11th International Conference
on Advanced Materials

ICAM2009

Rio de Janeiro Brazil
September 20 - 25

Intrinsic defects and charge transport mechanism in BTO

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Abstract – Bismuth oxide compounds exhibit a number of interesting properties, including: piezoelectric, electro-optical, elasto-optical, optical activity and photoconductive properties. After deriving a reliable potential model, the intrinsic defects in $Bi_{12}TiO_{20}$ and $Bi_4Ti_3O_{12}$ phases were calculated, ranging from Schottky, Pseudo- Schottky, Anti-Schottky, and Frenkel defects. The result shows for the $Bi_{12}TiO_{20}$ that the predominant defect is $(Bi'_{Ti}+h^{\bullet})$ + $(Ti^{\bullet}_{Bi}+e')$. In $Bi_4Ti_3O_{12}$ (both phases) the pseudo-Schottky Bi_2O_3 type defect is the one with lower energy at all temperature (0K, 293K and 965K). The activation energy was calculated, where the value found were 1.11eV.

Bismuth oxide compounds exhibit a number of interesting properties, including: piezoelectric, electro-optical, elasto-optical, optical activity and photoconductive properties. Due to these properties, sillenite crystals are useful for many advanced and promising applications, such as a reversible recording medium for real-time holography or for image processing applications. In the present work we employed computer modelling methods that are based on well established approaches using interatomic potentials to represent the interactions between ions, coupled with energy minimization. Defects can be modelled within the Mott–Littleton approach in which point defects are considered to be at the centre of a region where all interactions are treated explicitly, surrounded by an external region where approximate methods are employed. For the electron-hole formation, we used the model where the hole state is the Bi_{Ti} ion, while for the electron state it is the Ti^{3+} species sitting at the Bi site, a kind of neutralized anti-site defect [1]. These were all included in the GULP code [2] used in the present work. The first step, of the work consists of finding a suitable set of potentials to describe the system and that were done via a empirical approach where the potential parameters were fitted to the structures of $Bi_{12}TiO_{20}$ (cubic) and $Bi_4Ti_3O_{12}$ (orthorhombic and tetragonal). The potential parameter set was able to reproduce all the crystalline structures within 0-5%. Using these potentials, the intrinsic defects were calculated, ranging from Schottky, Pseudo-Schottky, Anti-Schottky, anti-site, and Frenkel defects in both materials at several temperatures. Apart from this typical intrinsic defect, two extra schemes were considered here to account for the formation of the $(Bi'_{Ti}+h^{\bullet})$ defect, following the reactions below. According to the energy obtained, we found that in $Bi_{12}TiO_{20}$ scheme (i) is more likely to occur at all temperatures (0K, 293K and 743K). In $Bi_4Ti_3O_{12}$ the Bi_2O_3 pseudo-Schottky type defect is the one with lower energy at all temperatures (0K, 293K and 965K). For the last one, the activation energy was calculated. The values found are comparable to the migration energies reported in ceramics sintered at 973K and possible mechanisms for charge transport related to the two processes found in the ceramics were proposed. (The authors are grateful to CNPq, FINEP and CAPES program for financial support).

(i) $$Ti_{Ti} + Bi_{Bi} \rightarrow \left(Bi'_{Ti} + h^{\bullet}\right) + \left(Ti_{Bi} + e'\right)$$

(ii) $$2Ti_{Ti} + 2Bi_{Bi} + 3O_O + \tfrac{1}{2}O_2(g) \rightarrow 2\left(Bi'_{Ti} + h^{\bullet}\right) + 2TiO_2 + 2V'''_{Bi} + 3V^{\bullet\bullet}_O$$

Table 1. Solution energies for $Bi_{12}TiO_{20}$ at different temperatures.

Temperature	0K	293K
Intrinsec Defect	Energy(eV)	Energy(eV)
Frenkel Bi	11.23	10.41
Frenkel Ti	11.67	9.26
Frenkel O	0.96	-1.10
Schottky	3.35	1.25
Pseudo-Schottky Bi_2O_3	3.31	1.20
Pseudo-Schottky TiO_2	3.99	1.96
Anti-Schottky	6.68	5.54
Anti-site	1.00	0.28
Reactions (i)	**0.70**	**-1.93**
Reactions (ii)	3.10	0.51

Table 2. Solution energies for $Bi_4Ti_3O_{12}$ at different temperatures.

Temperature	0K	293K
Intrinsec Defect	Energy(eV)	Energy(eV)
Frenkel Bi	14.84	9.99
Frenkel Ti	14.18	7.20
Frenkel O	2.39	-0.89
Schottky	2.03	-1.37
Pseudo-Schottky Bi_2O_3	**1.97**	**-1.40**
Pseudo-Schottky TiO_2	3.07	-0.36
Anti-Schottky	11.72	2.02

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