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Theoretical Study on $BaTiO_3$ Ceramic Nanoclusters

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In recent years, numbers of studies have been done on ceramic nanoparticles expecting their novel functional properties. In addition, much effort has been made for downsizing of nanoparticles. For $BaTiO_3$, the smallest nanoparticles of 6 nm size have been successfully obtained by Suzuki *et al*. [1] Precise understanding of atomic structures and electronic states of ceramic nanoparticles is very important for both basic materials science and applied industry. However, their details are still unclarified. First-principles theoretical calculations are expected to be very powerful technique for this purpose. In the present study, we investigated the atomic structures and electronic states of the $BaTiO_3$ nanoclusters in detail by first-principles calculations for the first time, to clarify their structural stability and various electronic properties.

We performed calculations by using the Vienna *Ab-initio* Simulation Package (VASP) program [2] based on the density functional theory. We systematically constructed the structural models for the $Ba_{8+x}Ti_{8+y}O_{24+z}$ nanoclusters from the cubic Perovskite $BaTiO_3$ crystal structure, which are about 1 nm size and consisting of $40+x+y+z$ atoms. Since the $BaTiO_3$ crystal structure has two nonequivalent cation sites, two types of structural models were constructed. One is the Ba-centered model and the other is the Ti-centered model, which are shown in FIG. 1. We put one isolated cluster model in the supercell, and examined the stable structure by fully relaxing all atoms.

For the atomic structures, it was found that the local coordinated structures of the Ti and O atoms are formed depending on the number of O atoms neighboring to Ti atom. The 2-, 3-, 4-, and 5-fold coordinated Ti atom forms the isosceles-triangular, triangular-pyramidal, tetrahedral, and square-pyramidal structure with O atoms, respectively. We also found that the stability of nanocluster increases with the increase of the number of tetrahedron. Thus, the tetrahedral structure was concluded to be important for the stability of the $BaTiO_3$ nanoclusters.

On the other hand, for the electronic states, the values of the energy gap widely varies from almost zero to values larger than that for the bulk $BaTiO_3$ depending on their structures. For the dielectricity, the 6-fold coordinated structure is unstable on the cluster surface, so that it is reconstructed to the the 4-fold cooredinated structure. Hence, the ferroelectricity was suggested to be suppressed. Furthermore, there exist the nanoclusters which show the magnetism, also depending on the structures.

References

[1] K. Suzuki, M. Terauchi, Y. Uemichi, and K. Kijima, Jpn. J. Appl. Phys. **44** (2005) 7593.
[2] G. Kresse and J. Furthmuller, Phys. Rev. B **54** (1996) 11169.

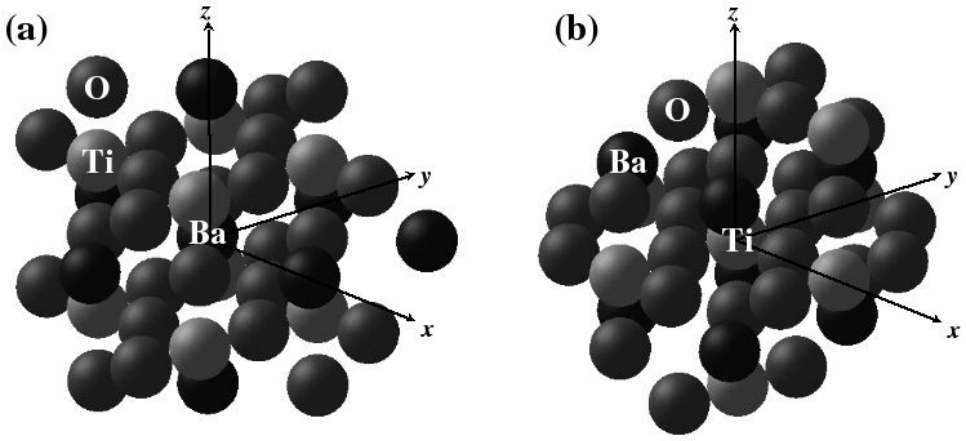

FIG. 1. The initial atomic structures of structural models for the $BaTiO_3$ ceramic nanoclusters (40 atoms) constructed from the cubic Perovskite $BaTiO_3$ crystal structure; (a) one of the Ba-centered model and (b) one of the Ti-centered model.