

First-Principles Calculations of Ferroelectricity in Wurtzite-Structured Simple Chalcogenides

Ayako Konishi¹, Hiroki Moriwake¹, Takafumi Ogawa¹, Koji Fujimura¹, Craig A. J. Fisher¹,
Akihide Kuwabara¹, Takao Shimizu², Shintaro Yasui², Mitsuru Itoh²

¹Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya 456-8587, Japan

²Materials and Structure Laboratory, Tokyo Institute of Technology, Yokohama 226-8503 Japan

A ferroelectric can be defined as a compound with a polar phase such that the electric polarization can be switched between two or more symmetry-related variants by application of an electric field, and is typically associated with a structural transition from a nonpolar high-symmetry paraelectric state. In well-known ferroelectrics, six oxygen ions forming an octahedron surround a cation. The cation displacement in the octahedron allows ferroelectric switching to occur. The addition of a new structural group to the ferroelectric family has important implications from the viewpoint of not only fundamental science but also technological applications.

In this study, we report the possibility that the wurtzite structure represents a new class of ferroelectric materials. As shown in Figure 1, binary compounds with the wurtzite structure (S.G. $P6_3mc$) have a polar crystal structure because the system is non-centrosymmetric. Such crystals have been assumed to be non-ferroelectric because of the rigid tetrahedral units held together by strong covalent bonding, so that its electric polarization cannot be switched by an electric field. For this reason, wurtzite-structured compounds are normally described as consisting of non-ferroelectric polar crystals. However, if we consider the relative displacement of the cation along the c axis, as illustrated in Figure 1, a centrosymmetric paraelectric state corresponding to space group $P6_3/mmc$ is found to exist between two polar states (the original $P6_3mc$ symmetry of wurtzite). If the potential barrier of this displacement is sufficiently low, the direction of electric polarization can be switched between these two equivalent polar states ($P6_3mc$) via this paraelectric state. For wurtzite-structured BeO, Sawada et al.,^[1] reported a D-E hysteresis loop with a relatively large polarization of 0.061 C/m² at 805 °C. However, the detailed mechanism of the ferroelectric-like behavior remains unclear. It is thus still not certain whether wurtzite-structured compounds can exhibit ferroelectricity or not. In this study we report a series of first-principles calculations of wurtzite-structured phases of MX chalcogenides (where M = Zn, and Be, X = O, S, Se, and Te), in an attempt to shed light on this issue.

The calculated potential surface of these compounds shows typical double well between two polar variants (Fig. 2). The potential barriers for the ferroelectric polarization switching were estimated to be 0.25 eV/f.u. for ZnO. This energy is only slightly higher than that of the common perovskite ferroelectric compound PbTiO₃.

Acknowledgements

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan through the Grants-in-Aid for Scientific Research (C) 24560833, (A) 23246113, Scientific Research on Innovative Areas "Nano Informatics" from JSPS, MEXT Elements Strategy Initiative to Form Core Research Center, and Green Network of Excellence (GRENE).

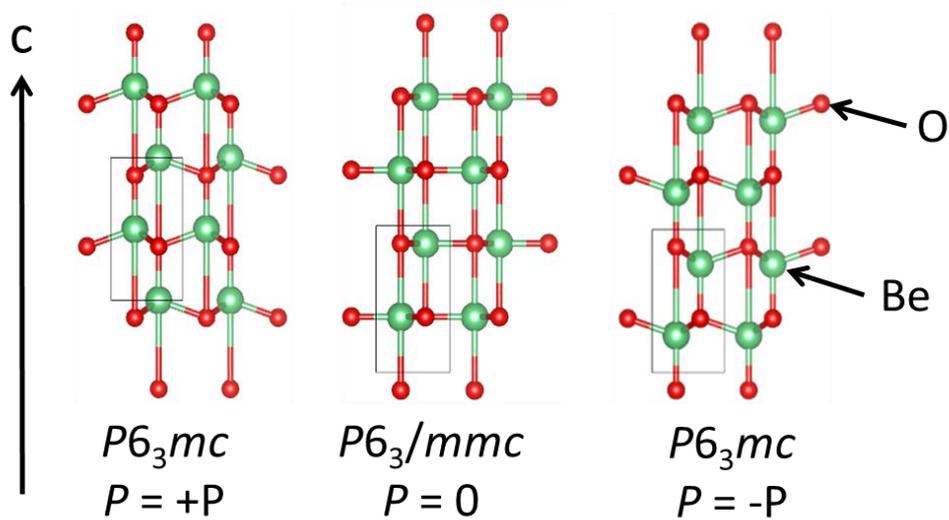


FIG. 1. Wurtzite-structured BeO in two polar states (left and right), corresponding to space group $P6_3mc$, compared with BeO in a non-polar state (center), corresponding to space group $P6_3/mmc$. If the potential barrier is sufficiently low, the electric polarization can be switched between the two polar states via the non-polar structure.

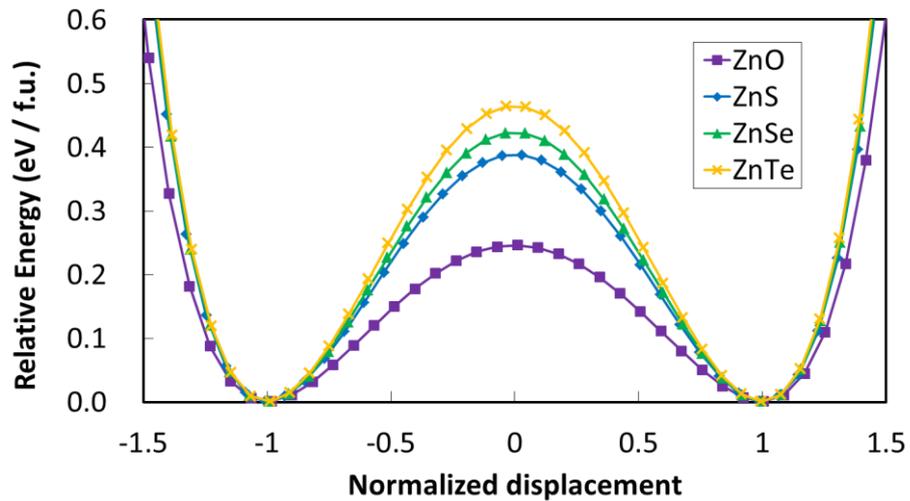


FIG. 2. Calculated slice of the potential surface for ferroelectric-type relative cation displacements in Zn chalcogenide compounds.

Reference

- [1] S. Sawada et al., J. Phys. Soc. Jpn., 1973, 35 946.