The Effect of Copper Oxide Addition on Sintering, Microstructure and Mechanical Properties of Ba_2HoSbO_6 Ceramics

Y.P. Yadava[1]; R.A. Sanguinetti Ferreira[1]; J.V. Barros[1]; E. Montarroyos[2]; J.M. Ferreira[2] and J. Albino Aguiar[2]

[1]Departamento de Engenharia Mecânica, Universidade Federal de Pernambuco, 50741-530 Recife, Brasil

[2]Departmento de Física, Universidade Federal de Pernambuco, 50670-901 Recife, Brasil

Abstract

Recently Ba_2HoSbO_6 ceramic has been reported as a potential material for substrate applications for high temperature superconducting films. As Ba_2HoSbO_6 is chemically inert with high temperature superconducting materials, it could be an excellent crucible material for single crystal growth of high temperature superconducting materials. For such applications high sintered density, homogenous microstructure and good mechanical strength are essential requirements. Principal limitation of ceramics is their brittleness, i.e., the tendency to fail suddenly with little plastic deformation. This is of particular concern when the material is used in crucible applications. In this work, we have studied microstructural characteristics and mechanical properties of the Ba_2HoSbO_6 ceramics. Single phase Ba_2HoSbO_6 and two another batches of Ba_2HoSbO_6 containing 1 and 2wt% of CuO as sintering aids, were sintered to study the liquid phase sintering behaviour. Surface morphology and microstructure of sintered materials were studied by scanning electron microscopy. XRD and EDX analysis show that there are no traces of impurity phases due to, up to 1 wt%, CuO addition in Ba_2HoSbO_6 samples. SEM micrographs reveal that CuO addition improves the microstructure and particle size distribution of the Ba_2HoSbO_6 ceramics. Mechanical hardness was determined by using Vickers indentor and this study shows an improvement in the hardness of the CuO added Ba_2HoSbO_6 ceramics. Our studies reveal that liquid phase sintering process, due to CuO addition, facilitates the sintering of Ba_2HoSbO_6 and improves the microstructure and particle size distribution of the Ba_2HoSbO_6 ceramics. An important observation is that higher wt% (> 1wt%) CuO addition destroys the crystallographic structural characteristics of the Ba_2HoSbO_6. Thus liquid phase sintering of Ba_2HoSbO_6 ceramic using CuO additives is limited to a maximum of 1wt% CuO. The microstructural modifications due to liquid phase sintering process, consequently, help in improving the densification and mechanical hardness of the Ba_2HoSbO_6 ceramics.

Keywords: Ba_2HoSbO_6, liquid phase sintering, microstructure, mechanical properties

Introduction

In recent years, complex cubic perovskite oxide ceramics are being investigated extensively for their use as substrate and crucible materials for high temperature applications [1-6]. Complex cubic perovskite oxides, normally, have $A_2BB'O_6$ or $A_3B_2B'O_9$ general formula and result from the ordering of B and B' cations on octahedral site of the basic ABO_3 perovskite unit cell [7-9]. Because of the increased complexity of the unit cell, a large variety of such materials could be synthesized. Recently Ba_2HoSbO_6, a member of the rare-earth based Ba-Ho-Sb-O ceramic family, is reported to be a potential ceramic material for such applications [10, 11].

For polycrystalline substrate and crucible applications high sintered density, homogenous microstructure and good mechanical strength are essential requirements. Principal limitation of ceramics is their brittleness, i.e., the tendency to fail suddenly with little plastic deformation [12, 13]. This is of particular concern when the material is used in structural and crucible applications. The theoretical strength of a material is the tensile stress that would be needed to break the bonds between atoms in a perfect solid and pull the object apart. But all materials, including ceramics, contain minuscule structural and fabrication flaws that make them significantly weaker than the ideal strength. Any flaw, such as a pore, crack or inclusion results in stress concentration, which amplifies the applied stress. Pores also reduce the cross-sectional area over which a load is applied. Thus, denser, less porous materials are generally stronger. Similarly, smaller grain size give rise better mechanical properties [13, 14].

Densification of ceramics requires either pressure assisted or liquid phase sintering [12-15]. Hot pressing and hipping are costly batch processes [16, 17]. For the densification of oxide ceramics, transition metal oxides are normally used as sintering aids for liquid phase sintering processes [18]. In this work, we have used CuO as a sintering aid for the densification of Ba_2HoSbO_6 and studied the microstructure and mechanical properties of the Ba_2HoSbO_6 ceramics.

Materials and Methods

Ba_2HoSbO_6 oxide ceramics were prepared by solid-state reaction process. Stoichiometric mixtures of high purity (99.99%) constituent chemicals Ho_2O_3, BaO and Sb_2O_3 were mixed thoroughly in an agate mortar. The mixture was dried in an oven for 6h at a temperature of 200°C and pelletized as circular discs, using isostatic pressing technique, at a pressure of 5 ton/cm^2. The green compacts were ground with SiC paper to remove 0.15mm from the top and bottom surfaces. This procedure was adopted to avoid contamination. The size of resulting green compact discs were 10mm in diameter and ~2mm in thickness. These green compact discs were calcined at a temperature of 1100°C for 40h. The calcined material was reground and isostatically pressed as circular discs at a pressure of 5 ton/cm^2. These green compacted discs were again were ground with SiC paper to remove 0.15mm from the top and bottom surfaces and sintered at 1200°C for 60h. Another two batches of the Ba_2HoSbO_6 containing 1 and 2wt% CuO, as sintering aid, were pelletized and sintered in the similar conditions. CuO added Ba_2HoSbO_6 were prepared and sintered to study the effect of liquid phase sintering on microstructural and mechanical properties of the Ba_2HoSbO_6 ceramics. All the material processing was carried out in open air atmosphere.

X-ray diffraction patterns (XRD) of the sintered Ba_2HoSbO_6 materials were recorded by a Siemens D-5000 x-ray diffractometer, using Cu K_α radiation (λ = 1.5406 Å). Surface morphology and microstructure of sintered materials were studied by scanning electron microscopy (SEM), using secondary electrons. SEM micrographs were recorded by a Leico-Cambridge Stereoscan model 440 Electron Microscope. Quantitative elemental analysis of materials was carried out by energy dispersive x-ray (EDX) technique. EDX spectra of the samples were recorded using X-ray OXFORD model PENTAFET detector with Be-window and 128 eV resolution. The accelerating voltage used was 20KV, the beam current 200pA and the counting 100s. The density of the sintered samples was determined by the Archemedes method. Mechanical hardness of the specimens were measured by Vickers WEB WERKSTOPFFPRUF MASCHINEM, model WPM indentor.

Results and Discussion

Crystallographic structural characteristics of the pure and CuO added Ba2HoSbO6 sintered ceramics were studied by XRD technique. X-ray diffraction spectra of the sintered Ba2HoSbO6 materials are shown in figures 1-3, respectively for the pure, 1 and 2wt% CuO added Ba2HoSbO6 ceramics. As seen from these figures, it is clear that CuO addition up to 1 wt% does not affect the crystallographic structural characteristics of the Ba2HoSbO6 materials. These materials have standard A2BB'O6 type ordered complex cubic perovskite structure (1, 2). However, the addition of 2wt% CuO destroys the crystallographic structural characteristics of Ba2HoSbO6 and material crystallizes in an unknown impurity phase. In view of the XRD results, we confined our further studies only up to 1 wt% CuO addition in Ba_2HoSbO_6.

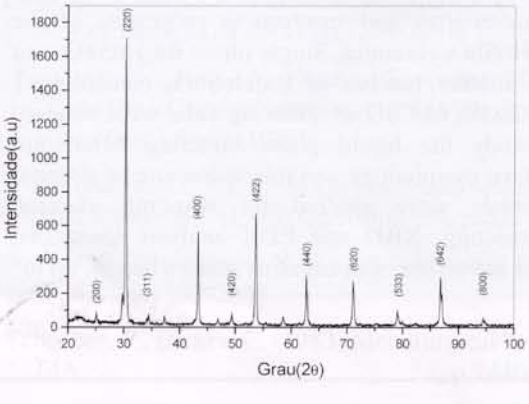

Figure 1 X-ray diffraction patterns of single phase Ba_2HoSbO_6

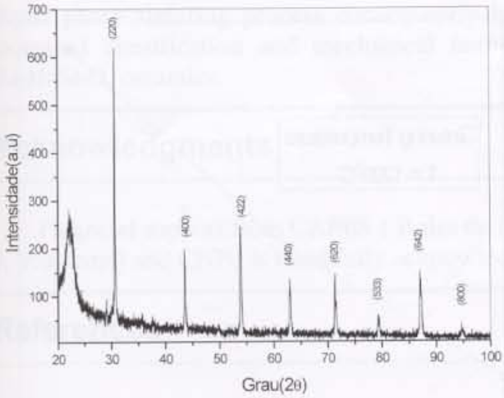

Figure 2 X-ray diffraction pattern of Ba_2HoSbO_6 added with 1 wt% CuO as sintering aid

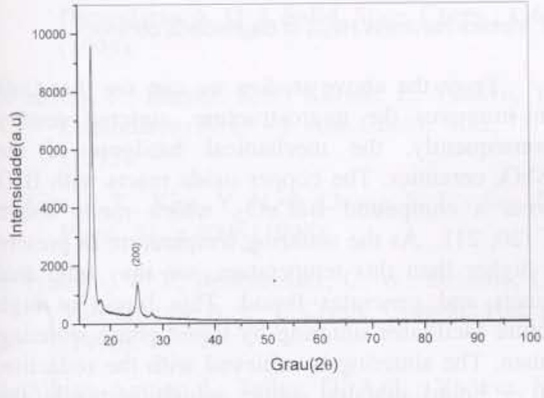

Figure 3 X-ray diffraction pattern of Ba_2HoSbO_6 added with 2 wt% CuO as sintering aid

SEM micrographs of sintered Ba_2HoSbO_6 and Ba_2HoSbO_6 added with 1 wt% CuO, shown in figs. 4 1nd 5, respectively, reveal that CuO addition improves the microstructure and particle size distribution of the Ba_2HoSbO_6 ceramics. Ba_2HoSbO_6 ceramics, added with 1 wt% CuO sintering aid, present a better homogenous surface morphology and particle size distribution, compared to the pure Ba_2HoSbO_6 sintered ceramics.

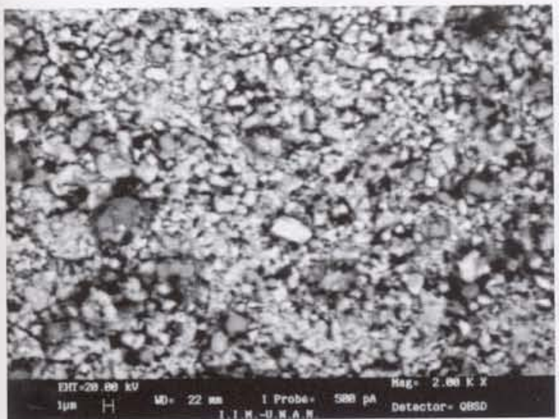

Figure 4 SEM microstructure of sintered Ba_2HoSbO_6 ceramic

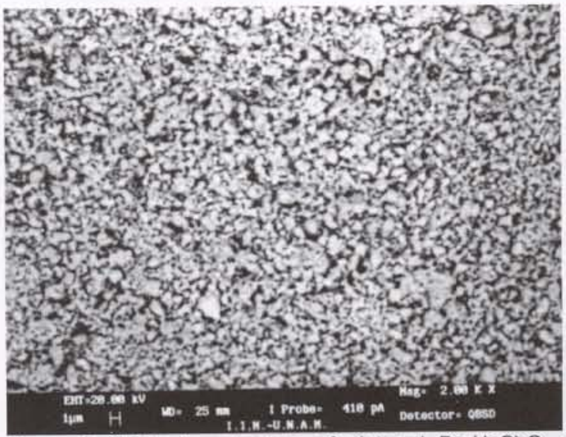

Figure 5 SEM microstructure of sintered Ba_2HoSbO_6 ceramic added with 1 wt% CuO as sintering aid

Results of quantitative elemental analysis by EDX of the sintered Ba_2HoSbO_6, added with 1 wt% CuO as sintering aid, is presented in Table 1 and EDX spectra of the same sample is shown in fig. 6. These results clearly show that the Ba_2HoSbO_6 sample contains only Ba, Ho, Sb and O elements and there are no traces of Cu element. It indicates that CuO works just as sintering aid and does not remain in the sample.

We obtained a sintered density of 7.03g/cm^2 for Ba_2HoSbO_6 ceramics sintered with an addition of 1 wt% CuO, while 6.64 g/cm^2 for Ba_2HoSbO_6 pure sintered samples. These values are 96% and 92%, respectively, of the theoretical density 7.36 g/cm^2 of Ba_2HoSbO_6.

Table 1. EDX data of the Ba_2HoSbO_6 ceramic sintered with 1 wt% CuO as sintering aid

Elements	Elements %	Atomics %
Ba	40.35	16.97
Ho	20.14	7.05
Sb	21.26	10.09
O	18.26	65.90
Total	100.00	100.0

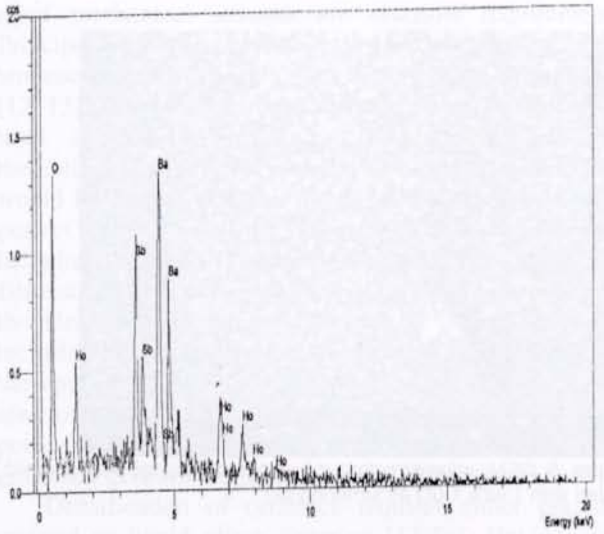

Figure 6. EDX spectra of Ba_2HoSbO_6 ceramic sintered with 1 wt% CuO as sintering aid.

Mechanical properties describe the way that a material responds to forces, loads, and impacts. In this work, mechanical hardness of the sintered Ba_2HoSbO_6 ceramics was studied by Vickers hardness test. The Vickers hardness test or the 136 degree diamond pyramid hardness test is a micro-indentation method. The indenter produces a square indentation, the diagonals of which are measured. Hardness is calculated by dividing the applied load by the surface area of the indentation. For calculating values of the Vickers hardness we used following equation [19]:

$$Hv = 1.8544\ P/d^2$$

where Hv – Vickers hardness, P – applied load and d – average of the diagonal of the indentation.

The results of the Vickers hardness test of Ba_2HoSbO_6 ceramics are shown in fig.7. As seen from the figure, hardness of the Ba_2HoSbO_6 ceramic is considerably improved with the addition of CuO sintering aid. These results are consistent with the results of microstructural studies where we observed a grain refinement and homogenous surface morphology of the 1wt% CuO added Ba_2HoSbO_6 ceramic. It may be noted that mechanical strength of sintered ceramics is strongly related with the microstructural characteristics of the material.

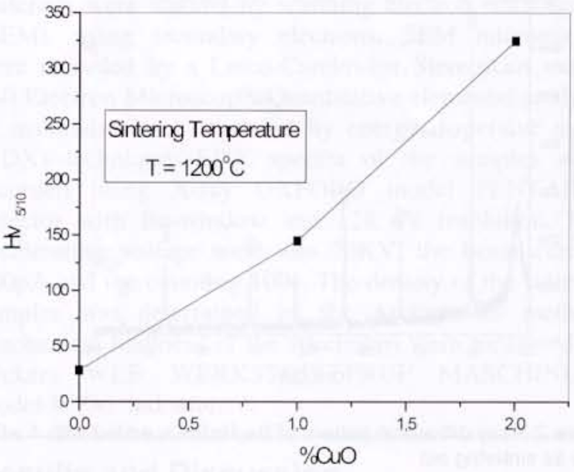

Figure 7. Vickers hardness $Hv_{5/10}$ of Ba_2HoSbO_6 ceramics

From the above studies we can see that CuO addition improves the microstructure, sintered density and, consequently, the mechanical hardness of the Ba_2HoSbO_6 ceramics. The copper oxide reacts with BaO and forms a compound $BaCuO_2$, which melts above 1000°C [20, 21]. As the sintering temperature in present case is higher than this temperature, we may infer that CuO reacts and generates liquid. This liquid at high temperature facilitates sintering by liquid phase sintering mechanism. The sintering is achieved with the reduction of solid – liquid dihedral angle, which increases the wettability and thus the liquid drags the grain towards each other. The sintering is enhanced by the formation of liquid phase and the increase in the wettability helps solution precipitation process to occur resulting in grain growth and improvement in the homogeneity of the grain size distribution. These microstructural modifications consequently help in the increase densification and mechanical hardness of the Ba_2HoSbO_6 ceramics.

Conclusions

In conclusion, we have studied sintering process, microstructural characteristics and mechanical properties of a high technology Ba_2HoSbO_6 ceramic. We also studied the effect of liquid phase sintering behaviour of Ba_2HoSbO_6 by adding 1 and 2wt% of CuO, as sintering aid, in the single phase Ba_2HoSbO_6. Our studies reveal that liquid phase sintering process, due to CuO addition, facilitates the sintering of the Ba_2HoSbO_6 and improves the microstructure and particle size distribution of the Ba_2HoSbO_6 ceramics. An important observation is that higher wt% (> 1wt%) CuO addition destroys the crystallographic structural characteristics of the Ba_2HoSbO_6. Thus liquid phase sintering of Ba_2HoSbO_6 ceramic using CuO additives is limited to a maximum of

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