

Anomalous Thermal Behavior of $\text{Cu}_x\text{Mg}_{1-x}\text{Nb}_2\text{O}_6$ ($x=0,0.4,0.6,1$) for LTCC Substrate

Jyotirmayee Satapathy, M. V. Ramana Reddy

Abstract—LTCC (Low Temperature Co-fired Ceramics) being the most advantageous technology towards the multilayer substrates for various applications, demands an extensive study of its raw materials. In the present work, a series of $\text{Cu}_x\text{Mg}_{1-x}\text{Nb}_2\text{O}_6$ ($x=0,0.4,0.6,1$) has been prepared using sol-gel synthesis route and sintered at a temperature of 900°C to study its applicability for LTCC technology as the firing temperature is 900°C in this technology. The phase formation has been confirmed using X-ray Diffraction. Thermal properties like thermal conductivity and thermal expansion being very important aspect as the former defines the heat flow to avoid thermal instability in layers and the later provides the dimensional congruency of the dielectric material and the conductors, are studied here over high temperature up to the firing temperature. Although the values are quite satisfactory from substrate requirement point view, results have shown anomaly over temperature. The anomalous thermal behavior has been further analyzed using TG-DTA.

Keywords—Niobates, LTCC, Thermal conductivity, Thermal expansion, TG-DTA.

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 as 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 $> 1100^\circ\text{C}$. 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 [1], [2].

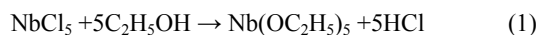
Furthermore, Circuit boards and packages undergo heat stress during assembly processes such as in solder reflow when LSI components and other electronic parts are mounted on them, and when reliability tests are performed before product shipment, so it is a concern that the interconnects between the board and components will lose their connection

reliability. As the thermal resistance of LTCCs is superior to that of resin materials, they offer better product reliability at high temperatures. In addition, the thermal expansion coefficient of LTCC is low compared with resin materials. Moreover, it has to be matched so that there should not be any deformation in the component as they all will be fired together. Greater thermal conductivity ensures no heat sink formation inside the layers. Thermal conductivity for LTCC substrate material should be greater than $1\text{-}2\text{ W/m}^2\text{K}$ and thermal expansion coefficient should be low which is $5\text{-}10 \times 10^{-6}/^\circ\text{C}$ [3].

In this present study, a series of $\text{Cu}_x\text{Mg}_{1-x}\text{Nb}_2\text{O}_6$ ($x=0,0.4,0.6,1$) has been prepared using sol-gel synthesis route. As the firing temperature of LTCC is around 900°C , these samples are sintered at a temperature of 900°C . Phase formation is characterized by XRD. To study the applicability in LTCC substrate materials, thermal behaviour such as thermal conductivity, specific heat and thermal expansion coefficient are measured over a temperature from room temperature up to 900°C . The anomalies have been justified by TG-DTA analysis.

II. EXPERIMENTAL

The starting materials used for preparation of powders $\text{Cu}_x\text{Mg}_{1-x}\text{Nb}_2\text{O}_6$ using sol-gel method for the present study were calcium nitrate $[\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ (FINAR), magnesium nitrate $[\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ (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 copper 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) [4]-[6]:



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 $A=(\text{Cu},\text{Mg})$ 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 10h, and then the $\text{Cu}_x\text{Mg}_{1-x}\text{Nb}_2\text{O}_6$ ($x=0,0.4,0.6,1$) 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 6h.

Ms. Jyotirmayee Satapathy and Prof. M.V. Ramana Reddy are with the Department of Physics, Osmania University, Hyderabad, 500007, India (e-mail: jsatapathy84@gmail.com).

The structural phase formation of the sintered samples was studied by XRD using Rigaku X-ray Diffractometer for 2θ values from 10° to 80° at a slow rate of $0.2^\circ/\text{sec}$. Thermal conductivity was calculated from thermal diffusivity and specific heat which are measured using LFA (Laser Flash Analysis) technique with instrument Netzsch LFA 427 over a temperature range from room temperature to 900°C using (2):

$$k(T) = K(T) \cdot d(T) \cdot C_p(T) \quad (2)$$

where k = Thermal Conductivity

K = Thermal Diffusivity

C_p = Specific heat

d = Density of the sample

T = Temperature

Thermal coefficient of expansion is a thermo mechanical parameter which is measured using Thermo Mechanical Analyser, TMA Q400, TA instruments, USA over a temperature from room temperature to 900°C .

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 ($A=\text{Cu, Mg}$). These peaks were matched with JCPDS file no. (CuNb_2O_6 : 39-0562, Pcan; MgNb_2O_6 : 88-0708, Pbcn) giving orthorhombic structure. The 2θ value shifts to the larger end for smaller lattice parameters. The splitting observed in the mixed compositions is perhaps due to the distortion produced due to different space groups of CuNb_2O_6 and MgNb_2O_6 . Also the red peaks indicate the presence of other phases of CuNb_2O_6 . Niobates give rise to columbite and perovskite phases like order-disorder transitions over temperature [7]-[9].

B. Thermal Conductivity

It can be seen from Fig. 2 that thermal conductivity has shown very non uniform and anomalous behaviour over temperature for different compositions. The anomaly due to Cu content may be due to the existence of secondary phases which can be related from the XRD result and the order-disorder transitions [10]. The phonon mean free path is hindered during the ordering of ions in the structure which is main cause of lowering of thermal conductivity [11]. Because, thermal conductivity is directly proportional to phonon mean free path [12], [13]. Other variations can be attributed to the porosity present in the sample as thermal conductivity is directly measured from the density using (2) because the specific heat of the samples have not shown much differences as shown in Fig. 3. From specific heat results, it can be inferred that there are no such phase transitions in these samples. Nevertheless, thermal conductivity of these samples varies from 1-3W/mK which is very much suitable for LTCC substrates. At lower temperature MgNb_2O_6 has a higher value

while at higher temperature CuNb_2O_6 has shown more satisfactory value for LTCC.

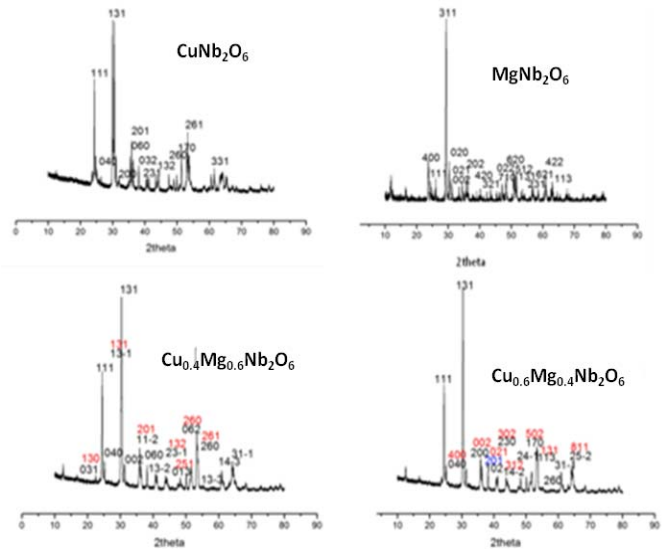


Fig. 1 XRD patterns of $\text{Cu}_x\text{Mg}_{1-x}\text{Nb}_2\text{O}_6$, ($x=0,0.4,0.6,1$)

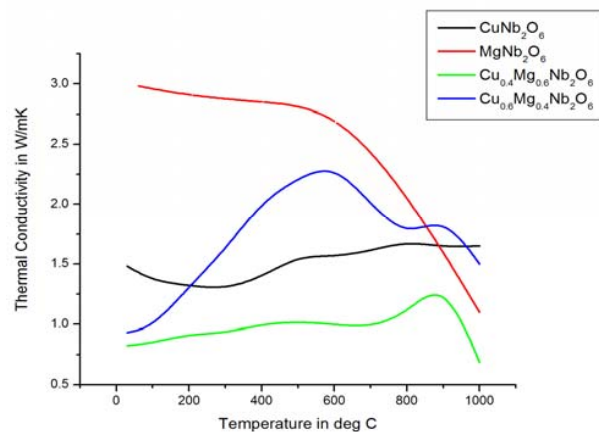


Fig. 2 Thermal conductivity over temperature of $\text{Cu}_x\text{Mg}_{1-x}\text{Nb}_2\text{O}_6$, ($x=0,0.4,0.6,1$)

C. Thermal Expansion Coefficient

From Fig. 4, it can be seen that thermal Expansion Coefficient of MgNb_2O_6 has a consistent value throughout the temperature scale which is very much accepted for LTCC. But peaks observed in copper doped as well as in CuNb_2O_6 perhaps due to the ordering of the perovskite to columbite phase and further disordering of columbite to other rutile phases at higher temperature [10]. The negative expansion coefficient can be attributed to the anisotropy property [13, 14] of the structure as well as due to the presence of secondary phases and symmetry variations.

The anomaly observed in $\text{Cu}_{0.6}\text{Mg}_{0.4}\text{Nb}_2\text{O}_6$ both in thermal conductivity and thermal expansion coefficient can be understood by TG-DTA analysis shown in Fig. 5. All the compositions have shown an endothermic peak at temperature

around 100°C which is attributed to the loss of organic compounds as there is no significant is observed. The exothermic peaks observed around 500-600°C for different compositions can be attributed to the crystallization or starting of the formation of the desired compound as there is no significant weight loss [15]. The stabilization in the curve at further temperature ensures that there is no phase transition other than the formation of the compound except that of $\text{Cu}_{0.6}\text{Mg}_{0.4}\text{Nb}_2\text{O}_6$. The huge weight loss and endothermic reaction observed in this composition at high temperature perhaps due to formation of different phase which can also be correlated with thermal conductivity and thermal expansion coefficient results.

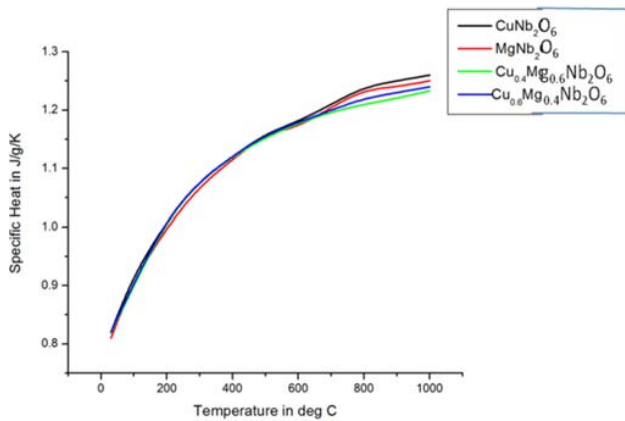


Fig. 3 Specific heat over temperature of $\text{Cu}_x\text{Mg}_{1-x}\text{Nb}_2\text{O}_6$, ($x=0,0.4,0.6,1$)

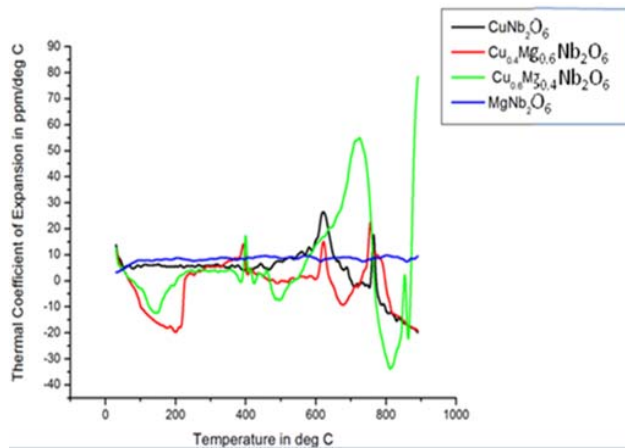


Fig. 4 Thermal coefficient of expansion over temperature of $\text{Cu}_x\text{Mg}_{1-x}\text{Nb}_2\text{O}_6$, ($x=0,0.4,0.6,1$)

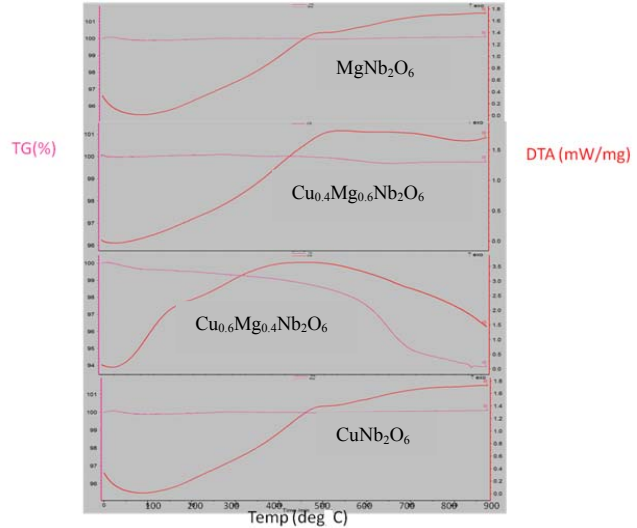


Fig. 5 TG-DTA analysis of $\text{Cu}_x\text{Mg}_{1-x}\text{Nb}_2\text{O}_6$, ($x=0,0.4,0.6,1$)

IV. CONCLUSION

In this present work, $\text{Cu}_x\text{Mg}_{1-x}\text{Nb}_2\text{O}_6$, ($x=0,0.4,0.6,1$) have been prepared using sol-gel route for the application towards LTCC substrate materials and sintered at a temperature of 900°C to match with the firing temperature of LTCC technology. Thermal behavior viz. thermal conductivity and thermal expansion coefficient have been studied over temperature up to 900°C. These values are mostly in regard with the required thermal behaviour of the materials for LTCC substrate. The anomalous behavior observed is analyzed with TG-DTA experiment.

REFERENCES

- [1] R. Pullar; D. Green; The Synthesis, Properties, and Applications of Columbite Niobates ($\text{M}^2\text{Nb}_2\text{O}_6$): A Critical Review; *Int. J. of Am. Cer.Soc.*, 92, 3, 2009, pp.563-762.
- [2] M. Sebastian and H. Jantunen; International Materials Reviews, 2008, 53.
- [3] Y. Imanaka, Fujitsu Laboratories, Multilayered Low Temperature Cofired Ceramics (LTCC) Technology, Ltd. Japan, ISBN: 0-387-23130-7, 2008, Springer.
- [4] Y. Hsiao, C. Liu, B. Dai, Y. Chang, Sol-gel synthesis and the luminescent properties of CaNb_2O_6 phosphor powders, *Journal of Alloys and Compounds*, 475, 1-2, 2008, pp.698-701.
- [5] Y. Hsiao, Y. Chang, G. Chen, Y. Chang, Synthesis and the luminescent properties of CdNb_2O_6 oxides by sol-gel process, *Journal of Alloys and Compounds*, 471, 2009, pp.259-262.
- [6] T. Fang, Y. Hsiao, Y. Chang, L. Ji, S. Kang, Luminescent and structural properties of MgNb_2O_6 nanocrystals, *Current Opinion in Solid State and Materials Science*, 12,3, 2009, pp.51-54.
- [7] H. Beck, H. Seup-Ra, R. Haberkorn, H. Kohlmann, M. Eul, T. Harmening, and R. Pöttgen, A Study on AB_2O_6 Compounds: Part I, Synthesis, Structure, Magnetic Properties and ^{151}Eu Mössbauer Spectroscopic Data of EuNb_2O_6 , *Z. Anorg. Allg. Chem.* 636, 2010, pp.1069-1073.
- [8] T. Chernaya, T. Volk, B. Maksimov, M. Blomberg, L. Ivleva, I. Verin, and V. Simonov, X-ray Diffraction Study of Cerium- and Thulium-Doped $(\text{Sr,Ba})\text{Nb}_2\text{O}_6$ Single Crystals, *Crystallography Reports*, 48, 6, 2003, pp. 933-938.
- [9] C. Lee, Y. Lin, and C. Huang, Cation Ordering and Dielectric Characteristics in Barium Zinc Niobate, *J. Am. Ceram. Soc.*, 90,2, 2007, pp. 483-489.

- [10] C. Santos, L. Zawislak, V. Antonietti, E Kinast and J. Cunha, Iron oxidation and order–disorder in the $(\text{Fe}^{2+}, \text{Mn})(\text{Ta}, \text{Nb})_2\text{O}_6$ – $(\text{Fe}^{2+}, \text{Mn})\text{Fe}_3(\text{Ta}, \text{Nb})_2\text{O}_8$ transition, *J. Phys.: Condens. Matter*, 11, 1999, pp.7021–7033.
- [11] R. Singh, S. Sanyal; Phonons in Condensed Matter Physics, 1990, Wiley Eastern Ltd, ISBN 81-224-0086-8.
- [12] J. Moreno-Piraján; Thermodynamics–interaction studies– solids, liquids and gases, 2011, *InTech, Croatia*; ISBN 978-953-307-563-1.
- [13] H. Ibach, H. Lüth; Solid-State Physics: An Introduction to Principles of Materials Science, 2009, *Springer Dordrecht Heidelberg London New York*, ISBN 978-3-540-93803-3.
- [14] B. Yates, Thermal Expansion, 1972, *Plenum Press*, New York-London; ISBN 0-306-30550-X.
- [15] Y. Zhanga, B. Fua, Q. Liua; Preparation of CuNb_2O_6 nanocrystalline powders by sol–gel method; *J. Alloys Compd.* (2008), doi:10.1016/j.jallcom.2008.10.108.