STUDY OF SINTERING BEHAVIOR AND MECHANICAL PROPERTIES OF Ba_2NiWO_6 CERAMICS

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Abstract: *Perovskite oxide ceramics have several uses in high technology industries as sensors, fuel cells, catalysts electronic packaging materials, substrates etc. Ni-perovskite oxide ceramics are reported as chemically inert and physically stable in hostile environment and due to this, these ceramics could be potential materials as ceramic components for temperature sensors for petroleum industries. Functional ability and performance of ceramics are highly dependent on their microstructure and mechanical properties, which in turn are greatly influenced by the sintering kinetics. In this context, we have carried out a study on sintering behavior and mechanical properties of Ni-perovskite oxide ceramics for sensor applications. In this work,* Ba_2NiWO_6 *ceramics were produced by solid-state reaction process. Fine-grained* Ba_2NiWO_6 *powders were compacted as circular discs (15 mm diameter, 5 mm thickness) at pressures of 7-10 ton/cm*^{2} *and sintered in the temperature range 1200 - 1600ºC for 48h in ambient atmosphere. Structural characteristics, studied by x-ray diffractmetry, show presence of the superstructural lines in XRD spectra revealing that* Ba_2NiWO_6 *ceramics have ordered complex cubic perovskite structure with lattice parameter a = 8.0748 angstroms. Microstructural features were investigated by scanning electron microscopy and mechanical hardness test was carried by Vickers micro-hardness tester. In this article, sintering kinetics of* Ba_2NiWO_6 *ceramics has been discussed in terms of microstructure, sintered density and Vickers micro-hardness variations in different sintering conditions.*

Keywords: *Ba_2NiWO_6 ceramics, sintering kinetic, microstructure, sintered density, Vickers micro-hardness*

1. INTODUCTION

Perovskite oxide ceramics have several uses in high technology industries as sensors, fuel cells, catalysts electronic packaging materials, substrates etc. (Tejuca and G. Fiero, 1993; Chandler, 1967; Brandle and Fratello, 1990; Kim and Chung, 1995; Fratello et al 1996; Hove and Riley, 1965). Ni-perovskite oxide ceramics are reported as chemically inert and physically stable in hostile environment and due to this, these ceramics could be potential materials as ceramic components for temperature sensors for petroleum industries (Fratello et al 1996). 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 embeddings Ni-based complex perovskite oxide ceramics

Functional ability and performance of ceramics are highly dependent on their microstructure and mechanical properties, which in turn are greatly influenced by the sintering kinetics. In this context, in the present work we have carried out a study on sintering behavior and mechanical properties of Ni-perovskite oxide ceramics, Ba_2NiWO_6, for such applications. In this work, Ba_2NiWO_6 ceramics were produced by solid-state reaction process. Fine-grained Ba_2NiWO_6 powders were compacted as circular discs (15 mm diameter, 5 mm thickness) at pressures of 7-10 ton/cm^2 and sintered in the temperature range 1200 - 1600ºC for 48h in ambient atmosphere. Structural characteristics, microstructural features and mechanical properties of sintered Ba2NiWO6 ceramics studied by x-ray diffractmetry, show presence of the superstructural lines in XRD spectra revealing that Ba_2NiWO_6 ceramics have ordered complex cubic perovskite structure with lattice parameter a = 8.0748 angstroms. Microstructural features were investigated by scanning electron microscopy and mechanical hardness test was carried by Vickers micro-hardness tester. In this article, sintering kinetics of Ba_2NiWO_6 ceramics has been discussed in terms of microstructure, sintered density and Vicker´s micro-hardness variations in different sintering conditions. This article reports these characteristics of Ba_2NiWO_6 ceramics and discusses its implications on application viability.

2. EXPERIMENTAL DETAILS

Ba_2NiWO_6 ceramics were prepared by conventional solid-state reaction route. High purity (99.99%) constituent oxides BaO, NiO and WO_3, were mixed in stoichiometric ratios, compacted at 4 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, Ba_2NiWO_6 ceramic powders were produced in a typical batch size of 5 grams. These ceramic powders were thoroughly milled in an agate mortar 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 Ba_2NiWO_6 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 7-10 ton/cm^2 for 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 temp eratures ranges, followed by furnace cooling till the ambient temperature. The flow chart of preparation and sintering processes are presented in Fig. 1.

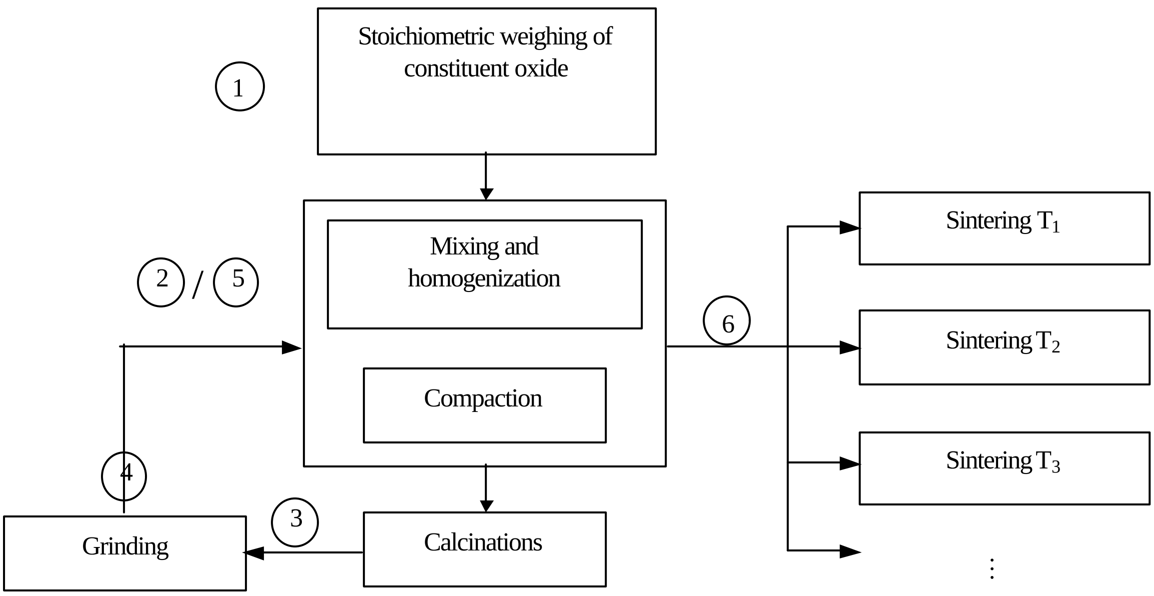

Figure 1 Flow chart for preparation and sintering of Ba_2NiWO_6

To evaluate the sintering behavior, determine the structural characteristics and phase identification we examined the sintered samples by powder X-ray difratometry (XRD) using a Siemens D-5000 Diffractometer, equipped with Cu - Kα radiation (ë = 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. Mechanical hardness of the sintered Ba_2NiWO_6 ceramics were determined by vicker´s microhardness tests.

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. The XRD spectrum of a typical Ba_2NiWO_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 (Wells, 1986).. No evidence for a distortion from the cubic symmetry is observed in the XRD spectrum. Presence of superstructural lines (111) and (311) in the XRD spectrum of Ba_2NiWO_6 ceramics reveal that it has an ordered complex cubic perovskite structure with lattice constant a = 8.0748 Å. The XRD data of has been given in Table 1

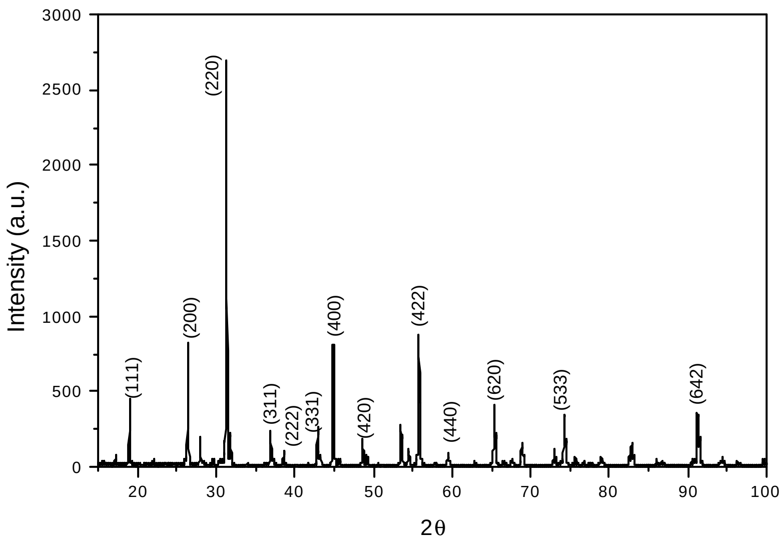

Fig. 1: Powder X-ray diffraction patterns of Ba_2NiWO_6 ceramic, sintered at 1200°C

Table 1. X-ray diffraction data of Ba_2NiWO_6

2θ	d (Å)	h	k	l	I/I0
18,9863	4,6705	1	1	1	0,1603
26,3914	3,3744	2	0	0	0,3060
31,2994	2,8556	2	2	0	1,0000
36,8963	2,4342	3	1	1	0,0877
38,5753	2,3320	2	2	2	0,0387
44,8611	2,0188	4	0	0	0,3018
48,6067	1,8716	3	3	1	0,0664
53,4286	1,7135	4	2	0	0,0970
55,7104	1,6486	4	2	2	0,3281
65,3542	1,4267	4	4	0	0,1531
74,2661	1,2760	6	2	0	0,1254
82,8337	1,1644	5	3	3	0,0607
91,1429	1,0787	6	4	2	0,1347

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 (Galasso, 1959; Galasso andKatz, 1961; Wells, 1986). 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. A disordered arrangement of B and B' should result in zero intensity. Therefore Ni^{2+} and W^{4+} cation ordering in Ba_2NiWO_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 indexed the XRD peaks of Ba_2NiWO_6 as an ordered complex cubic perovskite with $A_2BB'O_6$ crystal structure. The XRD data of has been given in Table 1.

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 (Richerdson, 1982; Reed, 1988). Typical microstructures of Ba_2NiWO_6 ceramics, sintered at 1300 and 1400^{o}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. 3(a), 4(a), and 3(b), 4(b), respectively, using secondary electrons, reveals that increase in sintering temperature up to 1400^{o}C improves considerably the surface morphology and increases the homogeneity of the particle size distribution. Ceramics sintered at 1500^{o}C presented undesirable grain growth, therefore their microstructures are not shown here.

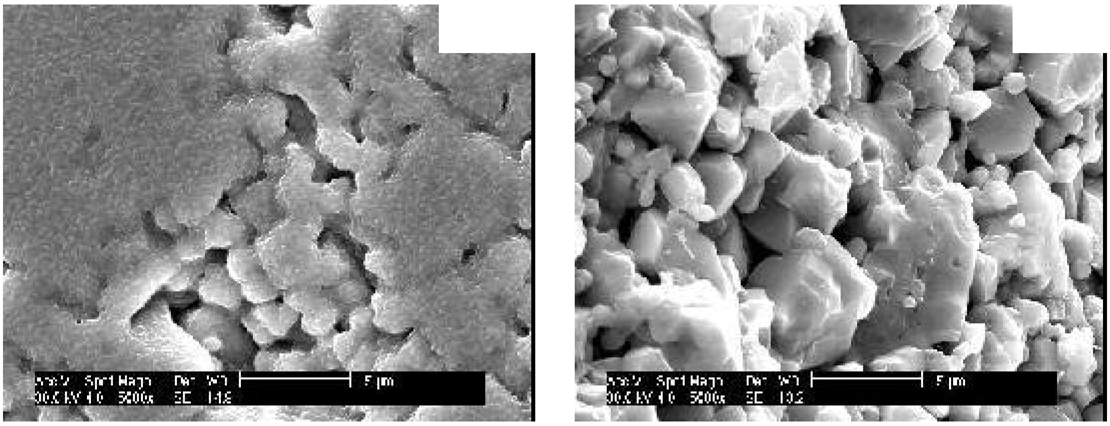

Fig. 3 SEM micrograph of Ba_2NiWO_6 ceramics sintererd at 1200^{o}C,
(a) polished surface (5000x); (b) fracture surface (1000x)

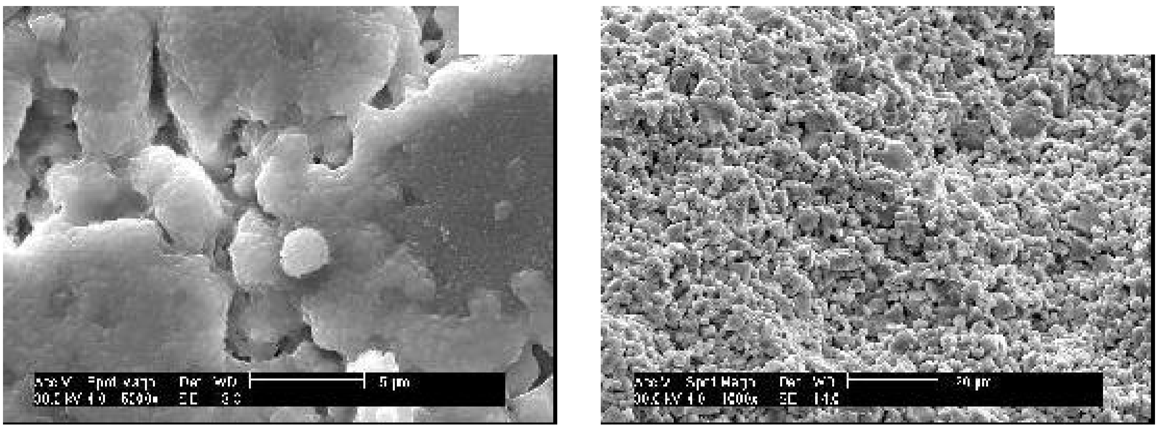

Fig. 4 SEM micrograph of Ba_2NiWO_6 ceramics sintererd at 1300^{o}C,
(a) polished surface (5000x); (b) fracture surface (1000x)

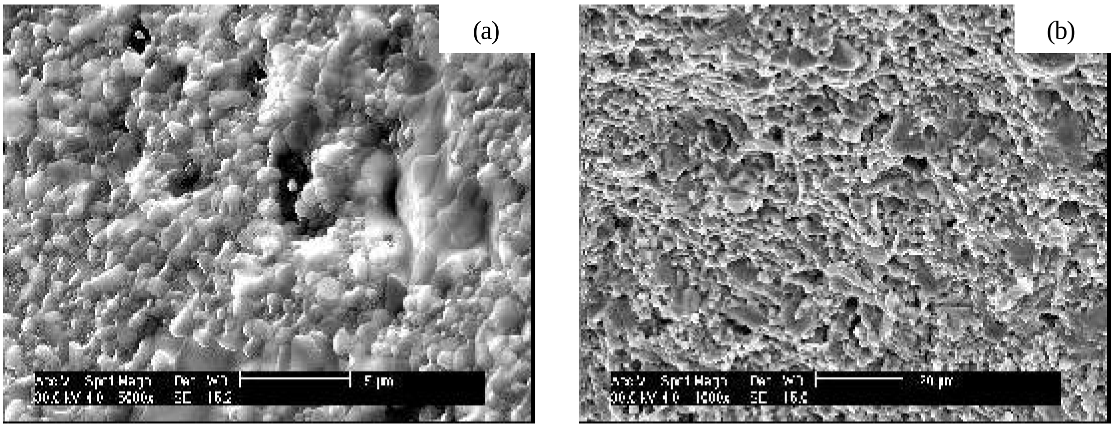

Fig. 5 SEM micrograph of Ba_2NiWO_6 ceramics sintererd at 1400ºC,
(a) polished surface (5000x); (b) fracture surface (1000x)

Sintered density of Ba_2NiWO_6 ceramics was measured by standard Archimedes technique. Sintered densities of Ba_2NiWO_6 ceramics and % densification values are tabulated in Table 2. Variation of sintered density with sintering temperature of Ba_2NiWO_6 ceramics has been shown in Fig. 6.

Table 2. Sintered densities of Ba_2NiWO_6 ceramics

Sintering temperature ^oC	Density (g/cm^3)	Standard deviation	Densification (%)
1200	6.54	0.09	90.45
1300	6.78	0.10	93.77
1400	7.08	0.10	97.98
1500	6.12	0.02	84.59

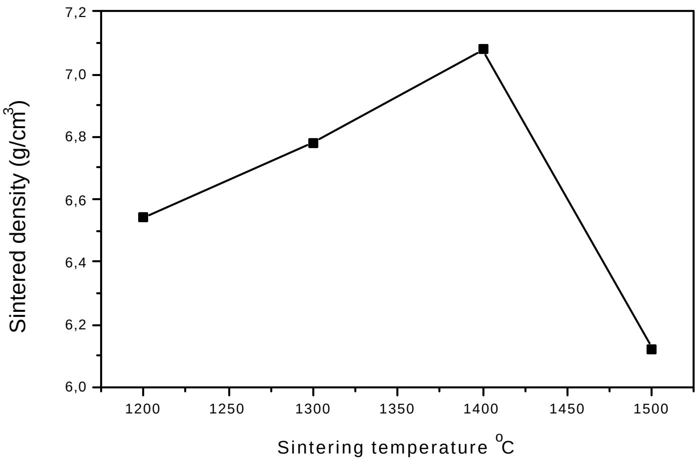

Fig. 6 Variation of sintered density as a function of sintering temperature
in sintered Ba_2NiWO_6 ceramics

As majority of ceramic products are of fragile nature, mechanical behavior of the sintered Ba_2NiWO_6 ceramics was studied by Vickers micro-hardness test, which is based on the mechanical resistance of the material to the penetration of a diamond pyramid with square base and 136º angles between the faces. The Vickers micro – hardness (H_v) is given by equation (Iost, 1996):

$$H_v = 1.8544P/d^2 \qquad (1)$$

Were *P* is the load and *d* is the average diagonal of the square identation produced by the pyramidal indentor in the sample [9]. In the present work, we used a load of 0.080 kg for 15 seconds and 5 measurements for each sample. Vicker´s hardness test values and standard deviation of sintered Ba_2NiWO_6 ceramics are tabulated in Table 3. Variations of Vicker´s micro-harness of Ba_2NiWO_6 ceramics is shown, in Figs. 7.

Tabele 3: Vicker´s hardness test values of sintered Ba_2NiWO_6 ceramics

Sintering temperature	Hv_5	Standard deviation
1200	172.74	14.78
1300	265.12	4.95
1400	322.58	2.27
1500	306.62	17.27

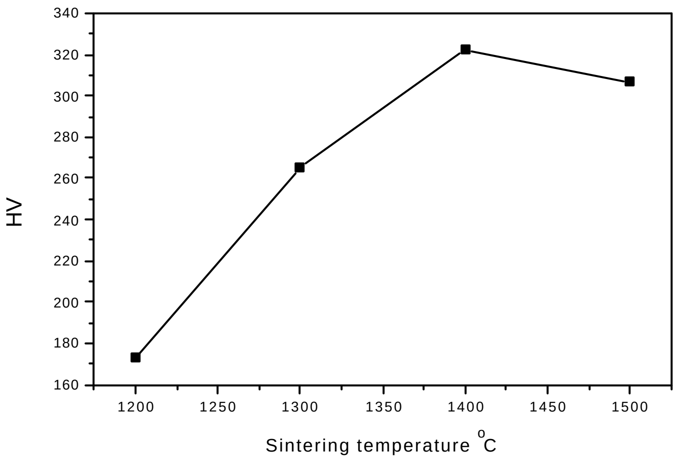

Fig. 7 Variation of Vicker´s hardness values as a function of sintering temperature in sintered Ba_2NiWO_6 ceramics

As it can be seen from Figs. 6 and 7, there is a gradual increase in mechanical hardness with the increase in the sintering temperature and densification of the materials also increases in the same manner, up to 1400°C. 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. Thus we may infer that gradual increase in the densification and mechanical hardness increases with sintering conditions as a result of better microstructural characteristics, as discussed earlier, obtained under these experimental conditions. At higher sintering temperature (1500°C) occurrence of abnormal grain growth deteriorates the homogeneity of microstructure with a consequence decrease in sintered density and mechanical strength of sintered Ba_2NiWO_6 ceramics.

4. CONCLUSIONS

In this work, we have produced Ba_2NiWO_6 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_2NiWO_6 has an ordered complex cubic perovskite structure. 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 and mechanical strength are of vital importance, we have studied sintering behavior and microstructural characteristics of these ceramics Our studies show a gradual improvement in microstructural characteristics sintered density and mechanical hardness of sintered Ba_2NiWO_6 ceramics with increase in sintering temperature up to 1400°C . Ba_2NiWO_6 ceramics sintered at 1400oC gave best results in terms of morphology and particle size distribution, densification and mechanical strength. At higher sintering temperature (1500°C) occurrence of abnormal grain growth deteriorates the homogeneity of microstructure with a consequence decrease in sintered density and mechanical strength of sintered Ba_2NiWO_6 ceramics. These favorable characteristics tend to show that Ba_2NiWO_6 ceramics sintered at 1400°C could be potential candidates for the fabrication of ceramic components for temperature sensors for temperature monitoring in petroleum wells.

5. ACKNOWLEDGEMENTS

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