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Linking sintering stresses to nano modification in the microstructure of $BaLa_4Ti_4O_{15}$ by transmission electron microscopy

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ABSTRACT

High quality factor and a temperature stable resonant frequency make $BaLa_4Ti_4O_{15}$ (BLT) ceramics attractive materials for microwave applications. Aiming to exploit the effects of external stresses on the development of textured and anisotropic microstructures to optimise MW properties, the influence of applied external pressure during sintering of BLT ceramics is analysed. HRTEM and geometric phase analysis (GPA) showed that stresses applied during sintering, trigger the nucleation and growth of faults hypothesised to be due to the errors in the AO_3 layer (basal plane) stacking sequence of the hexagonal perovskite structure. The results reveal a strong correlation between the high concentration of structural defects and the development of anisotropic microstructures, which tune the properties of BLT. Stresses applied during sintering are therefore a promising tool to design material properties.

1. Introduction

Advances during the last few decades in microwave (MW) technology have brought a revolution in telecommunication systems. The main criteria for the use of microwave materials in devices are compactness, low loss and reliability. The size of a MW component may be reduced by utilising high permittivity (ε_r) ceramics since the resonant frequency of a MW material is inversely proportional to ε_r. This is particularly important for dielectrically loaded Global Positioning Systems (GPS) antennas in handheld devices where space within the device casing is at a premium. However, for resonators and cavity filters in base stations the main technological driving force is the selectivity of the material to a narrow frequency range to maximise the usage of limited sections of the Electromagnetic (EM) MW spectrum and thus the MW quality factor (Qf) dominates innovation. Low temperature co-fired ceramic (LTCC) technology is used to create integrated MW circuits in which the EM radiation propagates through a sequence of waveguiding channels and filters embedded in ceramic layers [1]. In this technology, low cost and compatibility with Ag electrodes are critical.

Despite these diverse applications, one unifying material property is critical to all MW materials. The temperature coefficient of the resonant frequency (τ_f) must be close to zero. For modern cavity resonators and filters, the most stringent application for materials, $\tau_f = \pm 1$ ppm/°C, $Qf > 40{,}000$ GHz and $20 \geq \varepsilon_r \geq 50$. For dielectrically loaded antenna the requirements for τ_f and Qf are relaxed since loss is dominated by the ceramic/metallisation interface, $\tau_f = \pm 10$ ppm/°C, $20 \geq \varepsilon_r \geq 100$, $Qf = 10{,}000$ GHz, and for LTCC the presence of metallisations within the structure limits the Qf of the device, $\tau_f \pm 10$ ppm/°C $Qf < 1000$ GHz, and $8 \geq \varepsilon_r \geq 100$ [2].

There is considerable interest in titanate based electroceramics for microwave applications due to their exceptional dielectric properties [3–6]. Amongst titanate-based materials, compositions in BaO - Re_2O_3 - TiO_2 family are widely used in a broad range of applications such as dielectric resonators, microwave substrates for antennas and C0G (Electronic Industries Alliance standard for temperature compensating class 1 capacitors) temperature stable capacitors. There are many materials used for dielectric resonators but where a combination of medium to high permittivity is required with selectivity to a narrow frequency range, compositions based on $BaLa_4Ti_4O_{15}$ (BLT) are commercially competitive with MW properties reported as $\varepsilon_r \sim 45$, $Qf \sim 41{,}000$ and $\tau_f \sim -26$ ppm/°C.

BLT has a B-site deficient layered perovskite structure with a hexagonal *P*3*c*1 space group [5,6] (Fig. 1). AO_3 mixed layers are stacked to form the layered perovskite structure and the distance between these

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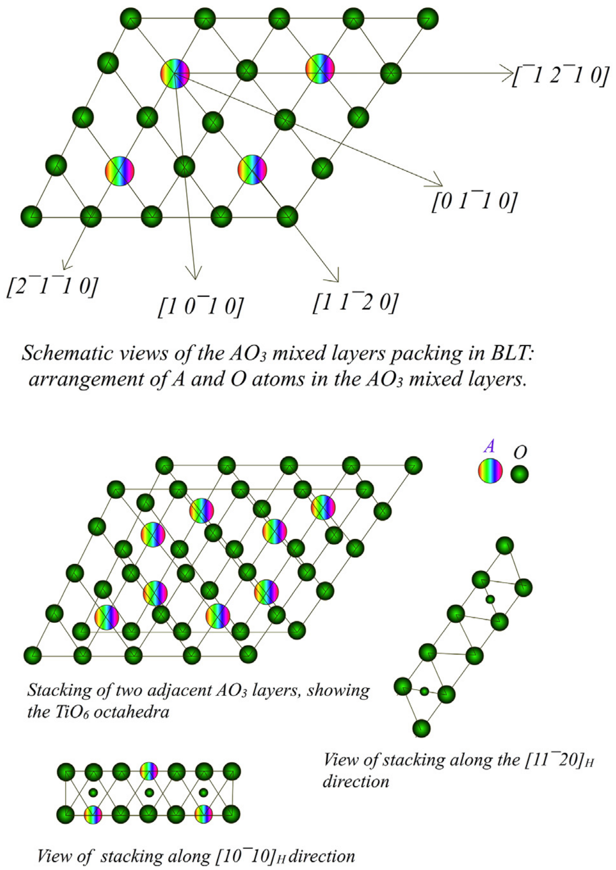

Fig. 1. Schematic representation of the layered perovskite structure of BLT in which A represents Ba and La ions in the structure [7,8]. The BLT structure exhibits some layers in which the octahedra are face rather than corner shared [7].

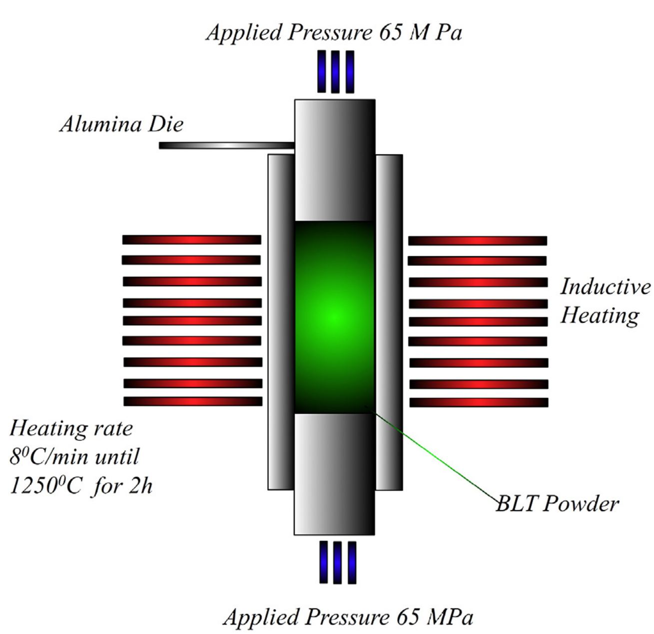

Fig. 2. Schematic of the preparation of HP BLT ceramics.

layers influences the properties of BLT [5,6]. Common crystal imperfections in such structures are stacking faults, which occur due to the disparities in stoichiometry of the AO_3 layers. The hexagonal structure of BLT essentially arises because at least two octahedral layers are face shared in contrast with cubic perovskites in which all octahedra are corner shared [7].

To control MW properties, it is imperative that ceramics attain an optimised microstructure. There have been several attempts to control the dielectric properties of microwave materials by using sintering variables, [3,4]. Temperature, heating/cooling rates and sintering atmospheres have been frequently used in titanates to change the microstructure and thus the dielectric properties [5]. In $SrTiO_3$, two sintering regimes exist and a slight variation in composition is enough to change the microstructure. The low temperature regime is dominated by grain boundary diffusion and at high temperature volume diffusion occurs [5]. In addition, depending on Sr/Ti stoichiometry the densification and microstructure may vary [5]. We have recently shown that a grain boundary (GB) anomaly can be triggered in $SrTiO_3$ by varying the sintering temperature [9]. Literature reports that in $SrTiO_3$ the grain growth anomaly may result from changes in grain boundary structure and stoichiometry with modification of the sintering temperature leading to changes in the grain boundary energy and/or mobility [10]. A TEM study on the grain boundary stoichiometry of $SrTiO_3$ [11] reports that Ti rich grain boundary regions diffuse slower than others, but no clear correlation to the grain growth anomaly has yet been obtained. The microstructure of ceramics is also controlled by the sintering atmosphere. For example, during the sintering of titanates at high temperature where reduction of Ti^{4+} may occur high oxygen partial pressure is utilised to maintain O stoichiometry.

Another way to control materials microstructure is by applying external stresses during the sintering. In functional thin films the role of stress is well known and used as an engineering tool to induce new physical phenomena. In $SrTiO_3$ thin films for example, ferroelectric behaviour may be induced through compressive in-plane strain [12]. However, the effect of stresses in the microstructure development of ceramics is not so well known and rarely documented. Since Abouaf et al. [13,14] first studied hot isostatic pressing of Al_2O_3 and observed that crystal imperfections are formed during sintering under stress, which relates to abnormal grain growth, no other systematic investigations have been conducted. Recently, however, Zhi et al. [15] and Amaral et al. [16] reported a marked effect of the mechanical stress on the microstructural development arising from the substrate during the constrained sintering of $BaNd_2Ti_5O_{14}$ (BNT) and BLT thick films. Zhi et al. [15] and Amaral et al. [16] hypothesised that tensile compatibility stresses induced by the geometrical constraint increase the mobility of grain boundaries or the driving force for grain boundary transport enhancing grain growth. However, a comprehensive understanding of the effect of stresses on the microstructure during sintering and its role and/or utilisation in the development/design of textured and anisotropic microstructures, is still missing.

In this work we link the microstructural changes in BLT ceramics to the external pressure applied during sintering. To this end, systematic HRTEM studies were conducted on BLT ceramics sintered under pressure and without external stresses with the results being used to develop a mechanistic understanding of the role of stress in sintering.

2. Experimental

Single phase $BaLa_4Ti_4O_{15}$ (BLT) powders, with 3 μm average particle size, were prepared through conventional solid state route by mixing the stoichiometric proportion of $BaCO_3$-La_2O_3-TiO_2 (< 99% purity, Merck) powders, in ethanol, and ball milling, for 24 h, in a Teflon jar before and after calcination at 1330 °C, for 3 h. Phase purity of the BLT powders were ensured with XRD. Powders were thermal consolidated by hot pressing (HP) in a hot press furnace (homemade by UIDM, Viana do Castelo) as schematically shown in Fig. 2. Alumina dies and punches were used and the thermal cycle conditions leading to near dense samples were: a constant heating rate of 8 °C min^{-1} up to a maximum temperature of 1250 °C, for 2 h, and 65 MPa of applied pressure. For a systematic and comparative study of the pressure