

Confined Electrons and Exotic Ions in Microporous $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$. Calorimetric Study

O. Trofymuk^{C,S} and A. Navrotsky

Thermochemistry Facility and NEAT ORU, University of California at Davis, Davis, CA, USA
otrofymuk@ucdavis.edu

Y. Toda, K. Hayashi, and H. Hosono

Materials and Structure Laboratory, Tokyo Institute of Technology, Yokohama, Japan

We present thermodynamic data for nanoporous calcium aluminates (CAAL) with a common formula $[\text{Ca}_{12}\text{Al}_{14}\text{O}_{33-\delta}]^{2\delta+}(2\delta\text{X}^-)$, (where $\text{X} = \text{H}^-, \text{OH}^-, \text{e}^-, \text{O}^{2-}, \text{O}_2^-, \text{O}^-$, $0 < \delta \leq 1$), that represent, as recently highlighted in a Nature publication by Hayashi et al. 2002 and a Science publication by Matsuishi et al. 2003, a new class of electrides and ionic conductors. The capability of CAAL to confine, conduct, and emit electrons arises from the unique microporous structure of the parent CAAL semiconductor $[\text{Ca}_{12}\text{Al}_{14}\text{O}_{32}]^{2+}(\text{O}^{2-})$, characterized by small interconnecting channels. We employed high temperature calorimetry to study the opposite process, i.e. oxidation of hydroxyl, hydride and electron-rich samples to eliminate electrons and obtain a stoichiometric compound. The enthalpies of oxidation and formation for hydroxyl, hydride and electron-rich, as well as the stoichiometric compound, relative to the most stable annealed calcium aluminate are measured. The study supports the idea that the oxidation of the stoichiometric $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ sample results in formation of extra-framework ions (O^{2-} and O^-). The unique structure of CAAL is able to stabilize both oxygen ions and electrons in cages at room temperature, and at the same time, provide the environment for ion and electron conductivity. The latter is strongly related to framework-ion vacancy geometry and ion-framework bonding, which is reflected in oxidation energetics.

The thermochemical study of $[\text{Ca}_{12}\text{Al}_{14}\text{O}_{33-\delta}]^{2\delta+}(2\delta\text{e}^-)$ samples presented provides not only insight into energetics of electron-framework binding and formation of extra-framework ions, but also sets the stage for future theoretical studies of electride-type structures and the search for new electrides and ionic conductors.