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Effect of consolidation parameters on structural, microstructural and electrical properties of magnesium titanate ceramics

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ABSTRACT

The aim of this study is to explore the influence of the processing route on the structural and physical properties of bulk $MgTiO_3$ ceramics. Commercially available MgO and TiO_2 powders were mechanically activated in a planetary ball mill. Green bodies were formed by an isostatic pressure of 300 MPa. The sintering of these samples was done either by the Two-Step Sintering (TSS) approach or by conventional pressureless sintering followed by Hot Isostatic Pressing (post-HIPing). The first set of compacts was sintered by TSS in air at 1300 °C for 30 min and the next step was performed at 1200 °C for 20 h. The density of the obtained samples after the two-step sintering reached almost 90% of the theoretical density (%TD). The second set of compacts was sintered at 1400 °C for 30 min in air. The samples without open porosity were post-sintered by the HIP at 1200 °C for 2 h in an argon atmosphere at a pressure of 200 MPa. The density significantly increased up to 96%TD. The differences between samples prepared by these two techniques were also analyzed by XRD and SEM. The lattice vibration spectra were obtained using Raman spectroscopy and they indicate a high degree of lattice disorder, as well as high values of the oxygen vacancy concentration. Electrical characteristic were established in the frequency range from 10 kHz to 10 GHz. The choice of the processing route had considerable influence on structural and physical properties of $MgTiO_3$ ceramics.

1. Introduction

Magnesium titanate, $MgTiO_3$, is a microwave dielectric material used in optical communication in planar light-wave circuits as a buffer layer, in multilayer capacitors, antennas for communication, direct broadcasting satellite and global positioning system, etc. [1]. A very important achievement in the fabrication of microwave ceramic components based on MgO-TiO_2 would be to improve the values of the relative permittivity (relative dielectric constant, ε_r) and the dielectric loss tangent ($\tan\delta$). It is well known that the density is one of the most relevant factors for the enhancement of ε_r. In addition, obtaining a greater level of ordering in the crystal lattice causes a decrease of unwanted dielectric losses. The major causes of the dielectric losses at microwave frequencies are lattice vibration modes, pores, chemical and phase impurities, as well as lattice defects [2].

The synthesis of $MgTiO_3$ with an appropriate structure and phase composition is a complex and still unresolved problem. The preparation of magnesium titanate was discussed in several papers and several methods were proposed, such as solid-state reaction, thermal decomposition of peroxide precursors, hydrothermal mechanochemical complexation routes, etc. [3]. The main problem associated with the application of the sold-state reaction is the appearance of $MgTi_2O_5$, which persists to a certain extent in the final product as a metastable phase, as well as high sintering temperatures, above 1400 °C, and the holding time of a few hours [4]. Remains of metastable phase are also detected during the synthesis of magnesium titanates by mechanochemical complexation. The sol–gel method has advantages, such as good stoichiometry, particles with well-defined geometry and morphology, but this method is complex and expensive [3]. In addition, ceramic based on $MgTiO_3$ always tends to form the secondary phase $MgTi_2O_5$, which deteriorates dielectric properties (ε_r and $\tan\delta$) in proportion with its molar ratio [5,6]. In order to control the combined dielectric properties of a high dielectric constant and a low dielectric loss, it is necessary to produce $MgTiO_3$ powders with

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the highest possible purity, well-defined particle morphology, and small particle-size distribution.

Having in mind that consolidation parameters strongly affect properties of electro ceramics, it is very important to optimize conditions which would lead to obtaining ceramics with appropriate structural and electric properties. The process of mechanical activation has been widely used to enhance the reactivity of materials by particle-size reduction and the amorphization process [7]. This is also a well-known top-down process which enables the formation of submicrometer and/or nanostructured materials with desirable properties. This process is frequently used in many areas of science, material science, biomedicine, etc., because it relies on low-cost and widely available oxides as starting materials and skips the calcinations step at an intermediate temperature, resulting in a simplified and cheaper manufacturing process [8,9]. During mechanical activation, powder particles are subjected to severe plastic deformation that results in the formation of defects of high concentration. The mechanical activation induces an enhanced atomic mobility together with other accompanying phenomena depending on milled materials [10]. This process overcomes the kinetic constraints and the demand for high processing temperatures, which are typical for conventional solid-state synthesis methods. Moreover, the mechanical activation of powders promotes the diffusion rate of reactants across phase boundaries and represents a way to increase the kinetics of solid-state reactions. Many researchers have also emphasized the efficiency of mechanical milling of precursors in the densification and phase purity. It has been demonstrated that the mechanical activation decreases reaction temperatures for the formation of titanate-based materials as a consequence of the increased specific surface area and the total free (Gibs) energy of the system. Furthermore, there is an increase of the structural defect concentration in the near surface layers, which is also accompanied by a reduction of potential barriers for the process of nucleation of a new phase. The formation of mechanically activated titanate-based materials usually takes place through two or three elementary steps, via intermediate compounds [11–13]. Furthermore, the sintering process, as a method for consolidation of powder mixtures, is a very important step in ceramic densification. A change in the size and structure of the particles during mechanical activation causes instability of treated powders, which is reflected in the changed sinterability of samples, within the applied sintering regime. Consequently, this leads to changes in their final structure. An increased number of contacts achieved owing to an increased specific surface, as a consequence of mechanical treatment, promote the formation of intergranular contacts. The main contribution to and densification has transport mechanisms. The driving force for neck growth and sintering is the reduction of the system surface free energy. In addition, neck growth is controlled by numerous diffusion mechanisms (lattice diffusion, grain boundary diffusion, etc.) with rates determined by the total flux of atoms coming to the neck [14]. Therefore, it can be assumed that the dominant processes occurs at grain boundaries. A large number of sintering techniques, such as conventional sintering, spark plasma sintering, microwave sintering, two-step sintering, and hot isostatic pressing (HIP), were developed providing various conditions during this high-temperature process [15]. During the sintering of submicrometer and nanosized materials, mass transport occurs in a somewhat different way compared to micrometer-sized materials. In this type of materials, the control of porosity during densification is particularly important [16].

Hot Isostatic Pressing can be used as a post-sintering step in samples without open porosity. Such samples are usually obtained after a conventional pressureless sintering regime. The sintering temperature is maintained until all pores become disconnected from the surface of the sample – the porosity is closed. This point is mostly reached when the relative density is higher than 94%TD, but this value varies for different materials. In cases of samples of a lower pre-sintered density and pores that are not all closed, HIP sintering will not be effective [17].

The combination of an increased pressure and a lower sintering temperature (than in the first pressureless step) can be used to achieve a higher density, as well as a more appropriate microstructure (lower grain growth rate). HIP is largely concerned with the elimination of closed pores, which are always present during the final phase of the sintering process of oxide materials and the decrease of gas solubility during the solidification and cooling steps, agglomerations of vacancies generated by creep or during a variety of diffusion processes which occur when connecting dissimilar materials. The mechanical performance of these products depends on the distribution, morphology and volume fraction of porosity, which have a detrimental effect on properties like fracture toughness, fatigue resistance and tensile strength [18]. The surface energy is a driving force for pore closure. During the final stages of HIP densification, when only isolated pores are present, the surfaces of the pores are not simply pushed together to develop a planar crack. Bonding occurs, because atoms diffuse in both directions across the interface (a microscopic form of the diffusion bonding). At this stage, pore dimensions are small (1 μm or less) and the sustain time (one hour or longer) is more than adequate to allow the complete elimination of pores [19]. HIP sintering is usually applied in materials based on hydroxyapatite composites [20], carbides [21], and piezocomposites [22], but advantages of this technique have not yet been sufficiently exploited in the field of microwave electronic materials. It is highly beneficial to obtain ceramics without porosity, as the electric properties of these materials are significantly affected by the presence of pores.

The two-step sintering was mainly used for nanosized or submicrometer materials to avoid the final grain growth, namely, for many ceramic materials, such as barium titanate, strontium titanate, alumina, etc. [23–25]. The two-step sintering (TSS) approach was proposed by Chen and Wang [26]. TSS consists of two steps, where the first step involves constant-rate heating with no dwell time or a very short dwell time. In this stage, the densification and elimination of supercritical porosity dominate. A sufficiently high relative density (70%TD or higher) needs to be achieved during the first step (S1), so that the densification process may continue in the second step (S2). S2 is performed at a lower temperature with a long dwell – usually dozens of hours. The success of the two-step sintering is requires a sufficiently high starting density that should be obtained during the first step. When the density is greater than a critical value, the pores become subcritical and unstable against shrinkage induced by capillary action. These pores can be filled as long as the grain boundary diffusion allows [27]. The most important advantage of this approach over the conventional pressureless sintering is that the densification of samples continues with a significantly slower grain growth [28]. As Chen and Wang have postulated, there is an interval of temperatures where the densification occurs, while migrations of grain boundaries have not started yet [29]. This temperature interval, named “kinetic window”, and the sintering in it, is the key to densification without grain growth. It has been demonstrated that the efficiency of TSS is different for different groups of materials [30]. In addition, it is assumed that for some classes of materials, such as alumina, the “kinetic window” does not exist because the activation energy of densification is higher than the activation energy for grain growth [31]. In such cases, the densification with no grain growth would not be possible. To the best of our knowledge, not many attempts of applying TSS on microwave dielectric materials, such as $MgTiO_3$, have been reported and studies seeking to clarify the relationship between electrical properties and microstructures resulting from