PRODUCTION AND STUDY OF SINTERING BEHAVIOR OF Ca2AlZrO5,5 CERAMICS COMPONENTS FOR THE PRETROLEUM INDUSTRY

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Abstract. *Ceramic oxides of perovskite or derived from this structure are quite used for applications in high technology because of its enormous variation in physicochemical properties with little change in the characteristics structural. This paper proposes the creation of a temperature sensor encapsulated in pottery from the study of a new ceramic material, the ordered complex cubic perovskite* $Ca_2AlZrO_{5,5}$*. This pottery was prepared by solid state reaction. Stoichiometric amounts of products chemical constituents with a high degree of purity, were homogenized in a using a ball mill jar and high purity alumina balls, compacted by uniaxial pressing and fired at 1200 ° C for 24 hours. Structural characterization of the samples produced was analyzed by x –ray diffraction.The mechanical property of ceramics are being studied by Vickers microhardness test and the results will be represented at COBEM 2011.The results will be presented and discussed in terms of capability of ceremic components for applications such as temperature sensors.*

Keywords*:* $Ca_2AlZrO_{5,5}$*, oil industry, temperature sensor*

1. INTRODUCTION

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 produced and studied sintering behavior of a new complex cubic perovskite oxide ceramic $Ca_2AlZrO_{5.5}$ ceramics and corresponding effect on microstructural characteristics amd mechanical properties

2. METHODS

The $Ca_2AlZrO_{5.5}$ ceramics was prepared by conventional solid-state reaction route. High purity (99.99%) constituent oxides Al_2O_3, Cao 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, $Ca_2AlZrO_{5.5}$ 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. Thoroughly milled and homogenized $Ca_2AlZrO_{5.5}$ 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 1300ºC 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 microhardness 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.

3.RESULTS ANALYSIS

3.1 X-RAY DIFFRACTION

The XRD spectrum of a typical $Ca_2AlZrO_{5.5}$ 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]. 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 $Ca_2AlZrO_{5.5}$ 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 $Ca_2AlZrO_{5.5}$ 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) and (311) in the XRD spectrum of $Ca_2AlZrO_{5.5}$ 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 $A_2BB'O_6$ 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 Al3+ and Zr 4+ cation ordering in $Ca_2AlZrO_{5.5}$ 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 $Ca_2AlZrO_{5.5}$ as an ordered complex cubic perovskite with $A_2BB'O_6$ crystal structure.

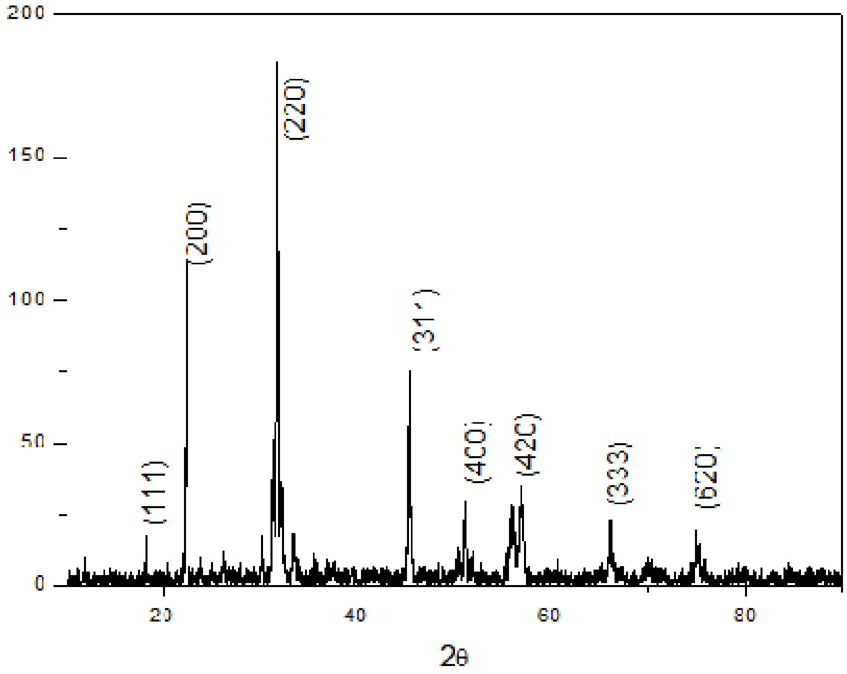
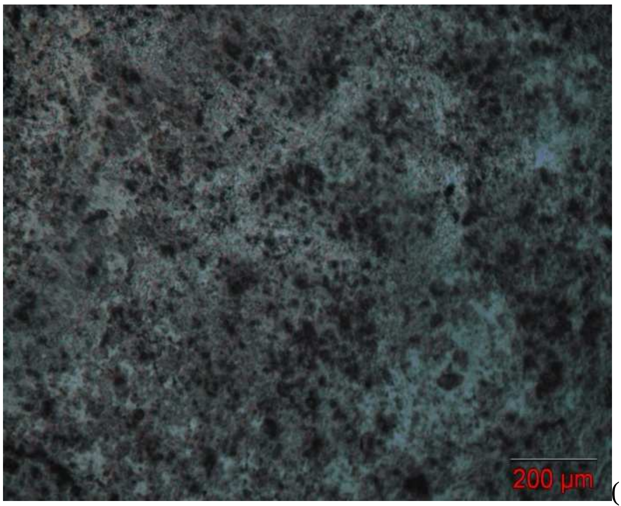


Figure 1. X-ray diffractogram pattern of $Ca_2AlZrO_{5,5}$

3.2. OPTICAL MICROSCOPY

Optical micrograph of a typical $Ca_2AlZrO_{5.5}$ ceramic compact sintered at a 1300°C is presented in Figure 1 which shows a considerable homogeneous character of the compact. So considering this fact of homogeneity through the Figure 2, is assured that the use of the high energy ball mill is very important to prepare the ceramic compacts.



(2)

Figure 2 . Optical Micrograph of $Ca_2AlZrO_{5,5}$ (magnification100x)

3.3. SCANNING ELETRONIC MICROSCPY

SEM is capable of producing high-resolution images of a sample surface. Because of the way images are created, SEM images have a characteristic three-dimensional appearance and are useful to evaluate the surface structure of a given sample.

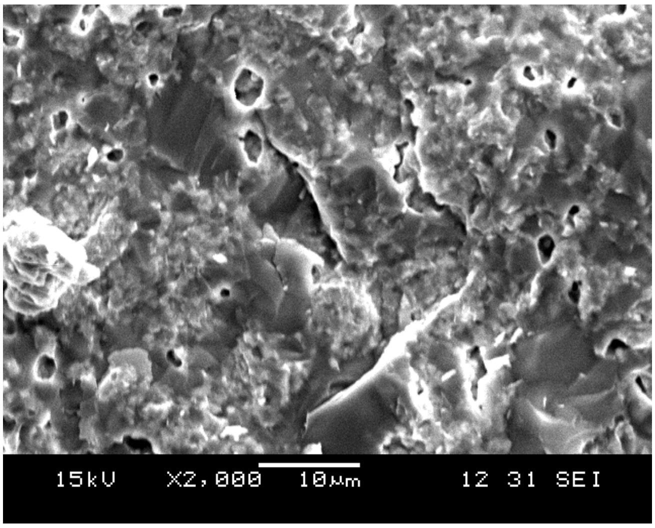


Figure 3.SEM of $Ca_2AlZrO_{5,5}$

A typical SEM micrograph of a sintered c $Ca_2AlZrO_{5.5}$ ceramic compact, is presented in Figure 3. Analysing the SEM images it can be observed that ceramics have a an uniform surface morphology and particle size distribution which guarantees that the ceramic have a good stability and mechanical resistance. .

3.4 MICROHARDNESS VICKERS

Table 1 presents the measurements of the Vickers microhardness of a typical sintered $Ca_2AlZrO_{5,5.}$ceramic compact. These results show a reasonable hardness of the $Ca_2AlZrO_{5,5}$, for encapsulation purposes.

Indentation	Diagonal 1 (micrometro)	Diagonal 2 (micrometro)	HV
1	80,16	86,28	267,76
2	80,59	76,63	300,09
3	84,27	84,03	261,88
4	84,75	81,72	267,66
5	79,09	83,45	280,76
6	76,38	79,05	307,04
7	80,50	76,91	299,36
8	73,59	81,78	307,28
9	80,22	75,48	305,98
10	84,77	82,34	265,62

At the moment ,the sample are submitted in crude oil originated from earthen and offshore petroleum oil wells from the northeastern region of Sergipe in Brazil to study their stability in crude petroleum.

4. CONCLUSIONS

In this work, we have produced polycrystalline $Ca_2AlZrO_{5,5}$, 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 $Ca_2AlZrO_{5,5}$, 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 $Ca_2AlZrO_{5,5}$, 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, $Ca_2AlZrO_{5,5}$, ceramics sintered at 1300^{o}C could be potential candidates for the fabrication of ceramic components for temperature sensors for temperature monitoring in petroleum wells.

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