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New insights into the 6H-type hexagonal perovskite solid solution $BaTiO_{3-\delta}$: Influence of acceptor and donor doping on crystal structure and electrical properties

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ABSTRACT

Polycrystalline 6H-type hexagonal Barium Titanate $BaTi_{0.5}(Fe_{0.33}M_{0.17})O_{3-\delta}$, where M = Mo or W was prepared by the solid state reaction method. The effects of the cationic substitution of Fe^{3+}, Mo^{6+} and W^{6+} for titanium in the B site for $BaTiO_3$ perovskite lattice on the symmetry and the electrical properties were investigated. It was found that the substitution of Ti^{4+} by ($Fe^{3+}Mo^{6+}$) gives a hexagonal perovskite structure, whereas the substitution by ($Fe^{3+}W^{6+}$) cations results in a mixture of double cubic and hexagonal pervoskite phases. The difference in the average radius of cations in the B site ($r_B = 0.50 \times r_{Ti} + 0.33 \times r_{Fe} + 0.17 \times r_{M,\ (M = Mo\ or\ W)}$) created the difference in cell parameters. The conductivity obtained for $BaTi_{0.5}(Fe_{0.33}Mo_{0.17})O_{3-\delta}$ sample at a temperature of 200 °C was $2.3 \times 10^{-3}\ S\ cm^{-1}$, which is much greater than that established by $BaTi_{0.5}(Fe_{0.33}W_{0.17})O_{3-\delta}$ sample at a temperature of 328 °C ($0.26 \times 10^{-3}\ S\ cm^{-1}$) This means that a mixed ionic-electronic conductor (MIEC) character may be present in the first compound. Impedance Spectroscopy data collected for our samples over a range of temperatures and frequencies showed the appearance of a phenomenon of blocking at the grain boundary level, which means that the compounds are highly influenced by the oxygen stoichiometry. The correlation between the electrical properties of grain boundaries and their chemical composition is consistent with the interpretation in terms of the space charge model with a positive excess charge in the grain boundary core.

1. Introduction

Ionic conductors, including pure ionic conductors (electrolytes) and mixed ionic-electronic conductors (MIEC), are key components in fuel cells, supercapacitors, batteries, sensors and other devices. Solid-oxide fuel cells (SOFCs) are electrochemical devices whose most advantageous features are converting fuel chemical energy directly into electricity at higher efficiency. Fuel cells are created, at a low-temperature of around 80–120 °C, from solid-polymer or alkaline electrolyte, whereas high temperature electrolytes, which operate in the temperature range generally higher than 800 °C, are constituted of ceramic oxides. However, in the oxide-based ionic conductors, high operating temperature limits their application due to rapid degradation, high cost, interface reactions between cell components, electrode sintering, and material compatibility challenges [1–5].

The emergence of new intermediate temperature SOFC (IT-SOFCs, 200–600 °C), in the last few years, was caused by the development of new electrolyte materials that are capable of conducting oxygen anions with lower activation energies, so as to increase the electrical conductivity and to improve the electrochemical kinetics. The family of oxide materials is considered as a large family to which the electrolytes belong. Paradigmatic examples are oxide ion conductors based on: zirconia (YSZ) with a composition $Zr_{1-x}Y_xO_{2-\delta}$ and fluorite structure [6,7], ceria (GDC) with a composition $Ce_{1-x}GdO_{2-\delta}$ and the same

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structure as that of YSZ [8], bismuth oxide δ-BiO_2 [9–11] and perovskite type [12–22].

$LaGaO_3$ perovskite materials discovered by Ishihara et al. [12] have been widely investigated owing to their high oxide ionic conductivity. By substituting or incorporating other chemical elements into the A and/or B sites in perovskites, a high ionic conductivity can be obtained, for example $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ (LSGM) [13–15]. SOFC cathodes, oxygen separation membranes and catalysts as oxidation reactions are applications for which many perovskites are good candidates. For example $(La_{0.75}Sr_{0.25})_{0.95}Cr0_{.5}Mn_{0.5}O_{3-\delta}$ (LSCM) [16] and $La_{0.8}Sr_{0.2}FeO_{3-\delta}$ (LSF) [17] are promising candidates for cathode materials. A symmetric solid-oxide fuel cell with $La_{0.8}Sr_{0.2}Sc_{0.2}Mn_{0.8}O_{3-\delta}$ perovskite oxide as both the anode and cathode was discovered by Yao et al. [18]. Recently, novel $La_{x+1}Sr_{1-x}InO_{4+\delta}$ oxides with low activation energy and a competitive ionic conductivity at low temperature have been prepared. These oxides can be used as electrolyte for SOFCs [19]. Double perovskites, too, have become attractive materials for application in IT-SOFCs, demonstrating a very good electrochemical performance [20–22].

The nonstoichiometry in perovskites has been studied at large in numerous reviews [23–25]. Anion vacancies are more common than those containing cationic vacancies. $Ca_2Fe_2O_5$ [26,27] and $La_2Ni_2O_5$ [28,29], with the browmillerite structure, are the best-known examples of perovskite oxides with ordered oxygen vacancies. The structure can be considered as an anion-deficient perovskite with one-sixth of the oxygen ions being vacant ($A_2B_2O_{6-\delta}$ where $\delta = 1$). The δ oxygen deficiency exhibited by several perovskites far exceeds the maximum values reported in fluorite-based oxides.

One of the materials having an important value of δ is double perovskite-based oxides. For example, hexagonal $BaTiO_{3-\delta}$ (6H-$BaTiO_{3-\delta}$) is a potential candidate material for electronic devices [30,31]. The origin of the significant value of δ in 6H-$BaTiO_{3-\delta}$ is due essentially to its structure described as follows: 6H-$BaTiO_{3-\delta}$ with $P6_3/mmc$ space group, is composed of 6 closely-packed BaO_3 layers stacked in sequence $[cch]_2$, where c and h refer to cubic and hexagonal stacking, respectively. This results in two different crystallographic units for the Ti cations: Ti(1) occupies corner-sharing TiO_6 octahedra and Ti(2) is located in face-shared Ti_2O_9 dimers. Ti_2O_9 units are positioned between two corner-sharing TiO_6 octahedra. The O(2) ions that connect the face-sharing octahedra, together with Ba cations, form the hexagonal stacking Fig.1 (a). In the Ti_2O_9 units, the highly charged Ti^{4+} ions are situated at unusual proximity of 2.69 Å [32], which is, because of the high electrostatic repulsion, unfavorable for the stability of the structure Fig.1 (b). 6H-$BaTiO_{3-\delta}$ is not stable at room temperature, but it can be stabilized by reducing Ti^{4+} or doping with acceptor ions. Sinclair et al. [32] reported that the bond length of Ti(2)–O(1) shrunk and that of Ti(2)–Ti(2) expanded due to oxygen vacancies which are stable at O(2). Consequently, it is broadly accepted that the hexagonal 6H-$BaTiO_{3-\delta}$ structure is stabilized by oxygen vacancies. The appearance of a concentration of oxygen vacancies will introduce into the research of these compounds the notion of migration of the ionic charge carrier and consequently the notion of a space charge zone located in the grain boundaries.

In the present work we describe the synthesis and characterization of a new family of oxides of a composition $BaTi_{0.5}(Fe_{0.33}M_{0.17})O_{3-\delta}$, where M = Mo or W. We report, precisely, the comparison of structural characterization of 6H-$BaTiO_{3-\delta}$ phase stabilized at room temperature by the substitution of larger and smaller cations, Fe^{3+}, Mo^{6+} and W^{6+}, for Ti^{4+}. We also used impedance spectroscopy to separate conductivity into bulk and grain boundary components. The analysis of ion transport properties was performed based on a Mott-Schottky type space charge layer. Dependences on dopant type and concentration were discussed.

2. Experimental procedure

The new polycrystalline ceramics of a nominal composition $BaTi_{0.5}(Fe_{0.33}M_{0.17})O_{3-\delta}$ (M = Mo or W) were prepared by conventional ceramic-making technique of solid-state reaction. Details of the sample preparation and structure characterization were described in our previous works [33,34]. Phase purity, structure, space groups, and lattice parameters were determined by powder X-ray diffraction (XRD) with a Siemens D5000 diffractometer using Cu-Kα radiation at room temperature. The powder was sintered into pellets of a diameter of 8 mm and a thickness of around 1 mm at a temperature of 1400 °C. The grain size and the micromorphology were detected on a fracture of surface by a scanning electron microscope (SEM) using a Philips XL30 equipped with energy dispersive X-ray detector (EDX). On both sides of the pellet we put a thin silver electrode through a circular mask of a diameter of 6 mm. Indeed, the opposite faces of the pellet was coated with high purity ultrafine silver paint, and then dried at 150 °C for 4 h to remove the moisture from the sample prior to electrical

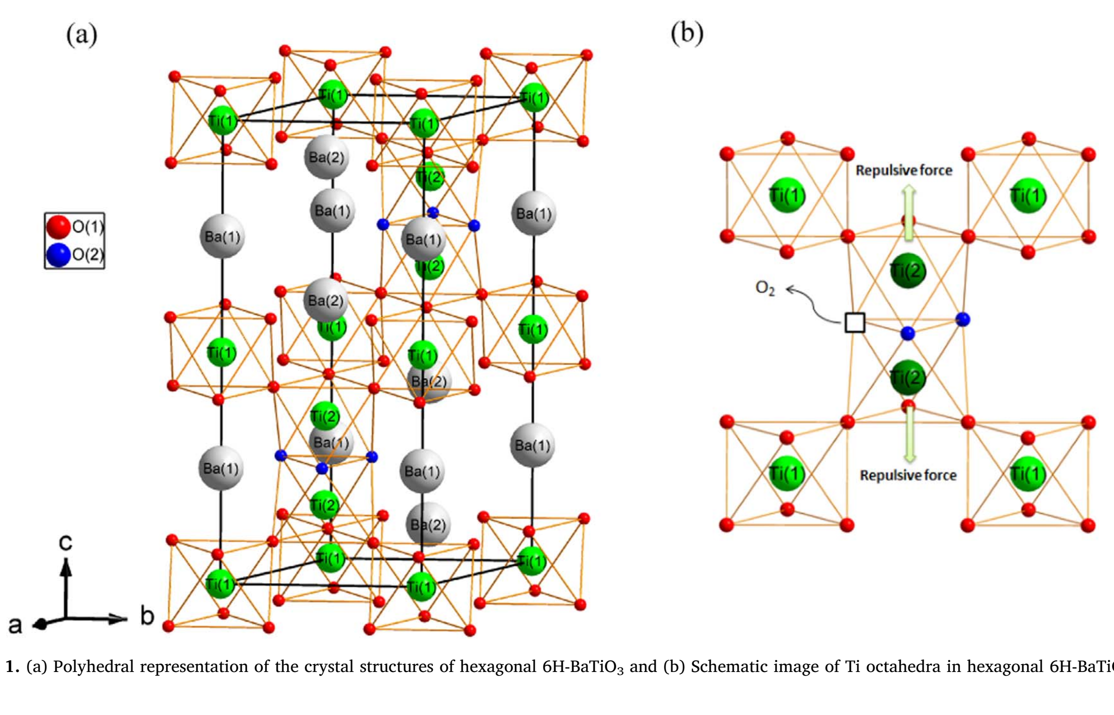

Fig. 1. (a) Polyhedral representation of the crystal structures of hexagonal 6H-$BaTiO_3$ and (b) Schematic image of Ti octahedra in hexagonal 6H-$BaTiO_3$.