thermal conductivity should be high, so that it can diffuse the heat. The Thermal conductivity of the available LTCC substrate in market is of >2 W/m.K[6].

Thermal conductivity measurement for four samples has been tabulated in table 2. This is measured from thermal diffusivity, density and specific heat of the sample. The relationship is given in equation 3.

$$K = \rho \times C_P \times \alpha \qquad (3)$$

where

K = Thermal conductivity
α = Thermal diffusivity
ρ = Density
C_P= Specific heat at constant pressure

The thermal conductivity has decreased with increase in temperature for all the samples which may be due to the reduction in phonon mean path[14]. It can be seen that thrmal conductivity varies linearly with density.

Densities of these samples were measured using Archimedes principle. They are tabulated in table 2. The nonlinear variation of density with the composition may be attributed to the porosity of the samples.

2) *Thermal Coefficient of Expansion(Tce) (α):*

Thermal coefficient of expansion (α) describes the amount of expansion takes place in the sample linearly at a particular temperature. LTCC substrate has to mount active elements on it. For better performance these elements are chosen to be of silicon. α of silicon is 3.5 x 10^{-6} /^{0}C. So the TCE of substrate material should be of 3-4 x 10^{-6} /^{0}C [6].

From the results tabulated in table 2, the inferences can be drawn as some of these samples have shown negative TCE values at 900^0C. There are four general mechanisms resulting in Negative Thermal Expansion(NTE): (i) shortening of bond lengths and phase changes; (ii) bridging atoms and rigid-unit vibrational modes (RUMs);(iii) magnetostriction; and (iv) electronic effects[15]. During phase transition, the perpendicular vibration along bond axis leads to the contraction of the sample[16]. Transverse low–energy phonon modes of two–coordinate oxygens may be responsible for this phenomenon. Also, it is generally assumed that polyhedra in the structure of the sample are inherently distorted in order to make a framework connected via vertices. However, these assumptions have never been quantitatively evaluated at structural level, although it has been strongly suggested that stretching and bending modes (high–energy optical phonons) tetrahedra contribute to negative value of TCE [17]. This NTE behaviour of these samples may restrict their firing temperature for LTCC fabrication.

TABLE II: QF VALUES, DENSITY, THERMAL CONDUCTIVITY AND TCE

Sample	Qf values (GHz)	Density (gm/cc)	Thermal Conductivity (W/m.K)	TCE at 100^0C (x 10^{-6} /^{0}C)	TCE at 900^0C (m x 10^{-6} /^{0}C)
$CaNb_2O_6$	1500	3.655	1.2	9	-3.7
$MgNB_2O_6$	3000	3.759	1.5	8.3	7.8
$NiNb_2O_6$	9000	3.76	1.8	5.2	4.9
CuNb 2O6	17000	3.762	2	5.97	-15.86

IV. SUMMARIES

A series of ANb_2O_6 (A=Ca, Mg, Cu, Ni) and Ni doped with $CaNb_2O_6$,$MgNb_2O_6$ and $CuNb_2O_6$ have been prepared using sol-gel method and the samples are sintered at a temperature of 900^0 C. Columbite formation and crystallinity are studied by X-ray diffraction. The average grain size was found to be between 40 to 60 nm. Dielectric constants of the samples were found to be from 4.8 to 10 at ku-band. Thermal measurements like thermal conductivity and thermal expansion coefficient were carried out over temperature range from room temperature to 900 ^{0}C. Negative TCE values around 900 ^{0}C were obtained for some samples. Thermal Conductivity measured was of 1-2 W/^{0}K and TCE of 5-10 x 10^{-6} . Hence it is concluded that these samples can be sintered at 900 ^{0}C and all these dielectric as well as thermal properties measured are in good agreement for their use in LTCC technology

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