ANALYSIS OF CONDUCTIVITY PROPERTIES IN $LaScO_3$

Composition: $LaScO_3$

Space group number: 62

ICSD code: 258768

MAIN CALCULATION RESULTS:

E_g, eV	3.92		
Working ions	O^{2-}		
Migration map from GT*	3D		
R_{sd}, Å	1.581-1.617		
r_{chan}, Å	2.096-2.223		
Migration map from BVSE*	3D		
E_m, eV	1D	2D	3D
	1.05	1.05	1.22
Number of migration paths for DFT-NEB* calculation	3		
Path lengths, Å	2.8798–2.9862		
Ionic conductivity at 400 °C** from KMC*, S/cm	1.9×10^{-8}		

* - GT (geometrical-topological), BVSE (bond valence site energy), DFT-NEB (density functional theory - nudged elastic band), KMC (kinetic Monte Carlo);

** - the temperature range is set by the user, this table shows the initial temperature, below is the full range.

A DETAILED DESCRIPTION OF THE OBTAINED DATA IS GIVEN IN THE TABLE ABOVE:

1. Electronic structure analysis:

Density of state calculation details:

DFT calculation was performed as implemented in the VASP program [1]. The generalized gradient approximation (GGA) of the exchange-correlation functional in the form of the Perdew–Burke–Ernzerhof (PBE) [2] was used with a plane-wave kinetic energy cutoff of 600 eV. Convergence thresholds were 10^{-5} eV for energy and 10^{-4} eV $Å^{-1}$ for ionic forces. Density of states spectra is presented in Figure 1.

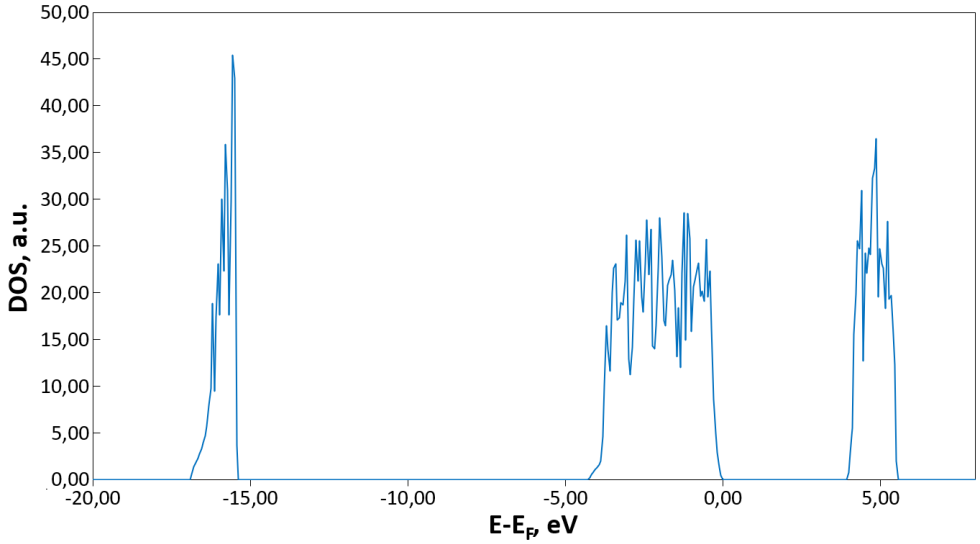

Fig. 1. Density of states (DOS) in $LaScO_3$.

The band gap is **3.92 eV**.

2. ***Ionic conductivity analysis:***

Working ions: $\mathbf{O^{2-}}$

The geometrical-topological (GT) analysis of ionic conductivity, which is based on the partition of the crystal space into convex Voronoi polyhedral, was carried out in the ToposPro program package [3], which is described in detail in the publications about oxygen-ionic conductivity [4–6]. Based on the results of the geometrical-topological analysis of eight voids, a **3D** periodic map of oxygen ions migration has been created (Figure 2). The geometric dimensions of the voids and channels are as follows: $\boldsymbol{R_{sd}}$ **= 1.581-1.617 Å** (voids) and $\boldsymbol{r_{chan}}$ **= 2.096-2.223 Å** (channels).

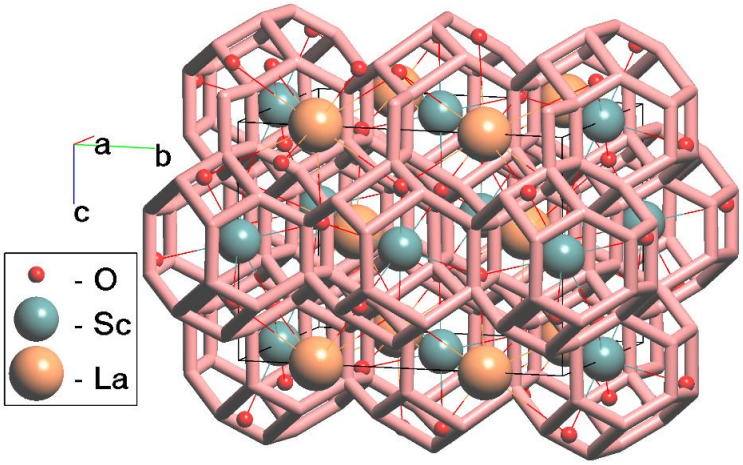

Fig. 2. 3D migration map of oxygen ions in $LaScO_3$ from geometrical-topological analysis.

The “PATHFINDER” service (https://pathfinder.batterymaterials.info/) allows users to generate all possible migration pathways for subsequent quantum chemical calculations. This service helped us to identify **three** non-equivalent migration pathways, which also formed a 3D representation of oxygen migration (Figure 3). PATHFINDER creates supercells for structures whose lattice parameters are less than 8 Å by default. Therefore, a **2×1×2** cell was created for $LaScO_3$.

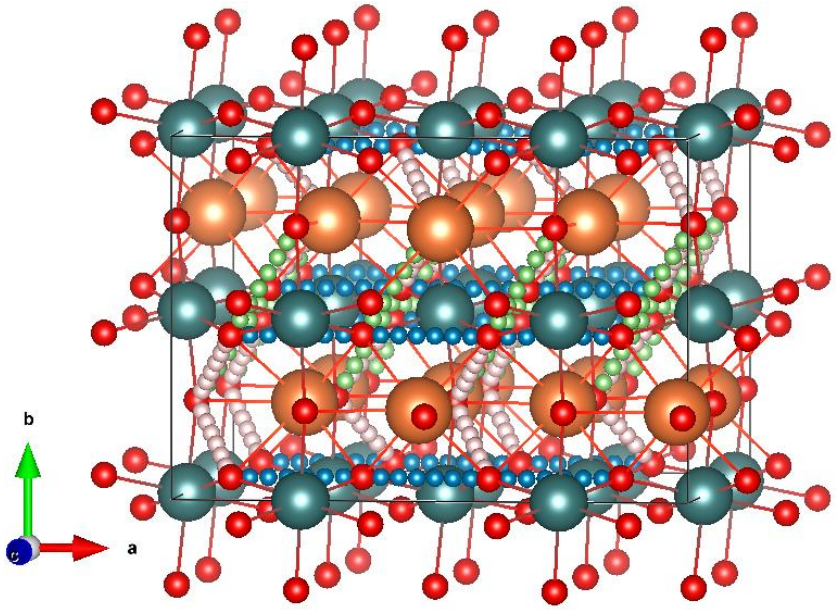

Fig. 3. Four nonequivalent migration paths in $LaScO_3$ (2×1×2 supercell) from the “PATHFINDER” service, forming a 3D oxygen migration map (the cif-file is attached to the report). The path lengths are less than 3 Å (pink path – 2.8798 Å, green – 2.9862 Å, blue – 2.9336 Å). The VESTA program was used for visualization [7].

The “Materials Analyzer” (https://materials-analyzer.info) service allows users to determine all interstitial oxygen positions during diffusion. Figure 4 shows the interstitial positions for the hops.

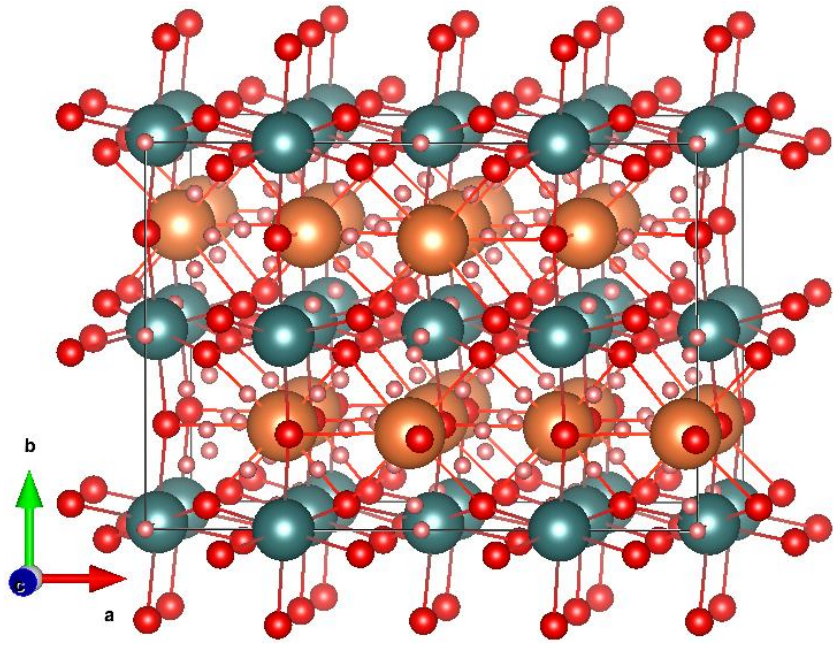

Fig. 3. All interstitial positions of oxygen ions in $LaScO_3$ (2×1×2 supercell) from the "Materials Analyzer" service, forming a 3D oxygen migration map (the cif-file is attached to the report). The VESTA program was used for visualization [7].

We also attach a merged file with interstitial positions and migration paths (Figure 4).

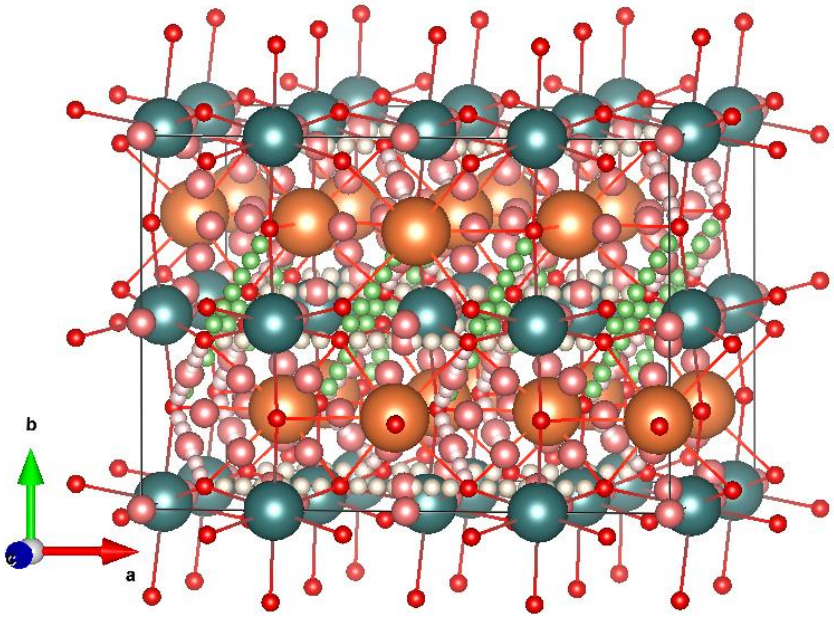

Fig. 3. All interstitial positions and pathways of oxygen ions in $LaScO_3$ (2×1×2 supercell, the cif-file is attached to the report). The VESTA program was used for visualization [7].

The bond valence sum (BVS) method was employed to analyze the ionic conduction properties. Bond Valence Site Energy (BVSE) modeling was performed

using softBV program [8,9] in order to calculate the migration energy that is related to the BVS through an interatomic potential. The default initial parameters for the calculations were described by *Adams et al.* [10]. Figure 5 shows an energy isosurface symbolizing the migration map of working ions. The BVSE calculation assumes a 3D mechanism of oxygen ion migration with energy barriers: **1D – 1.05 eV, 2D - 1.05 eV, 3D - 1.22 eV**.

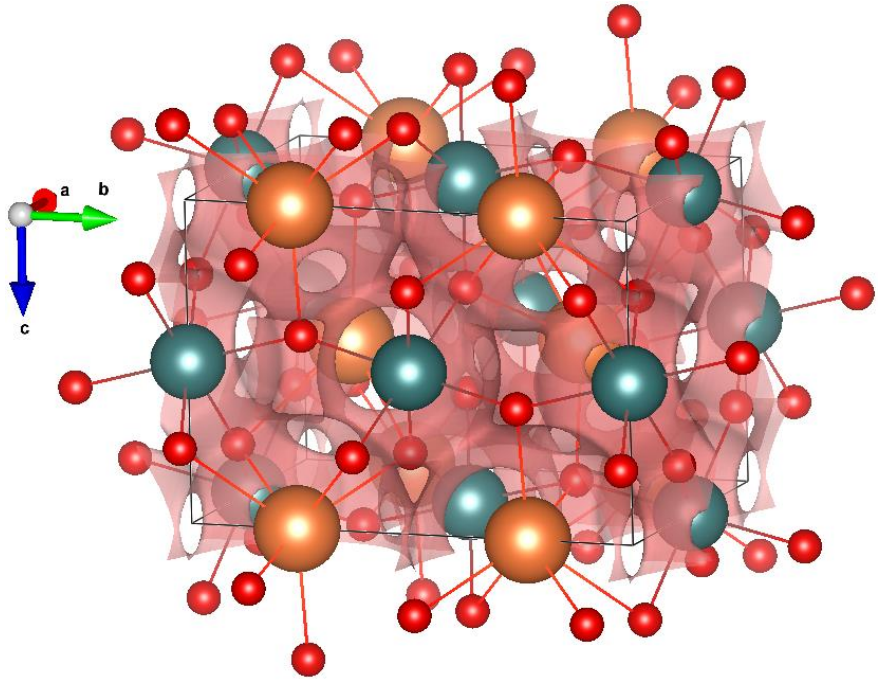

Fig. 5. 3D migration map of oxygen ions in $LaScO_3$ from bond valence site energy calculations (the cube-file is attached to the report). The VESTA program was used for visualization [7].

We also calculated the anion conductivity in the bulk structures using KMC simulations with the command-line version of softBV software package [9]. The conductivity was calculated over the temperature range of 400–900 °C, with a step size of 100 °C. To ensure the accuracy of the calculations, we created supercells with a size of 2 × 1 × 2 with a number of iterations from 1 to 10 million KMC steps. The initial migration energy value was obtained from the BVSE calculations, and the final conductivity value is the average of five independent calculations at each temperature. Below, the Arrhenius-type dependence of the calculated average ionic conductivity on temperature is presented for $LaScO_3$ from the KMC simulation (Figure 5).

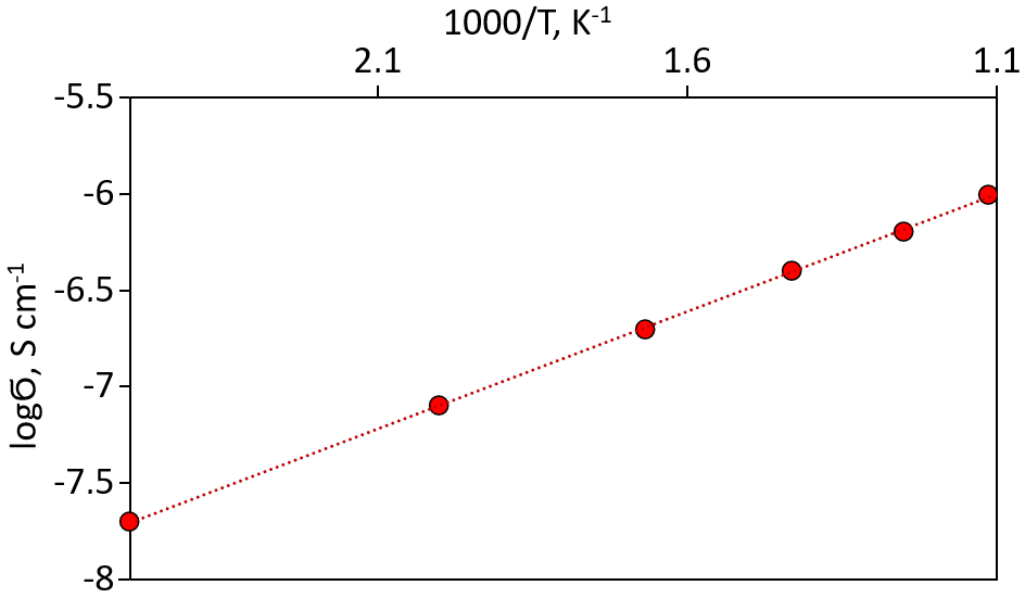

Fig. 5. Ionic conductivity as a function of temperature in $LaScO_3$ from KMC simulation.

References:

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