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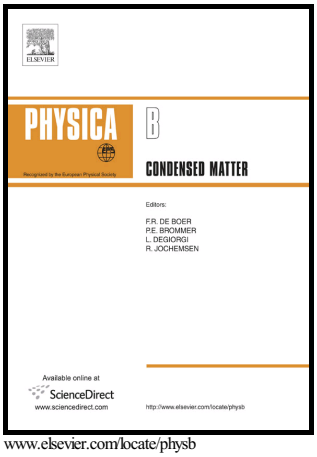

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Interstitial copper defect induced reconstruction of a new "CuO_4" quadrilateral in $CaCu_3Ti_4O_{12}$: A first-principles study

Haibo Xiao, Linfang Xu, Ruilong, Wang, Changping Yang[*]

Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Hubei Key Laboratory of Ferro & Piezoelectric Materials and Devices, Faculty of Physics & Electronic Science, Hubei University, Wuhan, 430062, People's Republic of China

[*]*Corresponding authors' information: Address: Faculty of Physics & Electric Technology, Hubei University, P.R. China, Wuhan, 430062. Phone: 86 27-8866-5447. Fax: 86 27- 8866-3390. E-mail : cpyang1011@126.com*

Abstract

The geometric structure, electronic structure and formation energy of $CaCu_3Ti_4O_{12}$ (CCTO) with interstitial copper atom have been studied using the density-functional method within the GGA approximation. Result of structural optimization shows that the interstitial Cu-atom (Cu_7) prefers to occupy a special location which is symmetrical with an intrinsic copper atom (Cu_{13}) deviated from the normal site. The mulliken analysis indicates the loss of electrons from interstitial atom (Cu_7) and Cu_{13} are only half more of the losing in other copper atom, which reveals a characteristics of covalent bonding between Cu_7/Cu_{13} and surrounding oxygen atoms respectively. Meanwhile, it is found from electron density difference (EDD) and orbital analysis that the introduction of interstitial Cu atom causes prominent structural reconstruction of a new "CuO_4" quadrilateral. Moreover, the new "CuO_4" planar leads to a corresponding electronic reconstruction in the hybridization between Cu_7/Cu_{13} 3d and O 2p at the vicinity of fermi surface, for which a new conductive filament channel comes into being. Besides, the formation energies of the interstitial defects in various charge states are corrected with the value of 2.18, - 4.17 and – 9.46 eV for charge of 0, 1+ and 2+, respectively.

Keywords: $CaCu_3Ti_4O_{12}$, Interstitial defect, first-principles, electronic reconstruction, formation energy;

1. Introduction

The multiple-perovskite $CaCu_3Ti_4O_{12}$ (CCTO) is one of the best known materials of possessing a giant dielectric constant, which has been interestingly attracted worldwide for applications in miniaturization of capacitor devices and