THERMO-MECHANICAL PROCESSING AND MECHANICAL PROPERTIES OF $BA_2ALWO_{5,5}$ CERAMICS FOR THE FABRICATION OF CERAMIC COMPONENTS FOR PETROLEUM INDUSTRIES

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Abstract. *Complex perovskites oxide ceramics based on tungsten are highly inert to hostile environmental conditions. For this reason, these types of ceramics have great potential for use in the petroleum industry where the corrosive environment is a constant problem for the manufacture of parts and components. We are working on the fabrication of temperature sensors encapsulated in ceramics for the petroleum industry. In this context, we produced $Ba_2AlWO_{5,5}$ ceramic by thermo-mechanical process using high energy ball mill and aluminum balls. $Ba_2AlWO_{5,5}$ ceramic components were manufactured through normal sintering of ceramic compacts. Sintering was carried out in a temperature range of 1200 to 1350°C during 24 hours in air atmosphere. Fabricated through thermo-mechanical process, the ceramic compacts showed high homogeneity in terms of size and distribution of the particles and presented desired mechanical properties required for ceramic encapsulation for the conservation of metallic parts in highly hostile crude petroleum environment.*

Keywords: $Ba_2AlWO_{5,5}$, ceramic components, thermomechanical processing, mechanical properties

1. INTRODUCTION

Nowadays, there is an increasing demand for sustainable materials and systems to operate in hostile environments such as high temperature or chemically aggressive environments of petroleum extraction industry. The ceramics are parts of a broad class of materials whose extremely vast characteristics such as: high thermal capacity, resistance to corrosion, the fact that they may be insulating, conducting or superconducting, they have magnetic properties or absence of magnetism, and to be hard and resistant but fragile make them interesting for various technological purposes. Thus, many of the new technology incorporate ceramic components in their activities due to these versatile characteristics. .(Schwartz 1985, Tejuca and Fierro 1993) We are working on fabrication of ceramic encapsulated temperature sensor for petroleum extraction industry, which present high degree of hostile environment. (Lapa et al 2005, Leonardo et al 2005, Yadava and Sanguinetti Ferreira 2008) in As tungustate ceramics present good resistant to hostile environment, in the same context, in this work we have produced tungustate based $Ba_2AlWO_{5,5}$ ceramics through thermomechanical processing using high energy ball mill and subsequent thermal treatment. Structural phase characterization was carried out using X-ray diffraction technique. Microstructural characteristics and mechanical properties of sintered $Ba_2AlWO_{5,5}$ ceramic powder compacts using scanning electron microscopy and Vicker`s micro-hardness tests. This article reports these results and discusses its implications on application viability of $Ba_2AlWO_{5,5}$ as ceramic components for the fabrication of temperature sensors encapsulated in ceramics for the petroleum extraction industry.

2. EXPERIMENTAL DETAILS

In the present study, $Ba_2AlWO_{5,5}$ ceramic powder has been prepared in a batch of 200 grams from the stoichiometric mixture of constituents chemicals: Ba2CO3, Al2O3 and WO3 through following relationship:

2Ba2CO3 + Al2O3+ 2WO3 = 2Ba2AlWO5,5 + 2CO2

These components were mixed in a high energy ball mill model with MA - 50, Marconi Equipments, São Paulo, Brazil equipped with a stainless steel milling chamber and alumina balls for a period of 24 h. For the efficient ball milling we had to analyze the number of alumina balls that are required to use in the mill of one liter capacity for milling 200gms of ceramic powder. The number of required balls for grinding was obtained by the following formula:

$$P(Kg) = V(L) \times d_b(Kg / L) \times p \times 0.6 ,$$

where P = amount of ball (kg), db = specific weight of the balls (kg / L), V = net volume of the ballmill (L), p = apparent occupancy rate of the balls (0.50 to 0.55), which made us conclude that the number of alumina balls to be used should be 31.

Ceramic mixture taken out from the ball mill was compacted as circular discs of 30mm diameter with a thickness of about 50mm. Powder compaction was carried out in a hydraulic press and hard steel mould made of abrasion resistant AISI A2 steel (HRC 58) at a pressure of 5ton/cm2. The compacted discs were taken to muffle furnace Jung model 0614 and calcined at a temperature of 1200°C for 24 hours in ambient atmosphere. After calcination, samples were furnace cooled to room temperature.

Calcined material was subjected X-ray powder diffraction analysis for structural characterization and phase identification studies. After the structural analysis and identification of Ba2AlWO5,5 single phase formation, calcined Ba2AlWO5,5 powder compacts were again subjected to high energy ball milling for 24h for grinding in fine particles and homogenization of particle size distribution for fabrication of ceramic components through normal sintering route.

Circular ceramic components of 10mm and 30mm diameter and 1 - 3mm thickness were fabricated by uniaxial pressing technique using the same above reffered mould and a hydraulic press at a pressure load of 10ton/cm2. For better compression, each fraction of pressure was applied for 5 minutes to stabilize the pressure load distribution in the chip and homogenize the necessary pressure load. The compressed ceramic components were subjected to the process of normal solid state sintering process in a temperature range 1200 - 1300ºC for 24h. Process of sintering of the samples was performed in high purity alumina crucibles in ambient atmosphere, using the same above reffered high temperature muffle furnace.

To evaluate the process of sintering, it is necessary to determine the structural characteristics and the long - range ordering of the lattice constituents and identifying the phase of sintered samples. The samples were investigated by X-ray diffraction technique using a Shimadzu, X-ray powder diffractometer, equipped with equipped with Cu - Kα radiation (λ = 1.5406Å). The analysis of microstructure of sintered ceramics were carried out by scanning electron microscopy(MEV) (model JEOL JSM-5900), using secondary electrons. To observe the microstructure, the samples were placed in a metal coating device to receive a thin layer of gold, since they aren't conducting, to getting the MEV.

Mechanical properties of the sintered ceramics were studied through Vicker's micro-hardness testing. For the indentation in Vicker's micro-hardness tester, the samples were polished with # 220, # 400, # 600, # 1200, # 1500 grade sand paper in granularity followed by mechanical polishing using diamond paste with 1 micron particle size. For micro-hardness testing a Vicker's hardness indentor model HVS-5 No 0021 was used.

3. RESULTS AND DISCUSSION

Among the various techniques for characterization of materials, the technique of X-ray diffraction is the most appropriate in determining the crystalline phases present in ceramics, as well as quantitatively analyze and determine the unit cell parameters and consequently, determines the crystalline structure, measuring the particle size, determines the existence of defects or disorder in the structure, and is a short-range order in non-crystalline solids. This is possible because in most solids (crystals), the atoms are arranged in crystalline planes separated by distances between them in the same order of magnitude of a wavelength of monochromatic X-rays.

The X-ray diffraction (XRD) spectrum of a typical $Ba_2AlWO_{5,5}$ ceramic sintered to 1300°C for 24 hours is shown in Figure 1. The XRD spectrum presents characteristics of a complex cubic perovskite structure, because it consists of strong peaks characteristics of the primary cubic perovskite and few weak lines arising due to the superstructure network. (wells 1989)

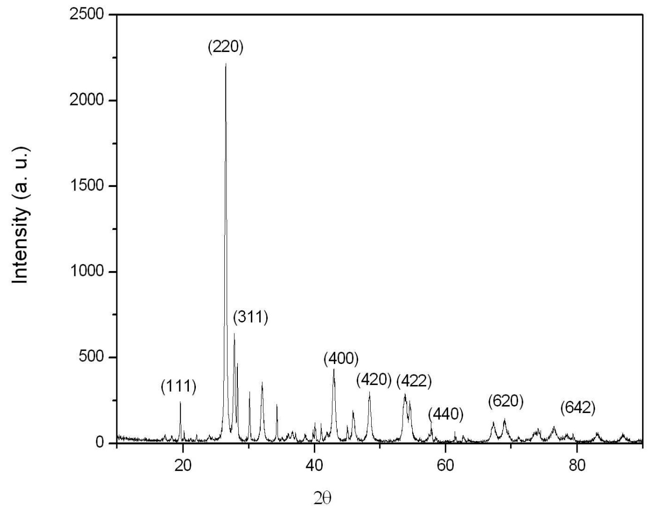


Fig.1. X-ray diffraction spectrum of $Ba_2AlWO_{5.5}$

The basic crystal structure of the perovskite is ABO_3, where A is a large ion placed in the 12 coordinates of the cube and octahedral B is placed on a lower case 6 octahedral site of the cube. The complex perovskite with different species in a place (especially the B site) can be represented by multiples of this formula unit (ABO_3) and a larger unit cell, for example, $A_2BB'O_6$ and $A_3B_2B'O_9$. The Presence of the superstructure reflection lines (111) and (311) in the XRD spectrum of $Ba_2AlWO_{5,5}$ is the confirmation of an ordering of a complex cubic perovskite structure . (Glasso et al 1961). Due to the ordering of B and B 'in the octahedral positions of ABO_3 cell, occurs a doubling of the parameter of the base of the network unit cell of cubic perovskite. Thus, all the XRD pattern of $Ba_2AlWO_{5,5}$ can be indexed in a cubic cell with an edge $A_2BB'O_6$ = 2ap where a_p is the parameter of the network base of the unit cell of cubic perovskite. The XRD spectrum of $Ba_2AlWO_{5,5}$ is similar to other complex cubic perovskite oxides having $A_2BB'O_6$ type crystal structure, shown in Figure 2, taking as an example, YBa_2NbO_6, $ErBa_2SbO_6$, $DyBa_2NbO_6$, among others.

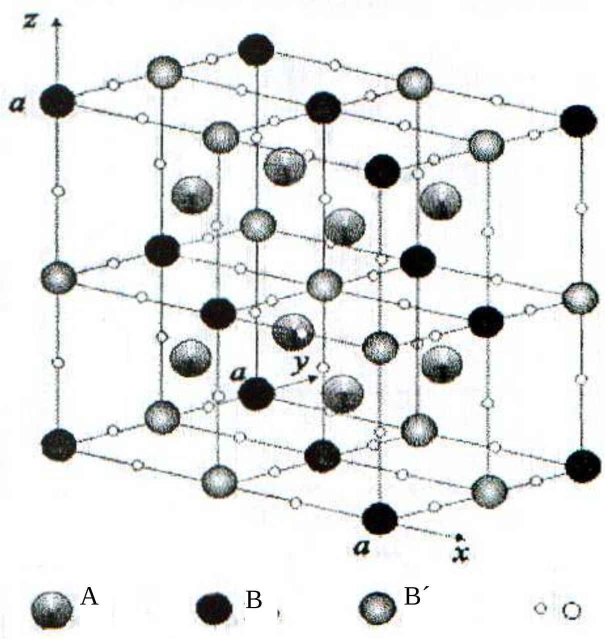


Fig. 2: Complex cubic ordered perovskite crystal $A_2BB'O_3$structure

Before being sintered, the ceramic is composed of a solid solution with random arrangement of B and B' in equivalent positions in the crystal structure. After an appropriate heat treatment, the random solid solution rearranges into a structure in which B and B 'occupy the same positions, but on a regular basis, that such a structure is described as superstructure. In the superstructure, the positions occupied by B and B 'are no more equivalent and this feature appears in the XRD spectrum of the material by the presence of lines of superstructure reflections.

A disordered arrangement of B and B 'should result in zero intensity. Therefore the cations Al^{3+} and W^{6+} in concerned $Ba_2AlWO_{5,5}$ in positions of B and B 'is clearly distinguished by the presence of significant intensity of (111) and (311) of lines of superestruture reflection. Based on the above discussion, we have now indexed the XRD peaks of $Ba_2AlWO_{5,5}$ as a ordered complex cubic perovskite A2BB'O6 crystal structure.. The unit cell parameter a of $Ba_2AlWO_{5,5}$, calculated from the experimental XRD data is a_{exp} = 8.4524 Å.

With following relations ,

$$aA = \frac{2(RA+RO)}{\sqrt{2}} \qquad (1)$$

$$aB = RB + RB' + 2\,RO \qquad (2)$$

$$acal = (aA + aB) / 2 \qquad (3)$$

We can calculate the parameter of network theory (ACAL) Ba2AlWO5.5 the compound under study. Where RA, RB, RB'and RO are ionic radii, as A, B, B' are a cation and oxygen anion. The network parameters aA and aB are calculated based on the cations A and B. The switch network acal is obtained from the relations above. Thus the radius of the barium, aluminum, tungsten and oxygen are 1.38 Å, 0.55 Å, 0.65 Å and 1.35 Å respectively and the parameter of network theory is calculated acal peroveskite = 2 x acal = 7.76Å. Data from XRD of $Ba_2AlWO_{5,5}$ are obtained in the Table(1).

Table 1 - Experimental XRD data of $Ba_2AlWO_{5,5}$

2θ	d(Å)	Int	hkl
19.57	4.5325	11.15	111
26.48	3.3633	100.00	220
27.82	3.2043	28.68	311
42.96	2,1036	19.66	400
48.49	1.8759	13.25	420
53,64	1.7073	13.47	422
57.84	1.5929	5.67	440
69.00	1.3560	6.88	620
79.33	1.2068	2.85	642

We also analyzed the density of sintered ceramics the method of Archimedes. In general, the high density ceramics are produced at sintering temperatures of between 0.5 to 0.8 TF TF (TF = temperature of melting) (2) of the ceramic in question. For density by Archimedes method was calculated as a = 29.9392 g, b = 30.0747 g, c = 79.2762 g, d = 79.1992g. Using the formulas of densities:

Density:

$$D = \frac{(b-a)}{b-a-c+d}$$

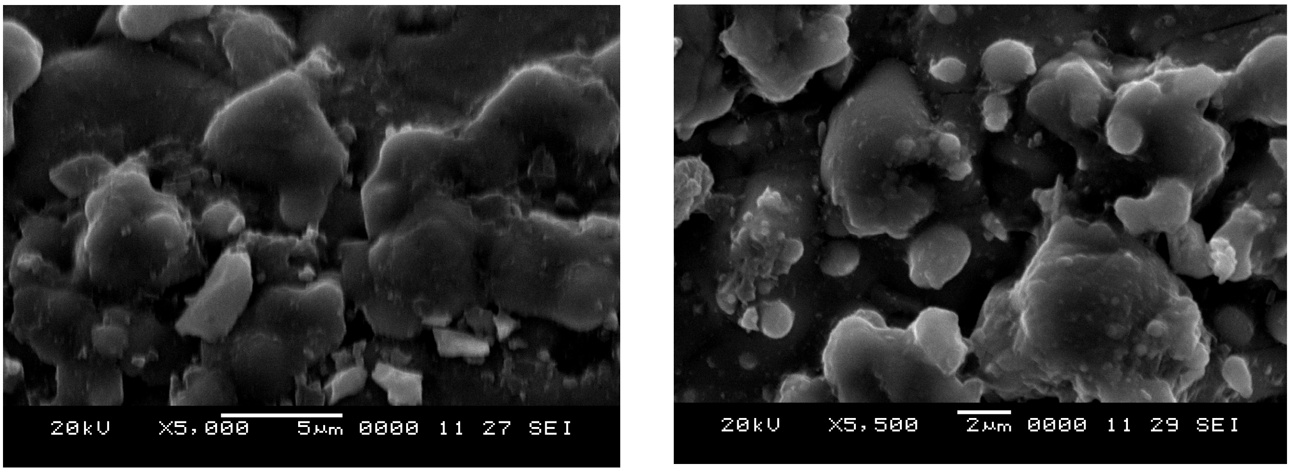
Density Fixed:

$$D_{corrigida} = \frac{(b-a)}{b-a-c+d} D'$$

Where: D = density or specific mass of solid particless, a = dried e empty specific gravity bottle, b = specific gravity bottle mass plus sample mass, c = specific gravity bottle mass plus sample and distilled hatter, d = specific gravity bottle mass fulled of hatter, D' = hatter specific mass in ambient temperature (for 22ºC, D = 0,99782 g/cm3).

It was obtained D = 5.7612 g/cm^3 and D '= 5.7487 g/cm^3.

The production and functional capacity of polycrystalline ceramics are highly dependent on their microstructural characteristics, which in turn are highly influenced by sintering kinetics. (Reed 1988, Richardson 1982) The microstructural characteristics define the quality of the final product of ceramics and its mechanical strength. The process of sintering of ceramics $Ba_2AlWO_{5,5}$ was made by the normal process of solid-state sintering. The microstructure, morphology and surface distribution of the particle size of the sintered ceramics, $Ba_2AlWO_{5,5}$, were studied using scanning electron microscopy (SEM), presented in (figure 3), and the elemental microanalysis was carried out by energy dispersion spectrometry (EDS), presented in figure 4.. This SEM characterization was carried out to evaluate the microstructure homogeneity, size and distribution of grains, porosity and the presence of phases in ceramics.



(a) (b)

Fig 3. SEM microstructures of Ba2AlWO5.5 ceramics sintered at 1300°C (a) increase of 5000x (b) increase of 5500x

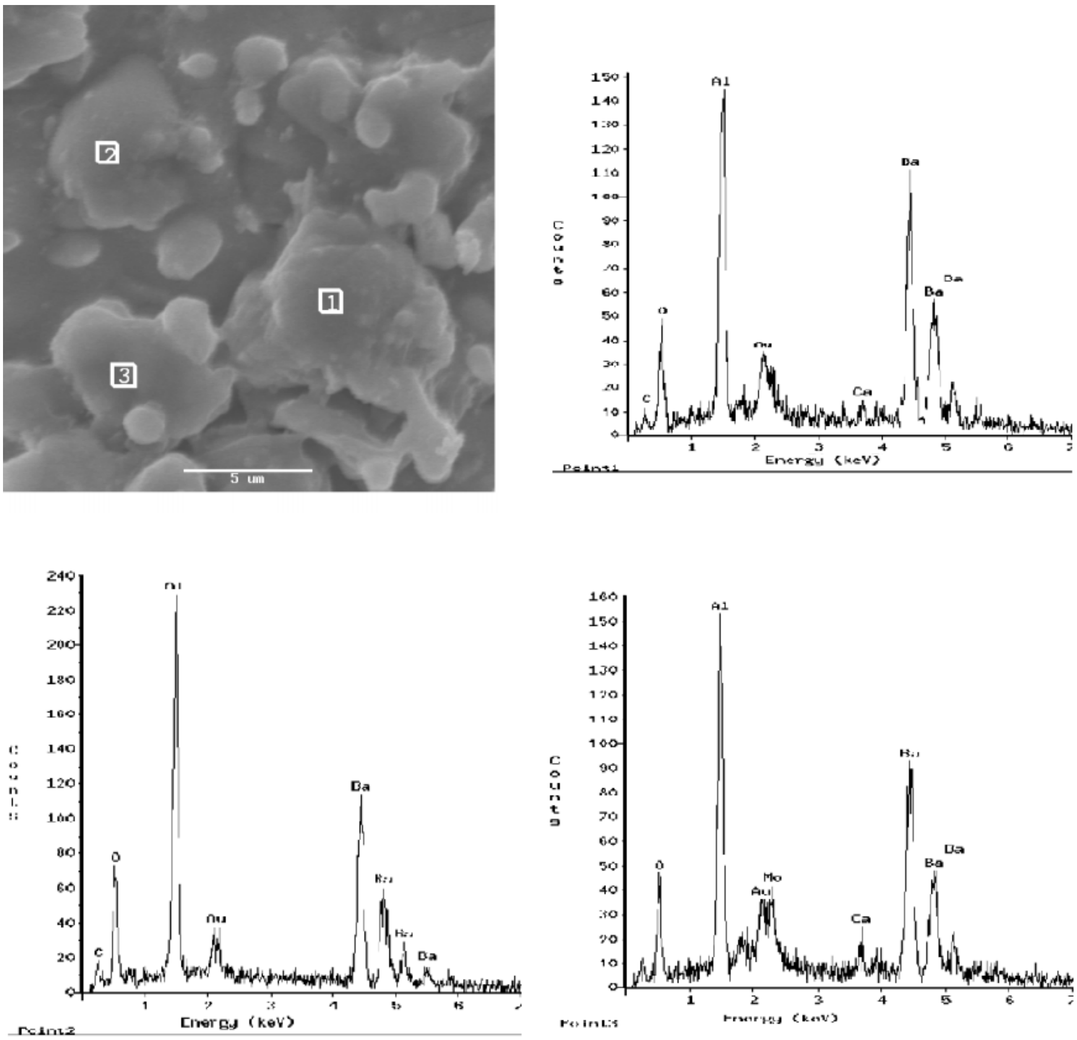


Fig 4. EDS energy dispersion spectrometry of Ba2AlWO5.5 ceramics sintered at 1300°C

For examining the sintered ceramics we had to deposit a thin layer of gold on a metal coating device which creates a vacuum for a half-time of thirty seconds and a current of 40 mA (model BAL-TEC SCD050), because our material is not conductive, then put in the equipment (model JEOL JSM-5900), to make the SEM studies. Mechanical properties of the sintered ceramics has been studied my measuring Vicker´s microhardness. To perform Vicker´s microhardness tests sintered ceramic discs were polished by # 320 to # 1500, grade sand papers successively, followed by mechanical polishing using dimond paste of 1 micron granularity.

The value of Vickers hardness (Hv) is calculated by the ratio of applied load by the area of the impression left in the body tested, which gives us the following equation: (Iost and Bigot 1996)

$$Hv(Kgf\ /mm2) = 1854.4 \times \frac{P(Kgf)}{d^2(mm2)}$$

Where: HV = Vicker's microhardness, P = applied load, d = average of diagonal indentation The microhardness was performed with a load of 200 grams for 15 seconds and an increase of 40x of indentation mark was used in the microscope. Vicker's microhardness test results are presented in Table 2 and Table 3. The average hardness of the 1st sample is HV 425.96 and average hardness of the 2nd sample is HV 449.00. It can be observed that the ceramics achieved a reasonable results in the hardness, to prove that there is a good homogeneity of the grains and the sintering behavior of $Ba_2AlWO_{5,5}$ ceramics.

Table 2. Vickers microhardness values of the first $Ba_2AlWO_{5.5}$ ceramic disc sintered at 1300^{0}C

	1st identation	2nd identation	3rd identation	4th identation	5th identation
D1	28,13	30,59	31,52	28,72	28,31
D2	31,28	28,84	32,91	27,81	28,00
HV	420,31	420,03	357,37	464,23	467,87

Table 3. Vickers microhardness values of the second $Ba_2AlWO_{5.5}$ ceramic disc sintered at 1300^{0}C

	1st identation	2nd identation	3rd identation	4th identation	5th identation
D1	29,83	28,73	26,06	27,80	31,44
D2	28,69	28,69	26,89	30,45	26,44
HV	433,20	402,64	529,13	437,22	442,83

4. CONCLUSION

In this work we have produced and studied structure, microstructure and mechanical properties a of a tungstate based $Ba_2AlWO_{5,5}$, ceramic through thermo-mechanical processing XRD studies showed that it has a complex cubic perovskite structure, with lattice parameter aexp = 8.4524 Å. Microstructural characteristics of sintered $Ba_2AlWO_{5,5}$ ceramics, studied by scanning electron microscopy, using secondary electrons, we verified that the sintered ceramics presented high microstructural homogeneity with uniform particles and particle distribution. Mechanical properties were studied through Vicker´s micro-hardness testing, presented a good hardness, sufficient for the fabrication of ceramic components. Results of these studies, showed that the fabricated through thermo-mechanical processing better results than the same ceramics produced through normal solid state reaction process. These characteristics, makes the $Ba_2AlWO_{5,\ 5}$ ceramics a strong candidate to be used in the manufacture of encapsulated temperature sensors for the petroleum industry.

5. ACKNOWLEGEMENTS

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