Supporting information

Mixed electronic and oxide ionic conduction and migration mechanism in digermanate $La_{2-x}Ca_xGe_2O_{7-x/2}$

Lu Liang,[a†] Xiaohui Li, [a,b†*] Xiaoge Wang,[c] Zhaoji Luo,[d] Kun Lin,[a] Qiang Li,[a] Sihao Deng,[e] Lunhua He,[e] Xiaojun Kuang,[b,d] and Xianran Xing[a*]

[a] Beijing Advanced Innovation Center for Materials Genome Engineering, Institute of Solid State Chemistry, University of Science and Technology Beijing, Beijing 100083, People's Republic of China.

[b] Guangxi Key Laboratory of Electrochemical and Magnetochemical Functional Materials, College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541004, People's Republic of China.

[c] College of Chemistry and Molecular Engineering, Peking University, Beijing National Laboratory for Molecular Science (BNLMS), Beijing 100871, People's Republic of China.

[d] MOE Key Laboratory of New Processing Technology for Nonferrous Metal and Materials, Guangxi Key Laboratory of Optical and Electronic Materials and Devices, Guangxi Universities Key Laboratory of Nonferrous Metal Oxide Electronic Functional Materials and Devices, College of Materials Science and Engineering, Guilin University of Technology, Guilin 541004, People's Republic of China.

[†] These authors contributed equally.

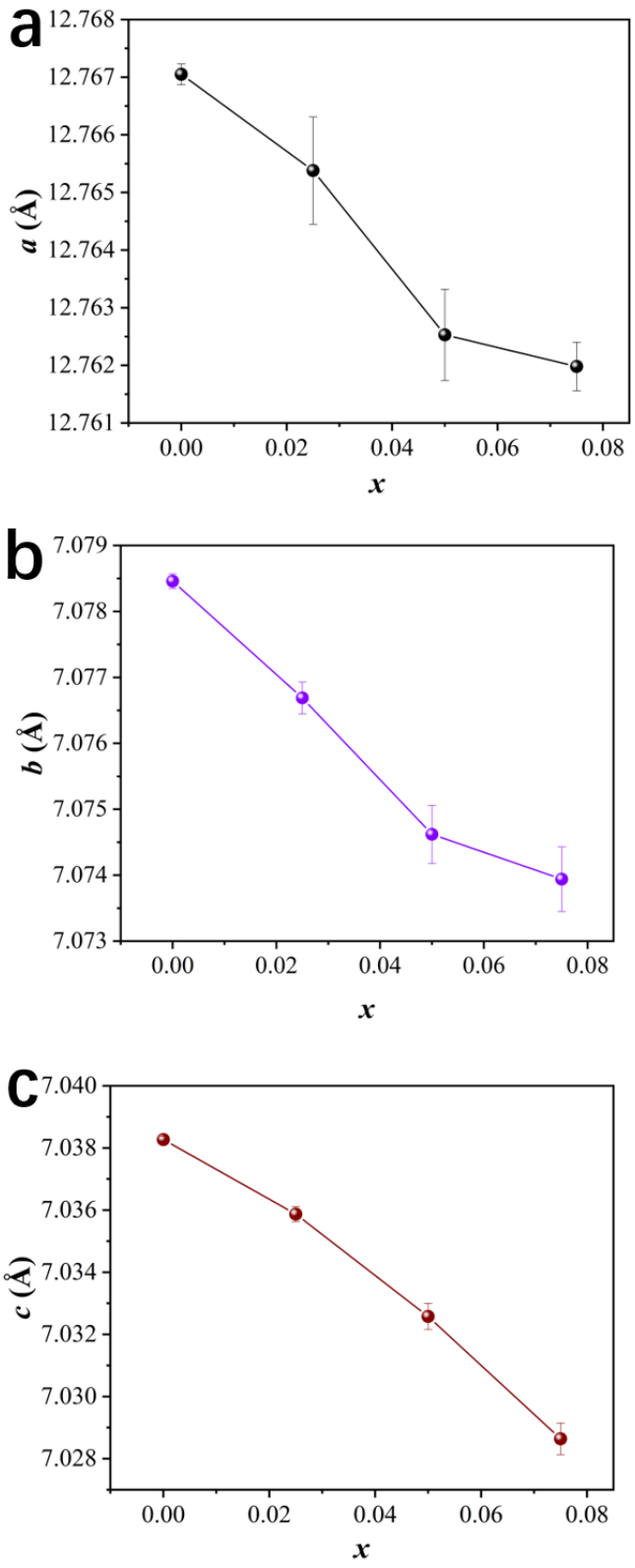

Figure S1. Refined cell parameters of $La_{2-x}Ca_xGe_2O_{7-x/2}$ as a function of Ca doping content.

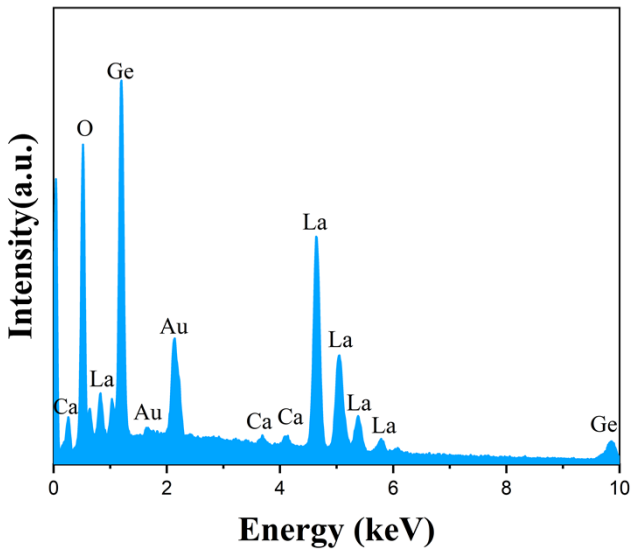

Figure S2. EDS spectrum of $La_{1.925}Ca_{0.075}Ge_2O_{6.963}$.

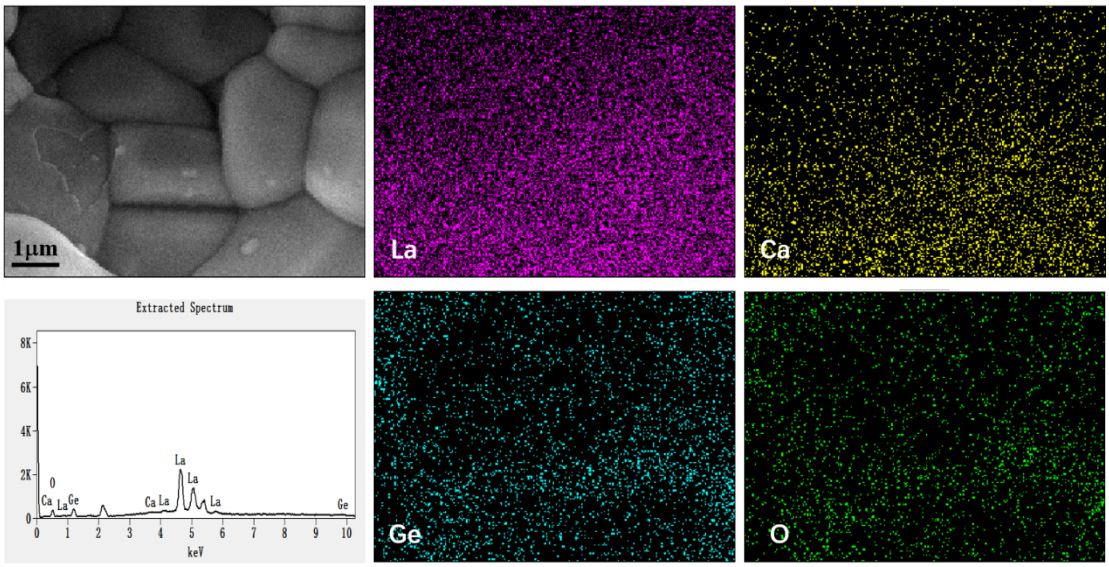

Figure S3. SEM elemental mapping and EDS spectrum of $La_{1.925}Ca_{0.075}Ge_2O_{6.963}$.

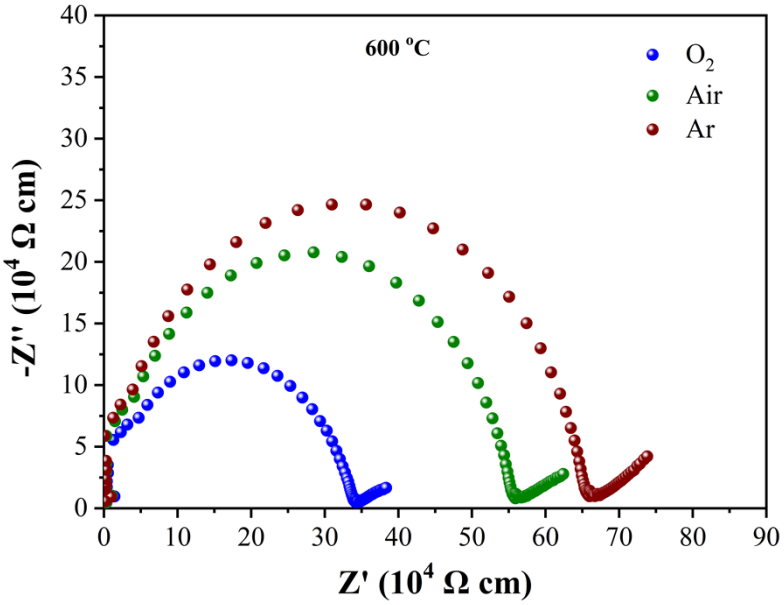

Figure S4. Complex impedance plots of $La_{1.925}Ca_{0.075}Ge_2O_{6.963}$ at 600 ºC under different oxygen partial pressures.

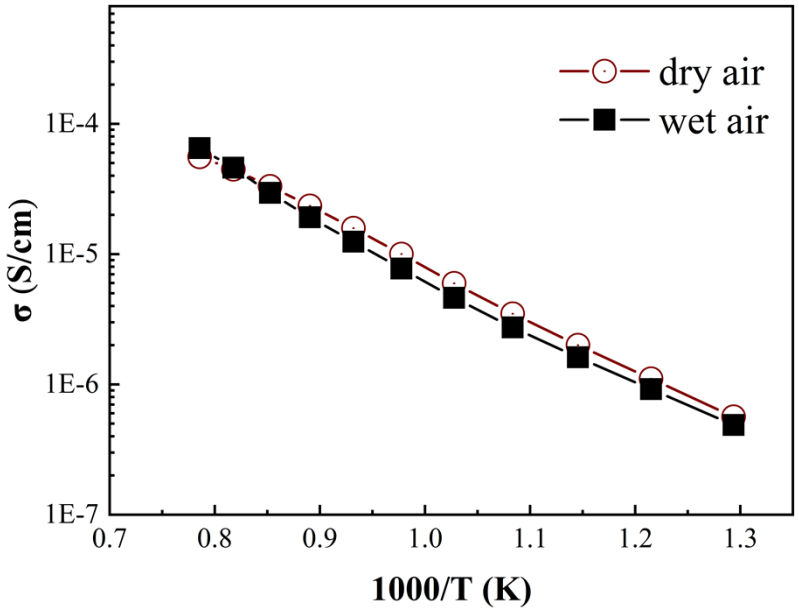

Figure S5. Bulk conductivities of $La_{1.925}Ca_{0.075}Ge_2O_{6.963}$ under dry and wet atmospheres.

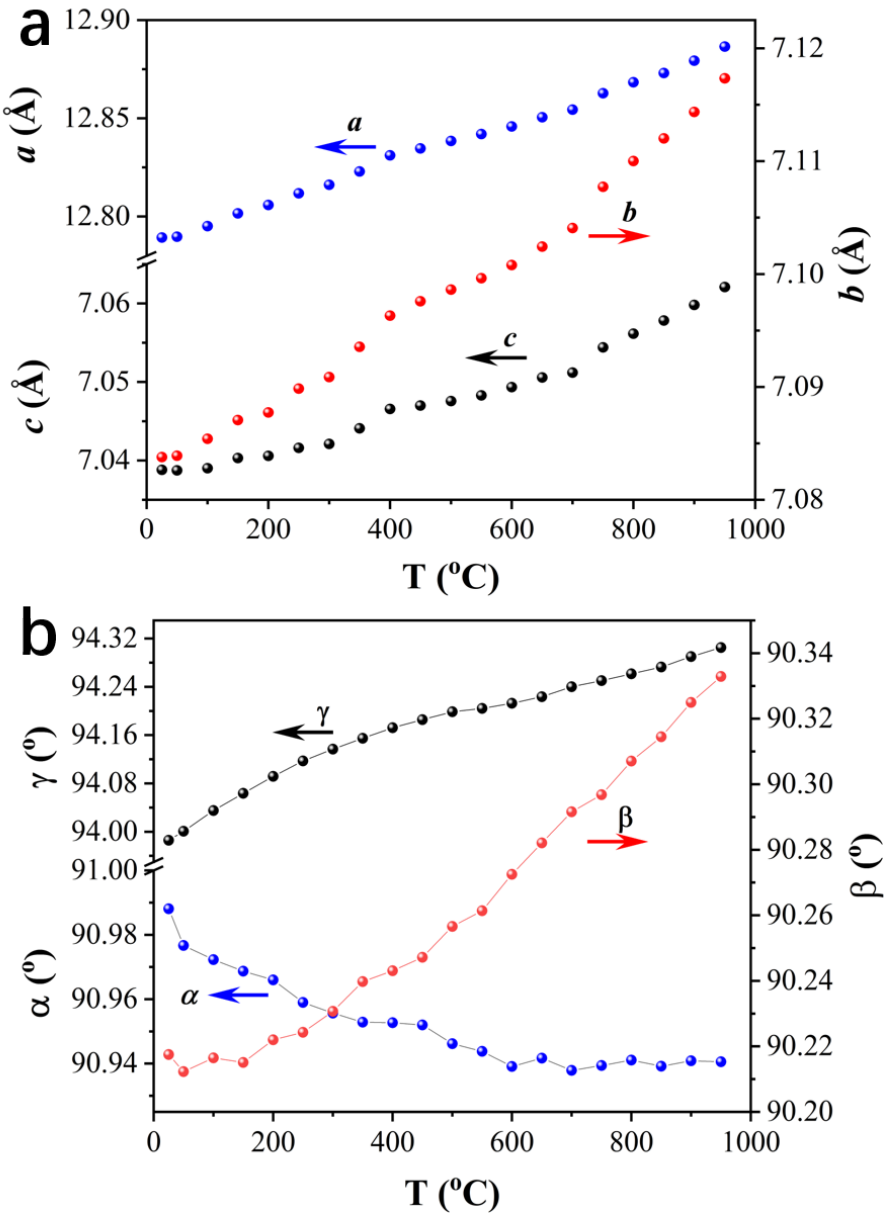

Figure S6. Refined cell parameters and angles versus temperatures of $La_{1.925}Ca_{0.075}Ge_2O_{6.963}$.

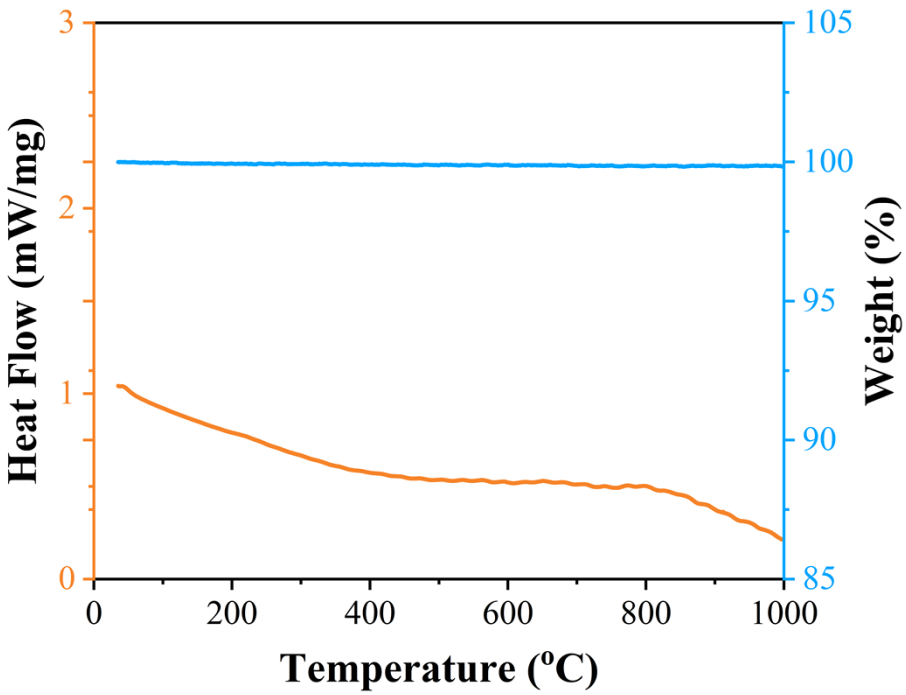

Figure S7. TG-DSC curves of $La_{1.925}Ca_{0.075}Ge_2O_{6.963}$.

Table S1. The anisotropic displacement parameters (ADPs) for $La_{1.925}Ca_{0.075}Ge_2O_{6.963}$ from the Rietveld refinement of NPD data in $P\bar{1}$.

Atom	Site	U11(Å^2)	U22(Å^2)	U33(Å^2)	U12(Å^2)	U13(Å^2)	U23(Å^2)
La1	2i	0.020(7)	0.005(5)	0.001(5)	0.002(5)	0.000(5)	-0.022(4)
La2	2i	0.041(10)	0.006(6)	0.004(7)	0.004(5)	-0.005(6)	-0.012(4)
La3	2i	0.008(7)	0.037(8)	0.005(6)	0.002(5)	-0.010(4)	-0.028(5)
Ca1	2i	0.008(7)	0.037(8)	0.005(6)	0.002(5)	-0.010(4)	-0.028(5)
La4	2i	0.020(8)	0.001(6)	0.010(7)	0.006(4)	-0.001(5)	0.013(4)
Ge1	2i	0.002(6)	0.013(6)	0.008(6)	0.004(4)	-0.017(4)	-0.026(5)
Ge2	2i	0.001(6)	0.001(5)	0.008(6)	-0.004(4)	-0.014(4)	0.002(4)
Ge3	2i	0.007(6)	0.002(5)	0.000(6)	-0.006(5)	0.004(5)	0.003(4)
Ge4	2i	0.007(6)	0.004(5)	0.003(5)	-0.002(4)	-0.001(4)	0.011(4)
O1	2i	0.039(11)	0.009(9)	0.033(10)	0.024(7)	-0.010(7)	-0.003(6)
O2	2i	0.030(13)	0.018(6)	0.009(8)	-0.004(7)	0.050(8)	-0.014(5)
O3	2i	0.007(11)	0.003(10)	0.026(5)	-0.020(7)	0.003(5)	0.002(5)
O4	2i	0.023(10)	0.005(8)	0.026(9)	0.013(7)	0.008(8)	0.008(6)
O5	2i	0.043(14)	0.018(12)	0.005(9)	-0.016(9)	0.016(8)	-0.022(7)
O6	2i	0.052(13)	0.023(10)	0.005(8)	0.018(8)	0.011(7)	0.032(6)
O7	2i	0.005(10)	0.011(9)	0.020(11)	-0.009(7)	-0.023(7)	0.015(7)
O8	2i	0.021(12)	0.013(6)	0.010(7)	0.010(7)	0.005(6)	0.006(5)
O9	2i	0.027(11)	0.004(7)	0.020(9)	-0.003(6)	-0.012(7)	0.027(6)
O10	2i	0.013(12)	0.006(7)	0.005(9)	-0.013(7)	-0.019(7)	0.008(6)
O11	2i	0.005(10)	0.005(10)	0.003(9)	-0.008(7)	-0.012(6)	0.008(7)
O12	2i	0.010(10)	0.037(12)	0.012(10)	-0.001(7)	0.020(7)	0.007(7)
O13	2i	0.057(15)	0.013(6)	0.010(8)	-0.005(7)	-0.007(7)	0.009(5)
O14	2i	0.024(12)	0.004(9)	0.022(11)	-0.034(7)	-0.029(7)	0.009(7)

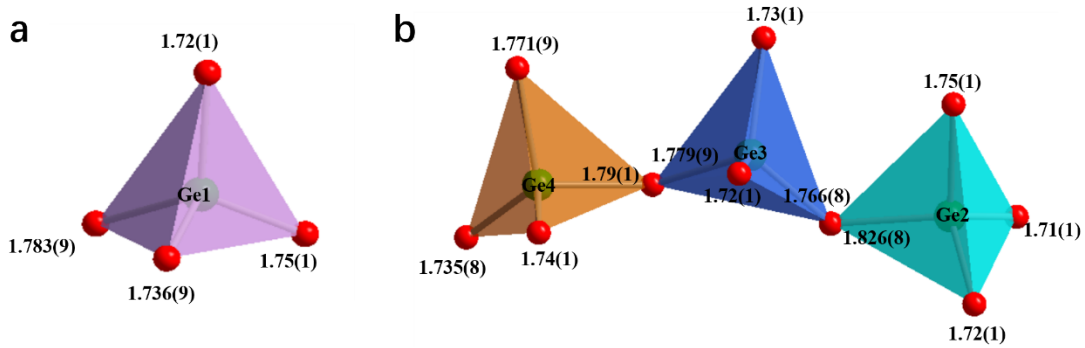

Figure S8. Coordination environments and bond lengths of (a) Ge1 and (b) Ge2, Ge3 and Ge4 in parent $La_2Ge_2O_7$.