Production and development of tungsten based complex perovskite oxide ceramic components for temperature sensors for petroleum wells

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Abstract

In petroleum production, different types of sensors are required in the petroleum wells to monitor temperature, pressure and other vital parameters. These sensors work in very hostile environmental conditions.. In case of temperature sensors, normally, sensing elements are metals, which are very sensitive to environmental conditions and in this way they need to be embedded in highly inert materials. Ceramic embedded temperature sensors, i. e. thermistors, are frequently used for these purposes. Commercially such sensors are available in the international market but at exorbitant prices. Presently we are working on development and fabrication of thermistors using different types of embedding of complex perovskite oxide ceramics, which are highly inert in hostile environment. In the present work we have developed and characterized tungsten based complex cubic perovskite oxide ceramics Ba_2MWO_6 (where M – Ni, Mg) for their use as ceramic components for temperature sensors. These ceramics were produced by solid-state reaction process and sintered at different sintering conditions. Structural and microstructural characteristics of single phase sintered Ba_2MWO_6 ceramics studied by x-ray diffractometry and scanning electron microscopy show a homogenous surface morphology and particle size distribution, which is of vital importance for quality and mechanical strength of ceramic products. Initial electrical characterizations reveal a quite stable behavior of dielectric constant and tangent loss values at 1-2 GHz frequencies of these sintered ceramics. These characteristics show great potential of these ceramics as ceramic components for temperature sensors. Results and implications of the present work are presented and discussed in this article.

Keywords: Ba_2MgWO_6, Ba_2MWO_6, Sintering, Electron microscopy, Dielectric properties

1. Introduction

In petroleum production, different types of sensors are required in the petroleum wells to monitor temperature, pressure and other vital parameters. These sensors have to work in very hostile environmental conditions. Thus it is of prime importance they should exhibit extremely inert and stable behavior in such environmental conditions. In case of temperature sensors, normally, sensing elements are metals such as Au, Pt, Nb etc. which are very sensitive to environmental conditions and in this way they need to be embedded in highly inert materials. Ceramic embedded temperature sensors, i. e., thermistors, are quite suitable and frequently used for these purposes. Commercially such sensors are available in the international market but at exorbitant prices. Presently, we are working on development and fabrication of parallel type of thermistors using different types of ceramic embedding of complex perovskite oxide ceramics, which are highly inert in hostile environmental conditions. Perovskite oxide ceramics have several uses in high technology industries as sensors, fuel cells, catalysts, electronic packaging materials, substrates, high temperature components for mechanical and metallurgical applications etc. [1-3]. Production and functional ability of polycrystalline ceramic products are highly dependent oh their microstructural features, which in turn is highly influenced by sintering kinetics. In this sense we are carrying out a study on sintering behavior and microstructural characterization of perovskite oxide ceramics [4, 5]

In the above context, in the present work we have developed, sintered and characterized tungsten based complex perovskite oxide ceramics, Ba_2MWO_6 (where M – Ni, Mg). Ba_2MWO_6 ceramics are abbreviated as BMW ceramics in this article. Structural and microstructural characterization of sintered BMW ceramics were carried out by powder x-ray diffractometry and scanning electron microscopy, respectively. Electrical characterization of BMW ceramics carried out by dielectric constant and tangent loss factor measurements. This article reports these characteristics of BMW ceramics and discusses its implications on application viability as ceramic components for the fabrication of Pt based thermistors to be used in petroleum industry as temperature sensors in petroleum wells. Based on above characterization, we are in the process of fabrication of Pt based thermistors using these ceramics, which will be reported in a separate article, elsewhere.

2. Experimental details

BMW ceramic powder was prepared by conventional solid-state reaction route. High purity (99.99%) constituent oxides BaO, WO_3, MgO and NiO (as the case may be) were mixed in stoichiometric ratios, compacted at 3 ton/cm^2 and calcined at 1200ºC for 48h in ambient atmosphere, using a microprocessor controlled high temperature muffle furnace. In the calcinations process, green compacts were heated up to 600^{o}C at a rate of 15ºC/min and then rate of heating was maintained at 5ºC/min till 1200^{o}C. After calcinations at 1200ºC, samples were furnace cooled to room temperature. After calcinations, samples were examined by x-ray diffractometry. The calcination process was repeated twice to obtain single-phase material.

For the study of sintering behavior, BMW ceramic powders were produced in a typical batch size of 5 grams. These ceramic powders were thoroughly milled in an agate mortar with pestle for 1 h. We used analytical grade acetone as mixing medium and consequently, ethylene glycol (analytical purity) as lubrificating agent, in order to achieve better homogeneity. Thoroughly milled and homogenized BMW powders were uniaxially compacted in a metallic mould to form circular discs with 15 mm of diameter and 2 mm thickness. We used a pressing load of 5 -7 ton/cm^2 for 5 – 10 minutes to stabilize the pressure distribution in the pressed compact, using a hydraulic press.

The green compacted BMW ceramic bodies were subjected to the sintering process at different temperatures, ranging from 1200º to 1400ºC, during different durations of times. Sintering process of the samples was carried out in ambient environmental atmosphere in high purity alumina crucibles, using a high temperature muffle furnace (EDG 1700). The heating rate of the furnace was fixed at 15ºC/min for the temperatures up to 600ºC and 5ºC/min for the higher temperatures ranges, followed by furnace cooling till the ambient temperature.

To evaluate the sintering process, determine the structural characteristics and phase identification we investigated the sintered samples by powder X-ray difratometry (XRD) using a Siemens D-5000 Diffractometer, equipped with Cu - Kα radiation (λ = 1.5406 Å). Microstructural characteristics of the sintered ceramics were studied by a scanning electron microscope (Philips XL30 TMP), using both secondary and back-scattered electrons on polished and fractured surfaces. For the observation of polished surfaces in the scanning electron microscope, samples were polished with #240, #320, #400, #600 grade sand papers and diamond paste with 3, 6 and 1 μm granularity. To observe the microstructure the samples were annealed at 1000ºC for 6 minutes and covered with thin gold coating.

Dielectric constant and tangent loss factor of sintered BMW ceramics were measured by impedance method. In this technique a metal plate was attached on both sides of the ceramic disc, using silver paint. After painting, the solvent is removed by heating the system. The plates have a circular shape and a diameter smaller than the diameter of the ceramic disc to reduce border effects. To complete the device, copper wires are attached to the metal plates. For our ceramics, a metal disc with 1cm diameter is pasted on both sides of the sample. In this work these measurements were carried out with an impedance analyzer for the measurements up to 2 GHz.

3. Results and discussion

Powder X ray diffraction studies were carried out on all the sintered ceramic samples. All the ceramics presented a well-defined complex cubic perovskite structure. Presence of superstructural lines in the XRD spectra of Ba_2NiWO_6 ceramics reveal that Ba_2NiWO_6 ceramics have an ordered complex cubic perovskite structure with lattice constant a = 8.0748Å. As the structural characteristics of Ba_2NiWO_6 ceramics are well reported in literature, we are not going here in further details.

The XRD spectrum of a typical Ba_2MgWO_6 ceramic, sintered at 1200°C for 48h, is shown in Fig. 1. It consists of strong peaks characteristics of primitive cubic perovskite plus few weak reflection lines arising from the superlattices. No evidence for a distortion from the cubic symmetry is observed in the XRD spectrum. The basic perovskite composition is ABO_3, where A is a large ion suitable to the 12-coordinated cube-octahedral sites and B is a smaller ion suitable to the 6-coordinated octahedral site. Complex perovskite with mixed species on a site (particularly the B site) may be represented by multiples of this formula unit and a larger unit cell, e.g. $A_2BB'O_6$, $A_3B_2B'O_9$ etc [7]. Thus in Ba_2MgWO_6 composition, Ba^{2+}, with largest ionic radius (1.43 Å) occupies position A, Mg^{2+} (ionic radius 0.78 Å) and W^{4+} (ionic radius 0.68 Å) cations occupy B and B' positions in the B site due to their smaller ionic radii compared to that of Ba^{2+} cation. Due to the ordering of B and B' on octahedral site of the ABO_3 unit cell there is a doubling in the lattice parameter of the basic cubic perovskite unit cell. Thus, the whole XRD pattern of Ba_2MgWO_6 can be indexed in a $A_2BB'O_6$ cubic cell with the cell edge $a = 2a_p$ where a_p is the cell lattice of the cubic perovskite. The XRD spectrum of Ba_2MgWO_6 is similar to $A_2BB'O_6$ type complex cubic perovskite oxides e.g. YBa_2NbO_6, $ErBa_2SbO_6$, $DyBa_2NbO_6$ etc. reported in the JCPDS file, as judged by the similarity in d-spacings and intensity ratios. Presence of the superstructure reflection lines (111), (311) and (331) in the XRD spectrum of Ba_2MgWO_6 is the signature of an ordered complex cubic perovskite structure. In a substitutional solid solution BB', there is a random arrangement of B and B' on equivalent lattice positions in the crystal structure. Upon suitable heat treatment, the random solid solution rearranges into a structure in which B and B' occupy the same set of positions but in a regular way, such a structure is described as superstructure. In the superstructure, the positions occupied by B and B' are no longer equivalent and this feature is exhibited in the XRD spectrum of the material by the presence of superstructure reflection lines [8]. For double cubic perovskite of the formula $A_2BB'O_6$ the intensity, in particular of the (111) and/or (311) superstructure reflection, is proportional to the difference in scattering power of the B and B' atoms, when all the atoms are situated in the ideal position [8]. A disordered arrangement of B and B' should result in zero intensity. Therefore Mg^{2+} and W^{4+} cation ordering in Ba_2MgWO_6 in B and B' positions is clearly distinguished by the presence of the significant intensity of (111) and (311) superstructural reflection lines. Based on above discussion we have now indexed the XRD peaks of Ba_2MgWO_6 as an ordered complex cubic perovskite with $A_2BB'O_6$ crystal structure. The lattice parameter of Ba_2MgWO_6, calculated from the experimental XRD data is a_{exp} = 8.0356Å. This value is in good agreement with lattice parameter value a = 8.099 Å of Ba_2MgWO_6 reported in literature [6].

Production and functional ability of polycrystalline ceramic products are highly dependent on their microstructural features, which in turn are highly influenced by sintering kinetics Microstructural features define the final product quality of the ceramic products and their mechanical strength. Typical microstructures of Ba_2NiWO_6 ceramics, sintered at 1200 and 1300°C temperatures for 48h are shown in Figs. 2 and 3, respectively. An analysis of the SEM micrographs taken on polished and fracture surfaces of the sintered Ba_2NiWO_6 ceramics, presented in figs. 2(a), 2(c), 3(a) and 3(c), using secondary electrons, reveals that increase in sintering temperature from 1200 to 1300^{o}C improves considerably the surface morphology and increases the homogeneity of the particle size distribution. On the other hand, SEM microstructures, figs. 2(b) and 3(b), recorded by back-scattered electrons show that increase in sintering temperature does not help much in decreasing the porosity. In conclusion, these studies reveal that sintering conditions (1300^{o}C, 48h) provides homogenous surface morphology and particle size distribution of Ba_2NiWO_6 ceramics. Ceramics sintered at 1400oC present undesirable grain growth, therefore their microstructures are not shown here.

Typical SEM micrographs of Ba_2MgWO_6 ceramics sintered at 1200^{o}C, 1300^{o}C and 1400^{o}C are presented in Figs 4, 5 and 6, respectively. These micrographs reveal a gradual improvement in the microstructural features of the Ba_2MgWO_6 ceramics with increase in the sintering temperature. Both polished surface and fracture surface micrographs show that surface morphology and particle size distribution homogeneity increases with increase in sintering temperature. As back-scattered electron SEM micrographs reveal more in-depth microstructural features, we subjected both polished and fracture surfaces for this microscopic examination. As we can see in fig. 6c, back-scattered electron micrograph reveals the abnormal grain growth and presence of some amorphous phase in the Ba_2MgWO_6 ceramics sintered at 1400^{o}C. In this way, both Ba_2NiWO_6 and Ba_2MgWO_6 ceramics presented best microstructural features, such as surface morphology, particle size distribution and homogeneity when sintered at 1300^{o}C for 48h.

The sintering process uses the heat and diverse mechanisms of material transport to convert after ceramic into dense polycrystalline solids. The driving force in the sintering process is obtained by the reduction of the total surface energy, which increases the contact and growth between the grains. The smaller grains are transformed in to the bigger grains and, consequently, the pores substituted by the solid materials. The necessity to get uniformity in the microstructure is for preventing the creation of tensions that make to appear (or they magnify) empty spaces, for being concentrative of tensions, assist in the propagation of cracks and micro-cracks in the sintered body.

Dielectric constant and tangent loss factor of sintered BMW ceramics were measured on typical ceramic discs of 15 mm diameter and 2 mm thickness, using silver paste and platinum foils as electrode materials. These results are presented in Figs. 7 and 8, respectively. As seen in Figs. 7 and, variations of both dielectric constant and tangent loss factor at GHz frequencies of BMW ceramics present a quite stable behavior between 1 to 2 GHz. This type of stability is quite important in the design and fabrication of strips of the temperature sensing elements [6, 7] such as Au, Pt, Nb etc.and further functioning of the temperature sensors.

4. Conclusions

In this work, we have produced polycrystalline BMW ceramics using solid-sate reaction process and studied its structural characteristics, in detail, using powder X-ray diffractometry. Presence of superstructural lines in the XRD spectrum reveals that Ba_2MgWO_6 has an ordered complex cubic perovskite structure. Experimental lattice parameters of BMW ceramics are in close agreement with the lattice parameter reported earlier in literature. As our aim of this study is to evaluate potential application of these ceramics for ceramic components for temperature sensors for petroleum industries, where microstructural characteristics are of vital importance, we sintered these ceramics and studied their microstructural characteristics using scanning electron microscopy. Electrical characteristics were evaluated using dieletric constant and loss factor measurements. Our studies show a gradual improvement in microstructural characteristics of sintered Ba_2MgWO_6 ceramics with sintering temperature. This homogeneity of grain sizes and particle size distribution increases with increased sintering temperature, which results in higher sintered density and increased mechanical hardness. BMW ceramics sintered at 1300oC gave best results in terms of suface morphology and particle size distribution. Dielectric constant and tangent loss factor show quite stable behavior at 1-2 GHz frequencies. These favorable characteristics tend to show that BMW ceramics sintered at 1300^{o}C could be potential candidates for the fabrication of ceramic components for temperature sensors for temperature monitoring in petrolium wells.

Acknowledgements

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Figure captions:

Fig. 1: Powder X-ray diffraction patterns of Ba_2MgWO_6 ceramic, sintered at 1200ºC.

Fig. 2: Microstructure of Ba_2NiWO_6 ceramics sintered at 1200°C for 48h. (a) polished surface, secondary electrons, (b) polished surface, back-scattered electrons and (c) fracture surface

Fig..3 Microstructure of Ba_2NiWO_6ceramics sintered at 1300°C for 48h. (a) polished surface, secondary electrons, (b) polished surface, back-scattered electrons and (c) fracture surface

Fig. 4: Microstructure of Ba2MgWO_6, sintered at 1200º C for 48h (a) polished surface, secondary electrons, (b) fracture surface, secondary electrons and (c) fracture surface, backscattered electrons.

Fig. 5: Microstructure of Ba2MgWO_6, sintered at 1300º C for 48h (a) polished surface, secondary electrons, (b) fracture surface, secondary electrons and (c) fracture surface, backscattered electrons.

Fig. 6: Microstructure of Ba2MgWO_6, sintered at 1400º C for 48h (a) polished surface, secondary electrons, (b) fracture surface, secondary electrons and (c) fracture surface, backscattered electrons.

Fig.7 Variation of (a) dielectric constant and (b) tangent loss factor with GHz frequencies of BMW ceramics

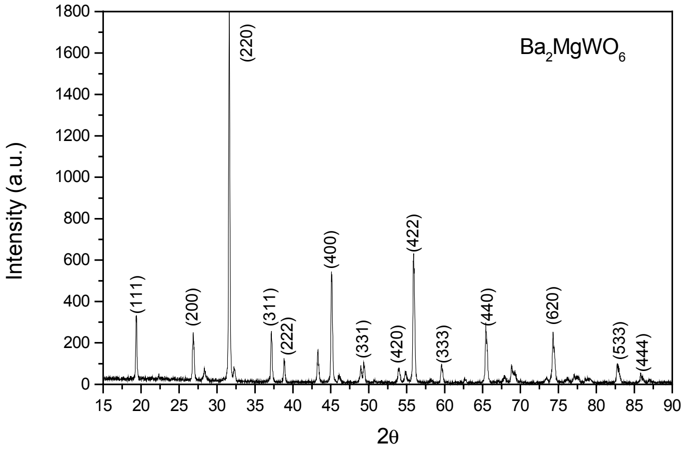


Fig. 1 – Yadava et al

(a) (b) (c)

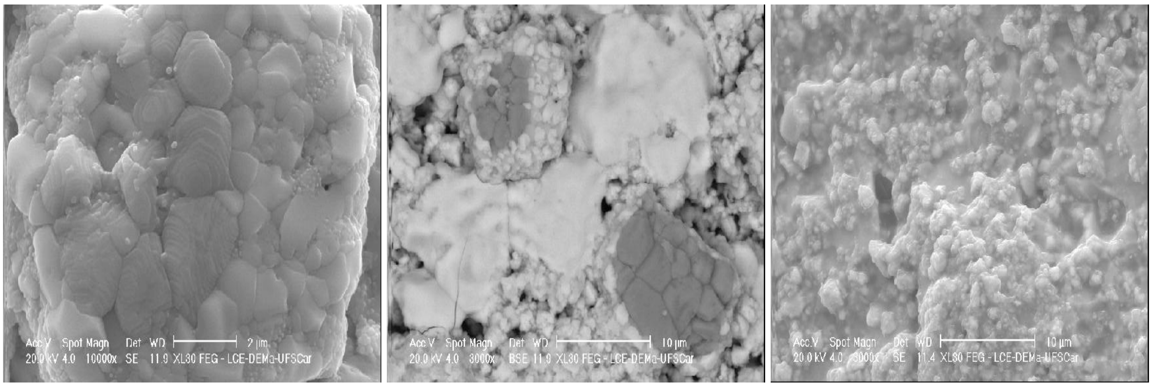
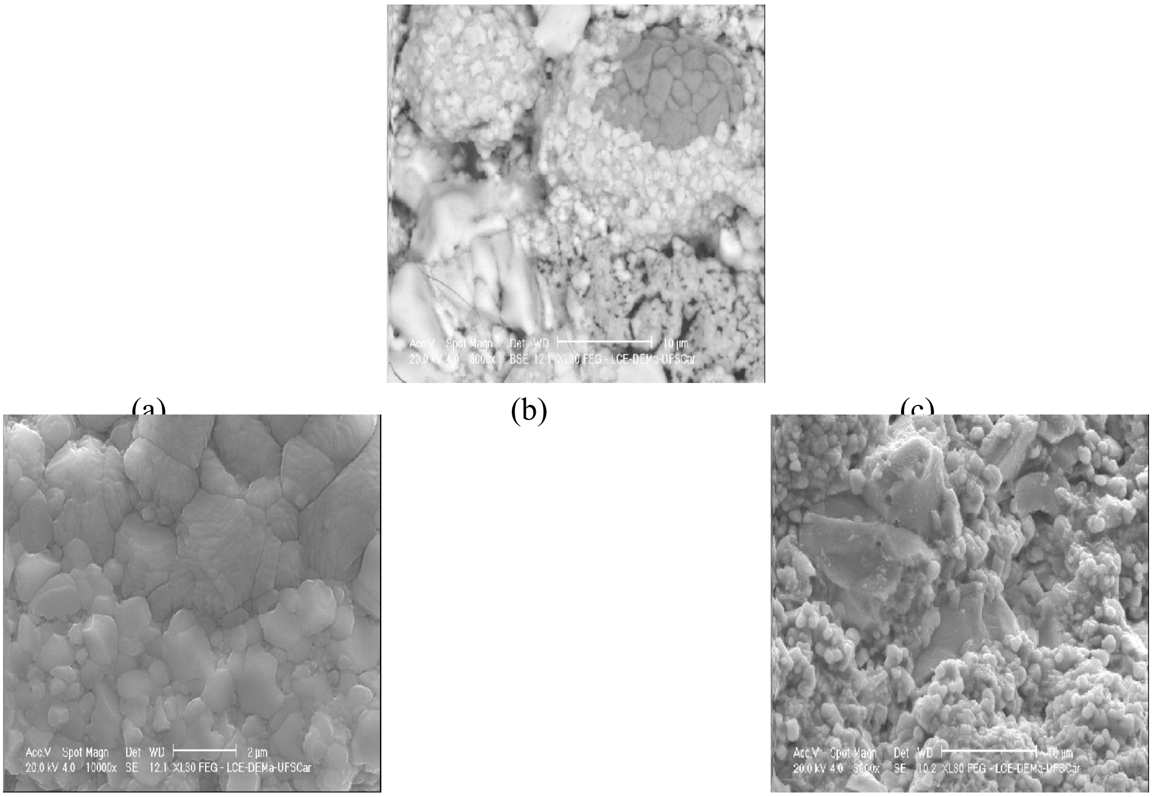
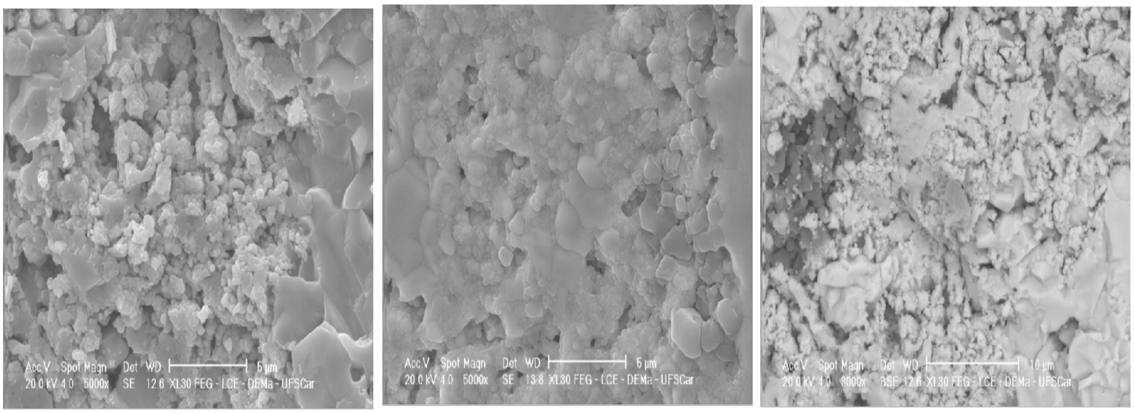


Fig. 2 – Yadava et al



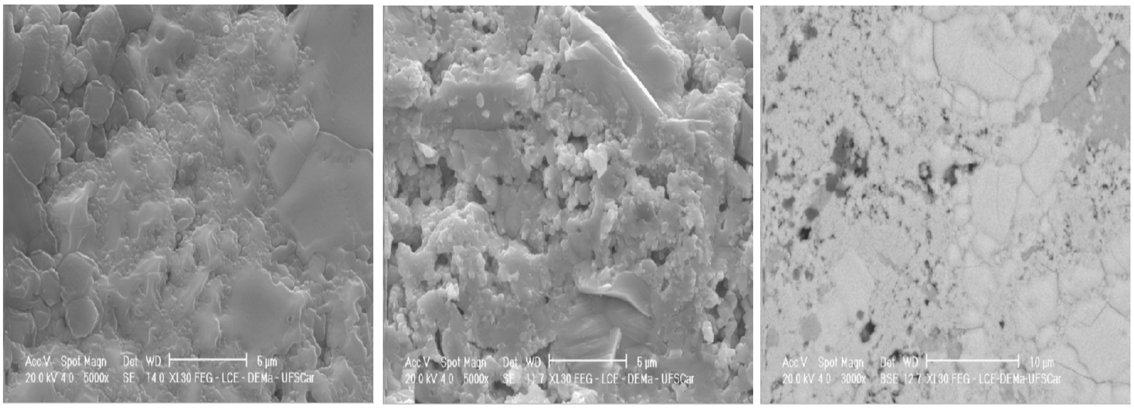
(a) (b) (c)

Fig. 3 – Yadava et al



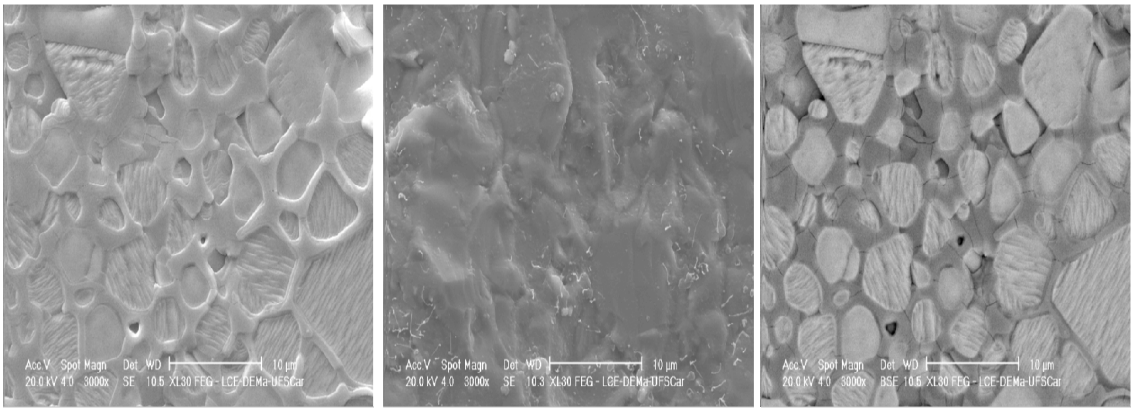
(a) (b) (c)

Fig. 4 – Yadava et al



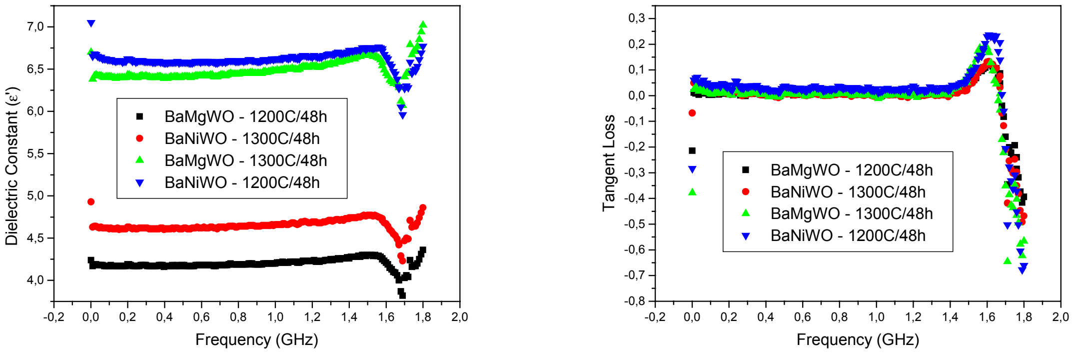
(a) (b) (c)

Fig. 5 – Yadava et al



(a) (b) (c)

Fig. 6 – Yadava et al



(a) (b)

Fig. 7 – Yadava et al