Supporting information

Title:

# Ionic conduction mechanism in Ca-doped Lanthanum Oxychloride

Kazuki Shitara[1,2], Akihide Kuwabara[2], Keisuke Hibino[3], Kotaro Fujii[3], Masatomo Yashima[3], James R. Hester[4] Masanori Umeda[5], Naoyoshi Nunotani[5], Nobuhito Imanaka[5]

[1] Joint and Welding Research Institute, Osaka University

[2] Nanostructures Research Laboratory, Japan Fine Ceramics Center

[3] Department of Chemistry, School of Science, Tokyo Institute of Technology

[4] ANSTO

[5] Department of Applied Chemistry, Faculty of Engineering, Osaka University

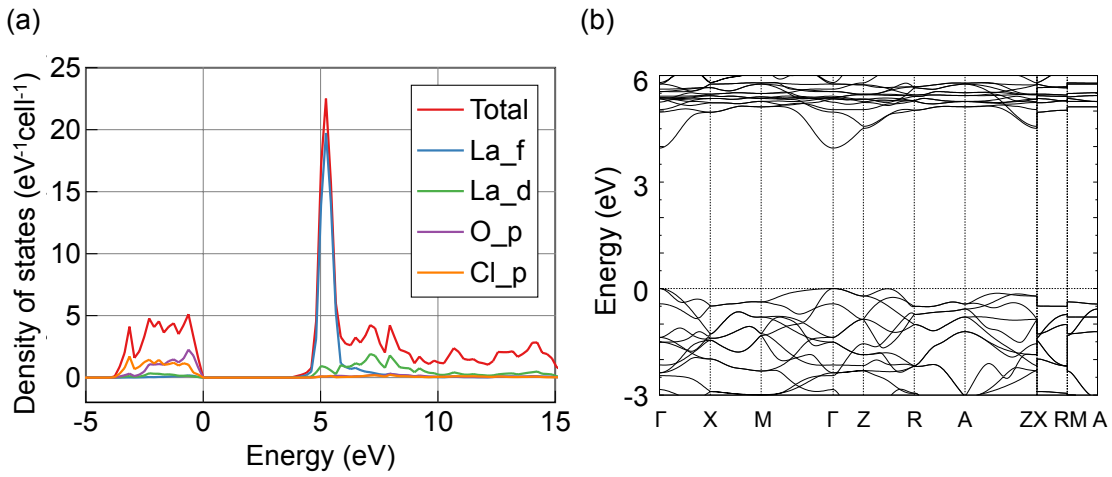


Figure S1 Calculated (a) density of states and (b) band structure of LaOCl

Figure S2 shows the atomic structures around $V_{Cl}^{\cdot}$ optimized by first-principles calculations. In the $V_{Cl}^{\cdot}$ model, there are three independent distances between the Cl vacancy site and surrounding ions: two types of distances between $V_{Cl}^{\cdot}$ and La, and one distance between $V_{Cl}^{\cdot}$ and Cl. The distances before and after the structure optimization are summarized in Table S1. The distance between La and $V_{Cl}^{\cdot}$ became shorter and the distance between Cl and vacancy became longer after structure optimization in this model. Attractive Coulomb interactions occur between $La^{3+}$ and $Cl^{-}$ ions. In contrast, $Cl^{-}$ ions have repulsive Coulomb interactions towards each other. Electrostatic interactions disappear owing to the Cl vacancy formation, as $La^{3+}$ ions move away from the Cl vacancy site and $Cl^{-}$ ions shift toward the Cl vacancy site. In the $V_{Cl}^{\cdot}$ model, the thickness of the Cl layer is expanded as the distance between $V_{Cl}^{\cdot}$ and La increases. This is possibly the reason for the conduction of $Cl^{-}$ ions.

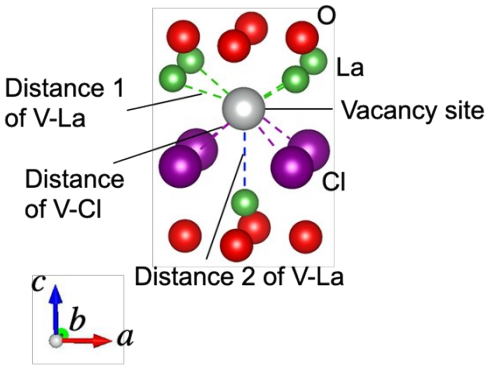


Figure S2. Local structure of a $Cl^{-}$ ion vacancy in LaOCl crystal

Table S1. Distances related to a $Cl^{-}$ ion vacancy before and after structure optimization

| | Distance before structure optimization (Å) | Distance after structure optimization (Å) |
|---|---|---|
| Distance 1 of V-La | 3.165 | 3.227 |
| Distance 2 of V-La | 3.107 | 3.181 |
| Distance of V-Cl | 3.389 | 3.168 |