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Microstructural and high-temperature impedance spectroscopy study of $Ba_6MNb_9O_{30}$ (M=Ga, Sc, In) relaxor dielectric ceramics with tetragonal tungsten bronze structure

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ABSTRACT

This work reports on the microstructural and high-temperature impedance spectroscopy study of a family of dielectric ceramics $Ba_6MNb_9O_{30}$ (M=Ga, Sc, In) of tetragonal tungsten bronze (TTB) structure with relaxor properties. For $Ba_6GaNb_9O_{30}$ and $Ba_6InNb_9O_{30}$ pellets, the SEM images have revealed good, dense internal microstructures, with well-bonded grains and only discrete porosity; in contrast $Ba_6ScNb_9O_{30}$ pellets had a poorer microstructure, with many small and poorly-bonded grains gathered in agglomerates, resulting in significant continuous porosity and poorly defined grain boundary regions. The electroactive regions were characterised by the bulk and grain boundaries capacitances and resistances, while their contribution to the electrical conduction process was estimated by determining activation energies from the temperature (Arrhenius) dependence of both electric conductivities and time constants. For Ga and In analogues the electronic conductivity are dominated by the bulk response, while for Sc analogue, the poorly defined grain boundaries give a bulk-like response, mixing with the main bulk contribution.

1. Introduction

Within ceramic materials, a very interesting and important class is represented by electroceramics, which have useful electrical, optical and magnetic properties. Generally, electroceramics are advanced materials that are used in high technology applications. Their properties depend on the complex interplay of structural, processing and compositional variables. Even simple single-phase ceramic materials (not composite materials) have complex behaviour, of which usually the bulk (intrinsic) properties of the crystal are those of interest; therefore, dense ceramics – free from extrinsic effects (*e.g.* grain boundary, surface and electrode interfaces, dopant segregation, *etc.*) – are desired. They are used for various applications, as insulators, capacitors, temperature sensors and varistors, gas sensors, ionic electrolytes in fuel cell and rechargeable battery applications [1,2].

Insulators are chemical compounds that have the outer shell electrons locked in either strong covalent bonds or are restricted to close regions to an atomic nucleus (if the case of an ionic compound), and are unable to move through the structure in order to facilitate electrical conduction [1,2]. They are often referred as dielectrics, with the only mention that the term "insulator" is generally used to indicate *electrical obstruction* while the term "dielectric" is used to indicate the material *capacity to store energy*, *i.e.* to become polarised under an applied field. In dielectrics, the valence band is usually full; the next energy band is separated by a large forbidden band gap. As the forbidden band gap is larger, fewer electrons from the valence band have enough thermal energy to pass into the conduction band, and thus such materials become very good insulators. Solid dielectrics are definitely the most used dielectrics in electrical engineering, generally as: (a) electrical insulating materials for coating or wrapping wires and cables that carry electric current (most plastics, electrical insulation paper, porcelain and glass) or (b) as dielectric components in electronic devices (ceramics), such as rectifiers, transducers and amplifiers [3]. The required properties for a "good dielectric" are: high dielectric constant, low dielectric loss, thermal stability, tuneable temperature coefficients, high quality factors at many frequencies, high intrinsic breakdown for pulse power applications and resistance to interference from electromagnetic fields [4].

Polar dielectrics such as piezoelectrics or ferroelectrics are useful in electronic devices, as capacitors or resonators, mainly to their high permittivities [5]; with the demand for increasing the

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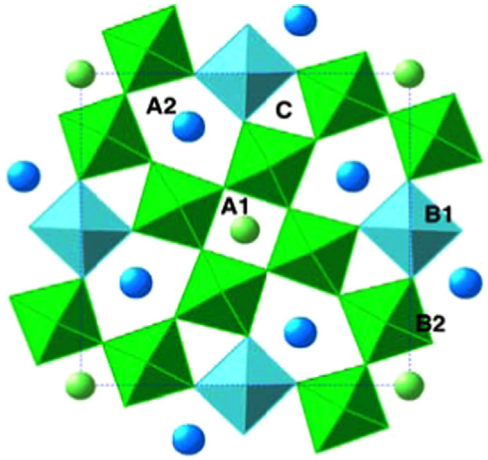

Fig. 1. Polyhedral representation of the tetragonal tungsten bronze (TTB) aristotype structure viewed down the c-axis.

power processing of computers, the market was flooded with various multi-layer ceramic capacitors that led to a greater appreciation of the research concerning the relationship between chemical composition, structure and electrical properties of new dielectric materials [6–9]. Relaxor ferroelectric phenomenon was observed in ceramics materials for nearly four decades [9–11]; for example, PMN-PT is a typical relaxor ferroelectric, with large piezoelectric effect and optical anisotropy [11].

More recently, besides the perovskite-based (ABO_3) materials, the tetragonal tungsten bronze (TTB) class of materials – Fig. 1 – which is related to perovskites [12], has begun to garner renewed interest in the research community [12–15]. The very versatile TTB structure: $(A1)_2(A2)_4(C)_4(B1)_2(B2)_8O_{30}$ allows for the inclusion of particular metals into the five different TTB sites [16] and offers the possibility of adjusting both electric and magnetic behaviour [17,18]. The TTB structure has a repetitive perovskite unit in the middle (A1), while the additional corner-sharing BO_6 octahedra create another two types of channels in the structure: the A2-site and the C-site. The A1 sites are 12-coordinated and defined by 8 octahedra, the four larger A2 sites are 15-coordinated and defined by 10 octahedra, while the four trigonal C-sites are 9-coordinated and defined by 6 octahedra; moreover, the BO_6 octahedra are non-equivalent (two B1 sites and eight B2 sites) – Fig. 1. This rich diversity of elements which can be incorporated into the TTB structure allows for compositional tuning that has been exploited for development of new phases [13,19] ranging from ferroelectrics [20–22] to microwave dielectrics [23,24] and to ionic conductors [25].

During the last few years, the research dedicated to novel TTB ferroelectric and ferroelectric-related materials resurrected [15–22,26–31], with the $Ba_6FeNb_9O_{30}$ (BFNO) [32–35] as starting point. Earlier data reported that BFNO is ferroelectric with T_C values either in the range 133–138 K [36] or 570–583 K [37,38], however being not electrically homogeneous [29] and with oxygen vacancy gradients due to the variable oxidation state of Fe (Fe^{3+}/Fe^{2+}); both low temperature dielectric spectroscopy and high temperature impedance spectroscopy measurements indicated more electroactive regions than anticipated [16].

A family of relaxor TTBs of composition $Ba_6M^{3+}Nb_9O_{30}$, where the trivalent species do not have variable oxidation states (*e.g.* Ga^{3+}, Sc^{3+}, In^{3+}) was chosen in order to avoid these additional complications during the study of this type of materials and reported by Arnold & Morrison [16]. Prior to this study, identical powders and pellets of these three Ga, Sc and In analogues of $Ba_6MNb_9O_{30}$ ceramic materials, prepared under the same conditions, were investigated by temperature-dependent powder neutron diffraction (TDPND) and by dielectric spectroscopy (DS); the confirmation of the phase formation and the crystallographic identification, but also the relaxor dielectric properties of these dense ceramic materials were already reported [39]. The analysis of dielectric data showed a systematic (almost linear) increase in the dipolar stability of these materials with increasing M^{3+}cation size. Characteristic temperature parameters for each compound were extracted from both dielectric and crystallographic data as a function of temperature: the Vogel-Fulcher dipole freezing temperature, T_{VF}; T_{UDR} corresponding to absolute flattening of the dielectric loss peak in the frequency domain; and $T_{c/a}$ corresponding to the maximum crystallographic tetragonal strain. These temperature parameters were essentially coincidental and describe the slowing of dipolar response on cooling and the eventual "locking" of the B-cation displacements along the *c*-axis, (*i.e.* dipole freezing) [39]. The dynamics of dielectric relaxation of dipoles was extensively investigated by fitting the dielectric permittivity data to the Vogel-Fulcher (VF) model in order to monitor the reproducibility and validity of the physical results. We have shown that Vogel-Fulcher fits are very sensitive. Constraining some of the fundamental relaxation parameters to physically sensible values or varying the fitting range itself, results in a large range of values associated with the dielectric relaxation processes; restriction of the frequency domain due to experimental noise or instrumentation limits also has a dramatic influence on the values obtained [40].

Recently, resonance ultrasound spectroscopy (RUS) investigation of our Ga-analogue revealed that the main relaxor behaviour is accompanied by both elastic and anelastic relaxations [41]. In addition to an understanding of the chemical bonding, crystal structure and macroscopic dielectric properties, it is very important to understand the ceramic microstructure [42] and to identify and characterise the electrical behaviour of micro-regions [1,43–45] in order to fully characterise these ceramic materials. For adjusting technological conditions to prepare electroceramic materials, microstructure (grain homogeneity, grain morphology – shape and size, grain orientation, grain boundaries) must be determined and understood. Moreover, imperfections and defects affect all sorts of properties, by changing electrical behaviour, creating dislocations and finally producing mechanical failure. In this paper, the ceramic microstructure for three compositions, $Ba_6MNb_9O_{30}$ (M=Ga, Sc, In) was investigated in order to identify the electroactive regions present within these materials, and identify their influence on the macroscopic dielectric response. The capacitances and resistivities for both bulk and grain boundaries were estimated using combined impedance and modulus spectroscopy. The electric conductivities and the time constants were determined for both bulk and grain boundary regions and their contribution to the overall electrical conduction processes were investigated.

2. Experimental

2.1. Materials

Three ceramic compositions: $Ba_6MNb_9O_{30}$ (M=Ga, Sc, In) [16] were synthesised by standard solid-state techniques. Stoichiometric ratios of dried $BaCO_3$, Nb_2O_5, Ga_2O_3, In_2O_3, (all Aldrich, 99+%) and Sc_2O_3 (Stanford Materials Corporation, 99.999%) were ball milled in ethanol until homogenized (5 min at 400 rpm, using a Fritsch Pulverisette 7 system with agate mortar and balls). Powders were placed on platinum foil in alumina boats inside a muffle furnace at 600 °C (static air atmosphere) and fired initially to 1000 °C, left to decarbonate for 1 h, and further fired for 12 h at 1250 °C (heating rates: 10 K min^{-1}). After quenched to room