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MANUFACTURE AND MECHANICAL PROPERTIES OF $Ba_2AlZrO_{5,5}$ CERAMICS COMPONENTS FOR THE PETROLEUM INDUSTRY

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Abstract. *Complex perovskites oxide ceramics based on zirconium 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* $Ba_2AlZrO_{5,5}$ *ceramic by thermo-mechanical process using high energy ball mill and aluminum balls.* $Ba_2AlZrO_{5,5}$ *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*:* manufacture, mechanical properties, ceramic components

1. INTRODUCTION

In high technology industries ceramics have several uses, especially at high temperature. The study of advanced ceramics makes it possible to develop new technologies, which could be inaccessible with conventional materials and also to substitute scarce materials, Lapa et al.(2005)

In recent years, complex cubic perovskite oxides are being extensively investigated as possible crucible and substrate materials for the production of single crystals and thin films of high Tc superconductors(Brandle and Fratello, 1990), Kim et al.(1995), Aguiar et al.(1998). Earlier research works in 1950 and 1960's , Galasso et al.(1959), identified a large group of materials, which have the basic ABO3 perovskite structure or a small distortion of that structure. These complex perovskite oxides generally have the formula A2BB'O6 or A3B2B'O9 and result from the ordering of B and B' cations on the octahedral sites of the basic perovskite unit cell. Due to the increased complexity of the unit cell, a large variety of such materials are possible and hence a more continuous progression of lattice parameter could be produced. In this context, we are working on production and development of new oxide ceramics, based on complex cubic perovskite structure for the fabrication of ceramic encapsulation components for the conservation of metallic parts in highly hostile crude petroleum environment. Earlier, we produced a new ordered complex cubic perovskite oxide ceramic $Ba_2AlZrO_{5,5}$, synthesized by solid-state reaction process Yadava et al.(2002). Sintering is an important stage in the manufacture of the majority of the ceramic products and in the sintering process the ceramic product suffers significant alterations as for example, reduction in the specific surface area and in the apparent volume and improvement in the microstructure and mechanical characteristics (James 1998), (Richerson 1982).

In the present work, we have studied sintering behavior of $Ba_2AlZrO_{5,5}$ ceramics and corresponding effect on microstructural characteristics and mechanical properties of these ceramics. We also studied the ceramic stability in crude petroleum. $Ba_2AlZrO_{5,5}$ ceramics were sintered at different temperatures and sintering conditions. Microstructural characteristics of sintered $Ba_2AlZrO_{5,5}$ ceramics were studied by scanning electron microscopy. The mechanical behavior was studied by Vickers micro-hardness tests and the stability was studied by microscopy comparison after the ceramic being submerged in ocean and earth crude petroleum.

2. MATERIALS AND METHODS

The $Ba_2AlZrO_{5,5}$ ceramic powder was prepared by conventional solid-state reaction route. High purity (99.99%) constituent oxides Al_2O_3, $BaCO_3$ and ZrO_2 were mixed in stoichiometric ratios, compacted at 4 ton/cm2 and calcined at 1200ºC for 24h in ambient atmosphere. To evaluate the solid state sintering process, determine the structural characteristics and long – range cation ordering, and phase identification we investigated the samples by powder X - ray diffarctometry (XRD) using a Shimadzu, equipped with Cu - Kα radiation (λ = 1.5406 Å).

For the study of sintering behavior, $Ba_2AlZrO_{5,5}$ ceramic powder was thoroughly milled in a ball mill using Marconi Equipments MA-50, equipped with an stainless steel milling chamber and alumina balls for a period of 24 h. After this was added to the ceramic 2% of CuO (mass) to work as liquid phase during the sintering which makes possible to sinter the ceramic in low temperatures. Thoroughly milled and homogenized $Ba_2AlZrO_{5,5}$ powders were uniaxially compacted in a metallic mould to form circular discs with 30 mm of diameters. We used a pressing load of 10-12 ton/cm^2 for 5 – 10 minutes to stabilize the pressure distribution in the pressed compact, using a hydraulic press.

The green compacted $Ba_2AlZrO_{5,5}$ ceramic samples were subjected to the sintering process at temperature 1350ºC during 24hours. Sintering process of the samples was carried out at ambient atmosphere in high purity alumina crucibles, using a high temperature muffle furnace (Jung 0614) followed by furnace cooling till the ambient temperature.

Microstructure of the sintered ceramics were studied by a scanning electron microscope (JEOL JSM-5900), using secondary electrons. To observe the microstructure, samples were covered with thin gold coating using a Sputter Coater BAL-TEC SCD050.

The mechanical behavior of the sintered ceramics was studied by measuring micro-hardness using Vickers hardness indentor model HVS-5 No. 0021. For the observation of polished surfaces in the microscope, samples were polished with #200, #400, #600, #100, #1200, #1500 grade sand papers and diamond paste with 1 µm granularity.

To stability study the ceramic samples were submerged in crude petroleum some in ocean petroleum other in earth petroleum where they stayed for 15 days. After this the ceramic was observed with microscopy and then returned to petroleum for more 15 days. The ceramic staid submerged an amount of 45 days.

3. RESULTS AND DISCUSSION

The XRD spectrum of a typical $Ba_2AlZrO_{5,5}$ ceramic, sintered at 1200ºC for 24h, is shown in Fig. 1. It consists of strong peaks characteristics of primitive cubic perovskite plus few weak reflection lines arising from the superlattice. No evidence for a distortion from the cubic symmetry is observed in the XRD spectrum. The basic perovskite composition is ABO3, 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. A2BB'O6, A3B2B'O9 etc [4]. Thus, in $Ba_2AlZrO_{5,5}$ composition, Ba2+, with largest ionic radius (1.38 Å) occupies position A, Al3+ (ionic radius 0.55 Å) and Zr 4+ (ionic radius 0.80 Å) cations occupy B and B' positions in the B site due to their smaller ionic radii compared to that of Ba2+ cation. Due to the ordering of B and B' on octahedral site of the ABO3 unit cell there is a doubling in the lattice parameter of the basic cubic perovskite unit cell. Thus, the whole XRD pattern of $Ba_2AlZrO_{5,5}$ can be indexed in a A2BB'O6 cubic cell with the cell edge a = 2ap where ap is the cell lattice of the cubic perovskite. The XRD spectrum of $Ba_2AlZrO_{5,5}$ is similar to A2BB'O6 type complex cubic perovskite oxides e.g. YBa2NbO6, ErBa2SbO6, DyBa2NbO6 etc. reported in the JCPDS file, as judged by the similarity in d-spacings and intensity ratios. Presence of the superstructure reflection lines (111) and (311) in the XRD spectrum of $Ba_2AlZrO_{5,5}$ 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.

For double cubic perovskite of the formula A2BB'O6 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 Al3+ and Zr 4+ cation ordering in $Ba_2AlZrO_{5,5}$ 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 $Ba_2AlZrO_{5,5}$ as an ordered complex cubic perovskite with A2BB'O6 crystal structure. XRD data of $Ba_2AlZrO_{5,5}$ obtained from the XRD spectrum are tabulated in Table 1. The lattice parameter of $Ba_2AlZrO_{5,5}$, calculated from the experimental XRD data is aexp = 8.38346 Å.

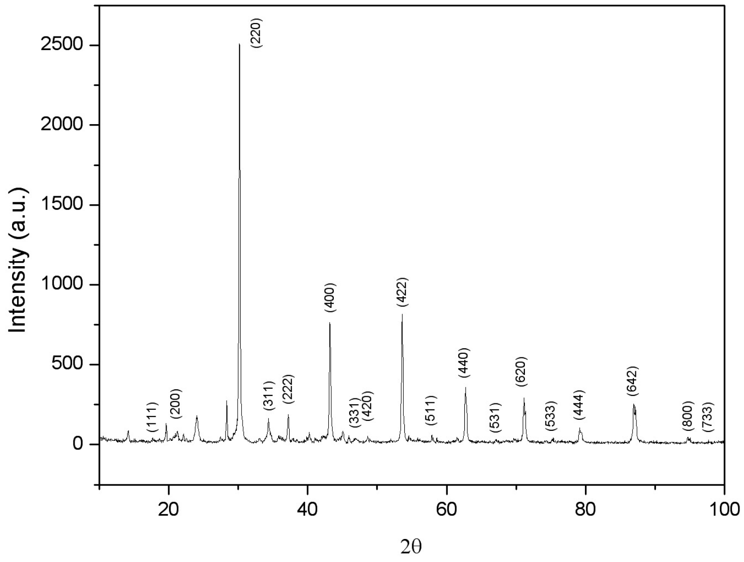

Figure 1. Powder X-ray diffraction patterns of $Ba_2AlZrO_{5,5}$ ceramic, sintered at 1200ºC for 24 h.

Table 1. X - ray diffraction data of $Ba_2AlZrO_{5,5}$

2θ	d(Å)	Int	hkl
19,64	4.5165	5.26	111
21,24	4.1797	3.35	200
30,16	2.9608	100.00	220
34,36	2.6079	6.53	311
37,16	2.4175	7.49	222
43,16	2.0943	30.44	400
46,76	1.9411	1.59	331
48,60	1.8719	2.04	420
53,56	1.7096	32.43	422
57,88	1.5919	2.39	511
62,68	1.4810	14.26	440
67,16	1.3927	1.27	531
71,08	1.3252	11.63	620
75,28	1.2613	1.67	533
79,12	1.2095	4.22	444
86,88	1.1203	10.04	642
94,68	1.0475	1.91	800
97,68	1.0231	1.19	733

As stated earlier, the objective of this work is to get $Ba_2AlZrO_{5,5}$ ceramics sintered with good mechanical properties in order to guarantee the required qualities that a final ceramic product must have. Microstructural features define the final product quality of the ceramic products and their mechanical strength, which in turn is heavily dependent on sintering behavior of the ceramic. In the present work $Ba_2AlZrO_{5,5}$ ceramics were sintered by liquid phase sintering at the temperature of 1350°C 24h at ambient air atmosphere. Microstructural features of $Ba_2AlZrO_{5,5}$ sintered ceramics, was studied by scanning electron microscopy, using secondary electrons. Typical SEM micrographs of the $Ba_2AlZrO_{5,5}$ ceramics, sintered at 1350°C is shown in Figs. 2 and 3.

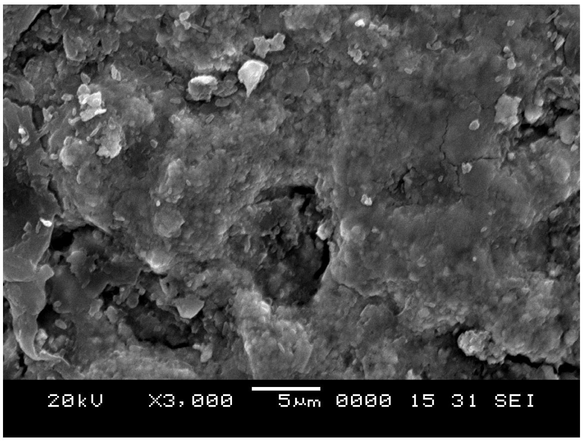

Figure 2. Microstructure of ceramic (X3000)

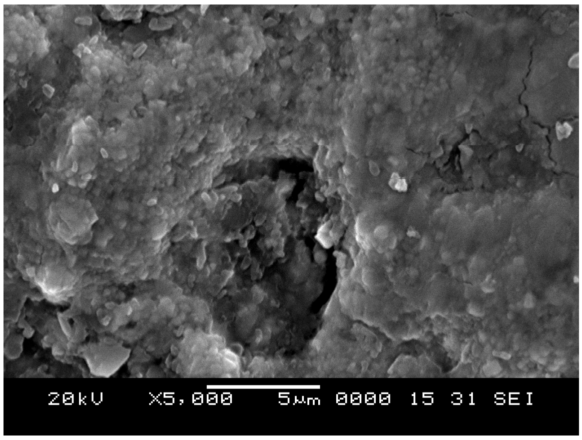

Figure 3. Microstructure of ceramic (X5000)

SEM micrographs (Figs.2 and 3) reveal that $Ba_2AlZrO_{5,5}$ ceramics sintered at 1350°C have a uniform surface morphology, grain homogeneity and particle size distribution.

As majority of ceramic products are of fragile nature, mechanical behavior of the sintered $Ba_2AlZrO_{5,5}$ ceramics was studied by Vickers microhardness 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. In the present work, we used a load of 0.500 kg for 15 seconds and 8 measurements for each sample (3 samples were idented). Datas of sintered micro-harness of $Ba_2AlZrO_{5,5}$ ceramics are shown Tab. 2,3,4.

Table 2. Micro Hardness data of sintered $Ba_2AlZrO_{5,5}$ ceramic sample 1

	1st identation	2nd identation	3rd identation	4th identation	5th identation	6th identation	7th identation	8th identation
D1	73.73	87.17	94.31	86.59	83.53	59.05	88.39	93.84
D2	85.88	80.19	91.44	89.97	88.00	60.13	94.52	83.27
HV	145.58	132.41	107.49	118.97	126.05	261.11	110.86	118.24

Table 3. Micro Hardness data of sintered $Ba_2AlZrO_{5,5}$ ceramic sample 2

	1st identation	2nd identation	3rd identation	4th identation	5th identation	6th identation	7th identation	8th identation
D1	99.08	86.42	90.73	71.10	89.55	81.58	92.64	75.56
D2	90.48	87.98	86.83	79.38	82.33	79.91	90.69	84.95
HV	103.21	121.94	117.64	163.72	125.54	142.21	110.35	143,96

Table 4. Micro Hardness data of sintered $Ba_2AlZrO_{5,5}$ ceramic sample 3

	1st identation	2nd identation	3rd identation	4th identation	5th identation	6th identation	7th identation	8th identation
D1	75.53	84.31	76.91	69.05	89.50	102.86	77.08	96.23
D2	79.70	84.86	74.88	77.94	92.59	86.59	82.16	92.31
HV	153.92	129.59	160.91	171.66	111.86	103.33	146.26	104.33

Tables 2, 3 and 4 shows a high micro-hardness of $Ba_2AlZrO_{5,5}$ ceramics, an average of 134.64 HV . It can be observed that the compound achieved a great result on the hardness, proving that despite the presence of other phases, there was a good homogeneity of the grains and the sintering stage.

After the mechanical characterization we submerged four samples in crude petroleum. Two of them in ocean petroleum and the other ones in earth petroleum. They stayed there for 30 days and we analyzed it by microscopy every 15 days. This analyses was made to compare the samples and observe if it suffered any change. As we observe on Figs. 4,5,6 and 7 the ceramics submerged in both type off petroleum didn't suffered changes.

Figure 4. Ceramic submerged in ocean petroleum for 15 days

Figure 5. Ceramic submerged in ocean petroleum for 30 days

Figure 6. Ceramic submerged in ocean petroleum for 15 days

Figure 7. Ceramic submerged in earth petroleum for 30 days

With this microscopy results we have that the ceramic $Ba_2AlZrO_{5,5}$ is stable to the aggressive petroleum environment so, this ceramic could be potential candidate for the fabrication of ceramic components for temperature sensors for temperature monitoring in petroleum wells.

4. CONCLUSIONS

In this work, we have produced polycrystalline $Ba_2AlZrO_{5,5}$ 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 spectra reveal that $Ba_2AlZrO_{5,5}$ have 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 are of vital importance. It was found through analysis, that the ceramic $Ba_2AlZrO_{5,5}$ showed a large increase in the micro hardness of the material and a very homogeneous microstructure, unlike the normal process of manufacturing of the ceramic disc, which is through the grinding using mortar and pistil. The analyses we did with the ceramic after being submerged showed us that its stable to crude earth and ocean petroleum. So, $Ba_2AlZrO_{5,5}$ ceramics sintered at 1350^oC could be potential candidates for the fabrication of ceramic components for temperature sensors for temperature monitoring in petroleum wells.

5. ACKNOWLEGEMENTS

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