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First principles study of the structural and electronic properties of double perovskite Ba_2YTaO_6 in cubic and tetragonal phases

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ABSTRACT

The Ba_2YTaO_6 double perovskite presents a transition from cubic ($Fm-3m$) to tetragonal structure ($I4/m$) at high temperature. In this work, we present a detailed study of the structural and electronic properties of the double perovskite Ba_2YTaO_6 in space group $Fm-3m$ and $I4/m$. Calculations were made with the Full-Potential Linear Augmented Plane Wave method (FP-LAPW) within the framework of the Density Functional Theory (DFT) with exchange and correlation effects in the Generalized Gradient (GGA) and Local Density (LDA) approximations. From the minimization of energy as a function of volume and the fitting of the Murnaghan equation some structural characteristics were determined as, for example, total energy, lattice parameter ($a=8.50$ Å in cubic phase and $a=5.985$ Å and $c=8.576$ Å in tetragonal), bulk modulus (135.6 GPa in cubic phase and 134.1 GPa in tetragonal phase) and its derivative. The study of the electronic characteristics was performed from the analysis of the electronic density of states (DOS). We find a non-metallic behavior for this with a direct band gap of approximately 3.5 eV and we found that the Ba_2YTaO_6 ($I4/m$) phase is the most stable one. © 2013 Elsevier Science. All rights reserved.

1. Introduction

Currently the complex perovskites with generic formula $A_2MM'O_6$ [1–3] have been subject of enhanced scientific studies because the wide range of applications that these materials present on an industrial scale, due to the variety of substitutions of alkaline earth elements at the crystallographic site A, and metals transition or lanthanide elements at the M and M′ sites [4]. A first study Ba_2YTaO_6 system, carried out by Layden et al. [4,5] showed that this double perovskite has a cubic structure. Zurmuhlen et al. [6] studied the structural and dielectric properties of this material and found that at a temperature of 253.1 K the compound undergoes a phase transition of the second order from a cubic structure, space group Fm − 3m with energy gap 4.6 eV, to a tetragonal structure, space group I4/m. The cubic structure of Ba_2YTaO_6 at room temperature was confirmed in numerous studies [7,8]. In 2006, Lufaso et al. [9] showed that the same transition occurs under the application of pressure up to 5 GPa, resulting in a tetragonal structure. Recent studies confirm the occurrence of this phase transformation at a temperature of 260 K [10]. Berger and Neaton, by means of theoretical calculations based on DFT, using the VASP code, found a gap of 4.3 eV [11], which is in a good agreement with the experimental value [6], which presents a good agreement with the value obtained from experiments [6].

In this paper, we present a first principles study of structural and electronic properties of the Ba_2YTaO_6 double perovskite for the cubic and tetragonal phases. The study was based on the Full-Potential Linear Augmented Plane Wave method (FP-LAPW) within the framework of the DFT with exchange and correlation effects introduced by the Generalized Gradient (GGA) and Local Density (LDA) approximations.

2. Theoretical calculations

In order to determine the electronic and band structures we applied the Full-Potential Linear Augmented Plane Wave method (FP-LAPW) within the framework of the Hohenberg and Kohn Density Functional Theory (DFT) [12], and adopted the Generalized Gradient (GGA) approximation for the exchange-correlation energy due to Perdew et al. [13] and also the Local Density (LDA) approximation [14]. The code wien2k allows the calculation of the

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total energy of the unitary cell [15]. Taking the experimental unit cell data as input, all the structures studied in this work were fully relaxed with respect to their lattice parameters and the internal degrees of freedom compatible with the space group symmetry of the crystal structure. The data of energies and volumes obtained have been fitted to the equation of state due to Murnagham [16] in order to obtain the minimum energy value, the bulk modulus, its pressure derivative and the equilibrium lattice parameters and associated volume. We used the following values for the muffin-tin radius of the elements: $R_{Ba}=2.3$, $R_Y=1.9$, $R_{Ta}=1.75$ y $R_O=1.6$ (in bohr) for atoms of Ba, Y, Ta y O respectively, angular momentum up to $I_{MÁX}=10$ inside the muffin-tin sphere, a maximum vector in the reciprocal space of $G_{max}=12.0$, $R_{MT}\times K_{max}=7.0$, which limits the size of the plane wave basis in the interstitial zone, i. e. for regions out of the muffin-tin sphere of the atoms in the unit cell. A mesh of 1700 and 700 k-points in the first Brillouin zone (equivalent to a maximum of 56 and 76 k points in the irreducible Brillouin zone for phase cubic ($Fm-3m$) and Tetragonal ($I4/m$) respectively). Finally, the convergence criteria for the self-consistent calculation was 0.0001 Ry for the total energies, 0.0001 a.u. in the charge and 1.0 mRy/a.u. in the internal forces.

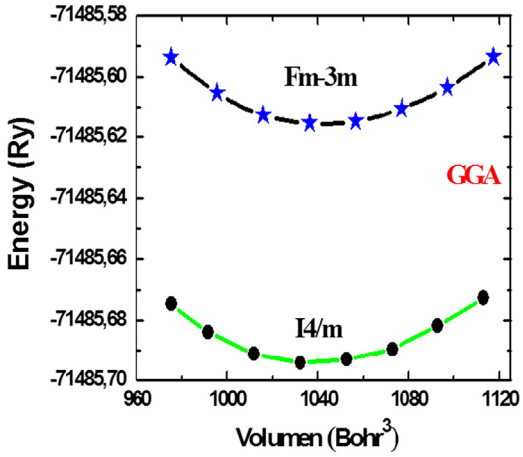

Fig. 1. Total energy as a function of volume for Ba_2YTaO_6 considering the $Fm-3m$ and $I4/m$ space group.

Table 1
Atomic positions obtained from the calculations for the Ba_2YTaO_6 complex perovskite.

Fm-3*m*	Site	*x* (Å)	*y* (Å)	*z* (Å)
Ba^{2+}	8c	0.2500	0.2500	0.2500
Y^{3+}	4a	0.0000	0.0000	0.0000
Ta^{5+}	4b	0.5000	0.0000	0.0000
O^{2-}	24e	0.2635	0.0000	0.0000
*I*4/*m*	Site	*x* (Å)	*y* (Å)	*z* (Å)
Ba^{2+}	4d	0.0000	0.5000	0.2500
Y^{3+}	2a	0.0000	0.0000	0.0000
Ta^{5+}	2b	0.5000	0.5000	0.0000
O^{2-}	4e	0.0000	0.0000	0.2385
O^{2-}	8h	0.2328	0.2954	0.0000

3. Results and discussion

Fig. 1 shows the energy as a function of volume. Each one of the squared points constitutes an individual calculation and the line corresponds to a fitting with the Murnaghan state equation, which was carried out by using the concept of the least-square fitting method [16,17]. These calculations were performed for the cubic structure ($Fm-3m$ space group) and for the tetragonal structure ($I4/m$ space group).

The minimum of the energy is obtained for a volume 1041.915 $Bohr^3$ for the $Fm-3m$ space group and 1037.470 $Bohr^3$ for the $I4/m$. From minimization of energy as a function of volume (Fig. 1) we calculate the lattice parameter $a=8.5023$ Å ($Fm-3m$) and $a=5.9871$ Å, $c=8.5783$ Å ($I4/m$), which is 99% in agreement with the predictions performed from the Structure Prediction Diagnostic Software *SPuDS*, $a=7.982$ Å [18]. The bulk modulus obtained from calculations were $B_o=135.2$ GPa and 134.1 GPa for the $Fm-3m$ and $I4/m$ space groups, respectively. In general, the ratio c/a of the tetragonal phase has a remarkable arrangement of less than 1% compared to the experimental value [10], obtained by the two approaches GGA and LDA. And in the case of the cubic phase, the lattice parameter has better agreement (within 0.7%) when using the approximation GGA. The crystallographic parameters are presented in Table 1.

Fig. 2 shows the structures of the Ba_2YTaO_6 double perovskite deduced from the calculations for the $Fm-3m$ and $I4/m$ space groups.

Fig. 3 shows a picture of pressure as a function of volume for both $Fm-3m$ and $I4/m$ space groups.

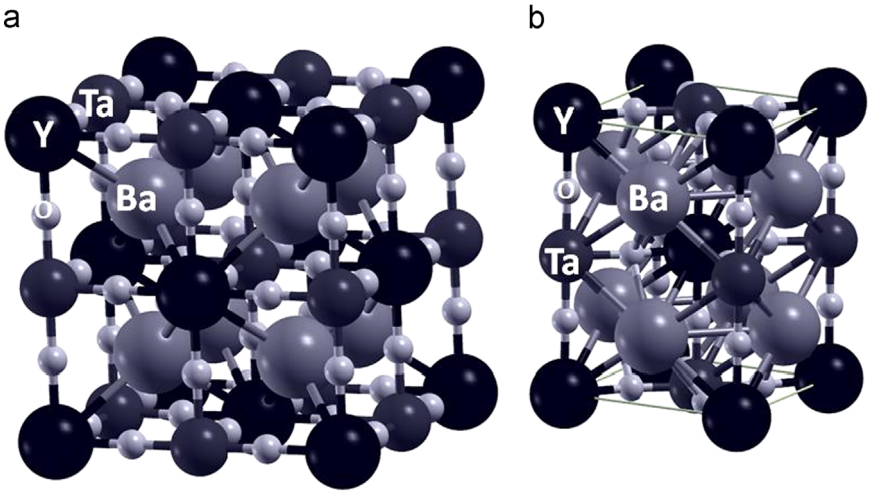

Fig. 2. Structure of the Ba_2YTaO_6 perovskite considering the (a) $Fm-3m$ space group and (b) $I4/m$ space group.