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$Bi_6Te_{2-x}R_xO_{13}$ (R=Ti, Si, Ce) Systems: A Investigation for Fuel Cell Applications

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Abstract. In recent years, the increase of economic and environmental problems related to energy generation has increased researches at renewable energy sources. Among others, the fuel cells excel as promising alternative technology of electricity generation and materials science is an ally in the search for better and more efficient materials for this application. In particular, solid-state ionic conductors represent functional materials with promising advantages for fuel cells, as is the case of Bi_2O_3-based oxygen ion conductors, however, they need to have its cubic phase stabilized at room temperature. This paper presents a study of the $Bi_6Te_{2-x}R_xO_{13}$ (R = Ti, Si and Ce) systems for such an application. Solid state reaction was used to materials synthesis. The $3Bi_2O_3:2TeO_2$ system present two phases, an orthorhombic one ($Bi_6Te_2O_{15}$) stable at room temperature and another high temperature cubic ($Bi_6Te_2O_{13}$). Experiments of substitution of Te ions by Ti, Si and Ce ions using the $Bi_6Te_{2-x}R_xO_{13}$ matrix were done intending to stabilize the cubic phase at room temperature and the results are presented as well as discussed here.

Key words. fuel cell, SOFCs, cubic phase, Bi_2O_3-based.

1. Introduction

In recent years has been heard about many economic and environmental problems arising from the increasing dependence on fossil fuels as primary source for power generation. Thus, the interest in research focused on renewable energy sources as alternative forms of electricity generation has been growing continuously. These new technologies include: micro-hydraulics, biomass, wind energy, photovoltaic cells, geothermal and fuel cells. Among these, fuel cells stand out as a very promising technology.

Fuel cell is a highly efficient electrochemical device that converts energy generated by an electrochemical reaction into electric energy. Among the different types of fuel cells are the solid oxide fuel cell (SOFC). These devices use oxygen ion conducting oxide materials that besides cell fuel applications can be applied also in several technological areas as chemical species sensors, oxygen pumps and oxygen permeable membranes [1]. High operating temperatures, between 600 and 1000°C, represent some of disadvantages for a solid oxide fuel cell related to the feasibility, thermal expansion and longevity [3]. Thus, a challenge for current research is in the study and development of solid oxide fuel cells able of operating at lower temperatures (400-700°C).

The conductivity is the essential property in the solid oxide fuel cell and in the oxygen ions conductor materials, it become of sequent jumps of oxygen ions in crystalline structure vacancies, therefore the conductivity depends on the high defects concentration. These vacancies are intrinsic or extrinsic, the last formed by addition purposely of others ions [2]. This ionic mobility required to obtain high conductivity values is observed in determined crystalline structures of some oxides. The cubic phase of δ-Bi_2O_3 (fluorite structure), for example, presents the highest ionic conductivity (~230S.m-1) at 800°C among the oxygen ion conductors [4]. In its structure, the δ-Bi_2O_3 have a quarter of its sites available with vacancies of O^{2-} ions [5]. Since the cubic phase is a high temperature phase, stabilize it at room temperature has demanded effort for some time. Binary system of Bi_2O_3 with another oxide, have been studied in the attempt this stabilization [4, 6-9], besides the use of dopants ions in binary oxide.

The $Bi_2O_3:TeO_2$ binary system presents many phases reported in the literature, although that for most of them there are no sufficient physical and chemical characterization. In particular, for the $3Bi_2O_3:2TeO_2$ composition there are two reported phases, the $Bi_6Te_2O_{15}$ orthorhombic one, stable at room temperature, and the high temperature cubic phase $Bi_6Te_2O_{13}$ [6, 11, 12]. This cubic-orthorhombic phase transition is accompanied by the oxidation of Te^{4+} ions to Te^{6+} ions, assimilating oxygen [11-12]. Ferreira *et al.* reports that the cubic phase can be kept at temperatures up to approximately 500°C during long time in a metastable condition due to the imposition of kinetic mechanisms [12]. Knowing that the Bi_2O_3-based cubic structure materials are oxygen ion conductors and they can be applied in the solid oxide fuel cells, bring an important challenge related to obtaining the stable cubic phase at room temperature.

In this work attempts to stabilize the high temperature cubic phase is presented. A study of partial replacement of the Te ions in the $Bi_6Te_{2-x}R_xO_{13}$ (R = Ti, Si and Ce) composition was done in order to minimize or avoid the oxidation of Te^{4+} to Te^{6+} during the cubic/orthohrombic phase transition. The addition of intentional impurities in crystalline compounds is an important tool in the materials chemistry and the object of numerous studies [13-24], in particular, there was an investigation of the stabilization of this cubic phase ($Bi_6Te_2O_{13}$) at room temperature by replacing Bi ions [24]. Here, Ti, Si and Ce ions have been chosen to replace Te ion site because all of these ions present the same oxidation state (IV) and ionic radius close.

2. Materials and Methods

A. Solid-state reaction synthesis

Solid state reaction was the synthesis method used to prepare the samples. Oxides of Bi_2O_3 (Sigma-Aldrich, 99.999%), TeO_2 (Aldrich, 99.995%), TiO_2 (Sigma-Aldrich, 99.9%), CeO_2 (Aldrich, 99.99 %) and SiO_2 (Aldrich, 99.99%) were used in the respective stoichiometric proportions. The $Bi_6Te_{2-x}R_xO_{13}$ (R = Ti, Si and Ce) compositions were synthesized using two temperatures (750°C and 870°C) and a rapid (quenching) or controlled (2°C/min) cooling rate was applied. The temperature of 870°C was chosen because is between cubic/orthorhombic phase transition temperature (856°C) and melting point (930°C) [12].

B. Characterization

X-ray diffraction (XRD) analyses were carried out on a Bruker D8 Discover diffractometer using CuKα radiation. Differential thermal analysis (DTA) and thermogravimetric analysis (TG) were performed in a Shimadzu DTG-60H using O_2 flux, temperature range from room temperature to 1000°C and heating rate of 10°C/min.

3. Results

A. $Bi_6Te_{2-x}Ti_xO_{13}$

To investigate the replacement of Te^{4+} by Ti^{4+} the $Bi_6Te_{2-x}Ti_xO_{13}$ compositions, with x = 0.2; 0.4; 1.0; 1.5 and 2.0, were synthesized. For all of them, two heat treatments were used: 750°C/24h with controlled cooling and 870°C/24h with rapid cooling. In the samples from first heat treatment formed a mixture of the $Bi_6Te_2O_{15}$ (orthorhombic), $Bi_{12}TiO_{20}$ (Sillenite) and β-$Bi_4Ti_3O_{12}$ (Perovskita) compositions. It is possible to visualize, from the analysis of the diffractograms (Figue 1), that the orthorhombic phase prevails in greater concentration for compositions with low concentration of Ti ions (x = 0.2; 0.4) and decreases as x increases. The phases $Bi_{12}TiO_{20}$ and β-$Bi_4Ti_3O_{12}$ coexist, even in small quantities, for low values of x, however, their concentrations increase as the value of x gets higher, until they become the only phases in the composition with x = 2.0. These two phases were the same as those reported by KARGIN et al. (2015) for the 3:2 stoichiometric ratio of the Bi_2O_3:TiO_2 phase diagram.

In the case of samples resulting from second heat treatment (rapid cooling), the cubic phase of composition $Bi_6Te_2O_{13}$ was formed instead of the orthorhombic phase. With the exception of this phase, the results presented in the diffractograms of figure 2 show a behavior similar to that observed for the treatment with controlled cooling: the $Bi_{12}TiO_{20}$ and β-$Bi_4Ti_3O_{12}$ phases have their concentration increased as x increases, until these phases are the only ones present in the mixture.

The thermal stability of the $Bi_6Te_{1.8}Ti_{0.2}O_{13}$ samples with both thermic treatment were investigated by simultaneous thermal analysis (DTA/TG), as shown in Figure 3. The DTA thermal profile to $Bi_6Te_{1.8}Ti_{0.2}O_{13}$ with controlled cooling (Figure 3(a) shows two transitions. The first of them, at 870°C, is related to an endothermic transition concomitant to a mass loss of 1.5%. This peak corresponds to process of the orthorhombic to cubic phase transition of $Bi_6Te_2O_{15}$ [12] as can be observed in the in inset box in figure 3(a), which is the phase mostly present in the mixture, as shown in the diffractogram of figure 1. The second peak with onset at 907°C corresponds to the melting point. The widest profile of this peak shows the overlap of thermal events related to the melting of the differents components present in the mixture. For the $Bi_6Te_{1.8}Ti_{0.2}O_{13}$ with rapid cooling (Figure 3(b)) the first process corresponds to exothermic transition at 668°C that starts at around 450°C, being completed at 700°C approximately. This transition was accompanied by a mass gain of 1.44%. The next two peaks correspond to endothermic events. Comparing these thermal analysis with that of the single cubic phase, $Bi_6Te_2O_{13}$, shown in the inset of figure 3(b), it is observed that the first two peaks correspond to events of this composition (transition from cubic metastable to orthorhombic phase followed of orthorhombic/cubic endothermic transition). The last peak is related to melting and its enlargement shows the overlap of thermal events related to the presence of mixtures in the sample.

The results demonstrate that, although the Ti^{4+} ion has the same oxidation state and ionic radius smaller than the Te^{4+} (Ti^{4+}= 0.61Å and Te^{4+}= 0.97Å), it does not replace the Te^{4+} ion in the investigated matrix, forming mixtures regardless heat treatment or concentration used.

B. $Bi_6Te_{2-x}Si_xO_{13}$

To explore the behavior of the replacing Te^{4+} with an isovalent ion, with an even smaller ion radius, an experiment was performed using the Si^{4+} ion (0.42 Å). The composition $Bi_6Te_{1.8}Si_{0.2}O_{13}$ (x=0.2) was synthesized from a heat treatment at 870 °C/24h with a controlled cooling rate of 2°C/min. The diffractogram of the resulting sample, shown in figure 4, shows the formation of a mixture of phases consisting of $Bi_6Te_2O_{15}$, Bi_2TeO_5, Bi_2O_3 and $Bi_2O_2SiO_3$. The result indicates that the replacement of Te by Si does not lead to the formation of a single phase with $Bi_6Te_{1,8}Si_{0,2}O_{13}$ composition.

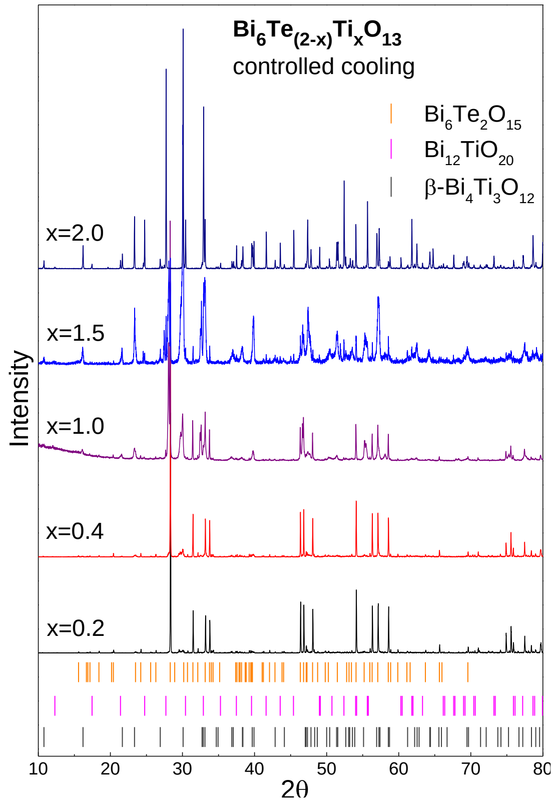

Figure 1- Diffractograms of $Bi_6Te_{2-x}Ti_xO_{13}$ samples with x = 0.2; 0.4; 1.0; 1.5 and 2.0, treated at 750°C/12h with controlled cooling (2°C/min). The Bragg angles of the $Bi_6Te_2O_{15}$ (orthorhombic), $Bi_{12}TiO_{20}$ (Sillenite) and β-$Bi_4Ti_3O_{12}$ (Perovskite) phases are shown below the sample diffractograms

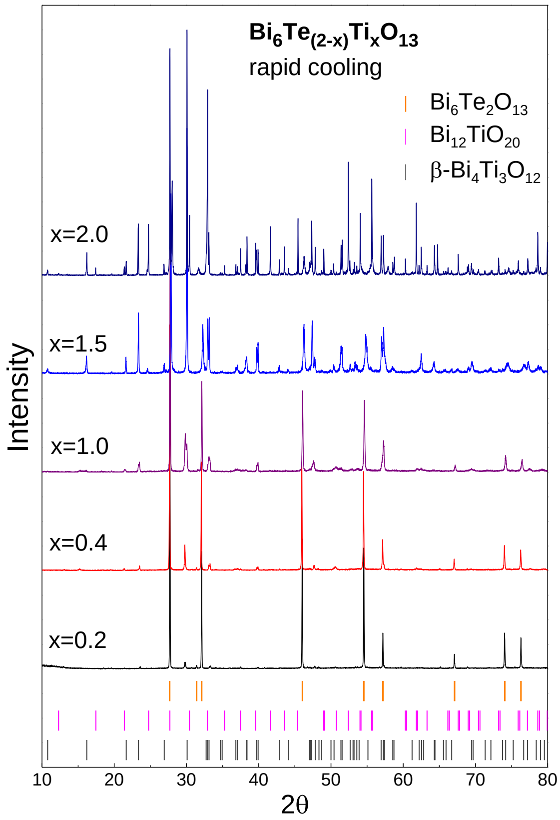

Figure 2- Diffractograms of $Bi_6Te_{2-x}Ti_xO_{13}$ samples with x = 0.2; 0.4; 1.0; 1.5 and 2.0, treated at 870°C /12h with rapid cooling (quenching). The Bragg angles of the $Bi_6Te_2O_{13}$ (cubic), $Bi_{12}TiO_{20}$ (Sillenite) and β-$Bi_4Ti_3O_{12}$ (Perovskite) phases are shown below the sample diffractograms.

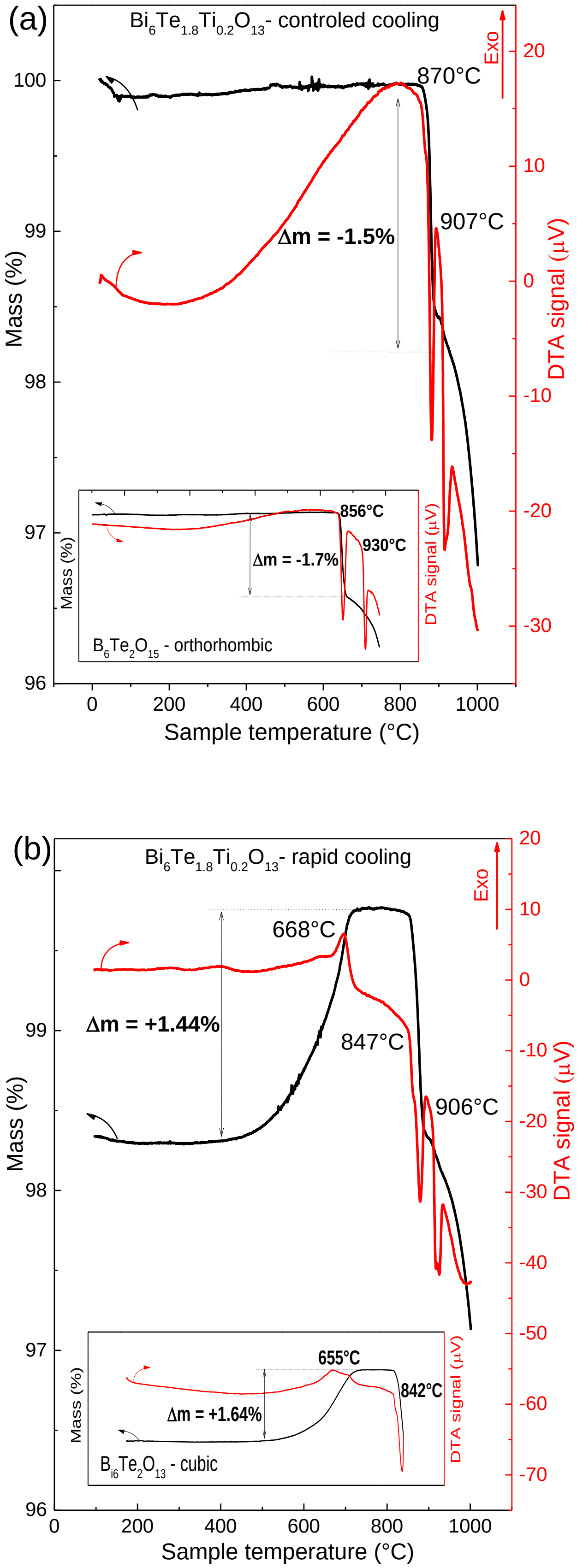

Figure 3- 3(a) Simultaneous thermal analysis (DTA/TG) of $Bi_6Te_{1.8}Ti_{0.2}O_{13}$ measured with O_2 flux and heating rate of 10°C/min. 3(a) Sample obtained by controlled cooling (2°C/min). The inset corresponds to the DTA/TG curve to $Bi_6Te_2O_{15}$ orthorhombic phase. 3(b) Sample obtained by rapid cooling (quenching) The inset corresponds to the DTA/TG curve to $Bi_6Te_2O_{13}$ cubic phase.

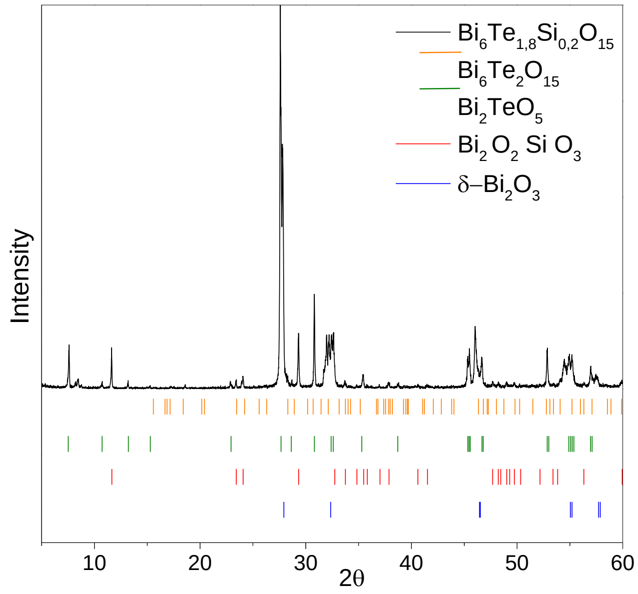

Figure 4- Diffractogram of $Bi_6Te_{1.8}Si_{0.2}O_{13}$ composition with treatment at 850 ° C and 2°C/min cooling rate

C. $Bi_6Te_{2-x}Ce_xO_{13}$

The Ce^{4+} ion (0.87Å) was tested as a substituent using the composition $Bi_6Te_{1.6}Ce_{0.4}O_{13}$ (x=0.4). The diffractogram of the sample treated at 870 °C/24h with a controlled cooling rate of 2 °C/min is shown in figure 5. The result indicates that there was no formation of a single phase for this composition, on the contrary, in an attempt to replace Te^{4+} by Ce^{4+} there was the formation of a mixture of phases composed of $Bi_6Te_2O_{15}$, Bi_2O_3 and CeO_2.

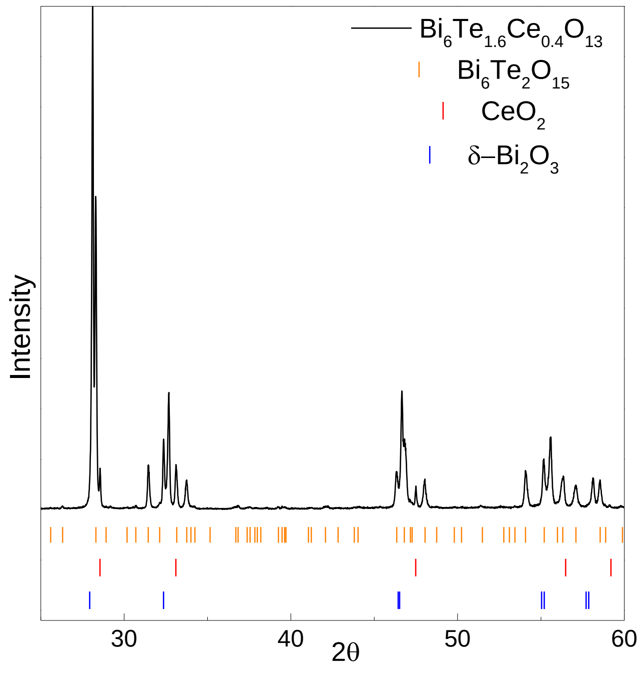

Figure 5- Diffractogram of the $Bi_6Te_{1.6}Ce_{0.4}O_{13}$ composition with treatment at 870°C and controlled cooling. The Bragg angles of the $Bi_6Te_2O_{15}$ (PDF 057-0107), Bi_2O_3 (PDF 52-1007) and CeO_2 (PDF 089-8436) compositions are identified below the diffractogram.

4. Conclusion

The attempt to stabilize the cubic phase of the $Bi_6Te_2O_{13}$ system at room temperature through the insertion of Ti, Si and Ce ions in $Bi_6Te_{2-x}R_xO_{13}$ (R = Ti, Si and Ce**)** compositions, resulted in mixtures the indicating that the substituent ions are not soluble in the studied matrices. There was no formation of a solid solution, but the formation of multiphase systems for any composition or heat treatment used. The formation of multiphase systems did not allow conductivity measures. This study is important to indicate these ions used do not replace Te ions in the matrix investigated and studies with others cations to replace Bi or Te are in progress intending to stabilize the cubic phase in lower temperatures to fuel cells applications.

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