Supplemental material

Mechanisms of Point Defect Formation and Ionic Conduction in Divalent Cation-Doped Lanthanum Oxybromide: First-Principles and Experimental Study

Kazuki Shitara[1,2], Akihide Kuwabara[1], Naoyoshi Nunotani[3], Muhammad Radzi Iqbal Bin Misran[3], Miki Inada[4], Tomoki Uchiyama[5], Yoshiharu Uchimoto[5], Nobuhito Imanaka[3]

[1]Nanostructures Research Laboratory, Japan Fine Ceramics Center, 2-4-1 Mutsuno, Nagoya, Aichi 456-8587, Japan

[2]Joint and Welding Research Institute, Osaka University, 11-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

[3]Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

[4]Center of Advanced Instrumental Analysis, Kyushu University, 6-1 Kasuga-Koen, Kasuga, Fukuoka 816-8580, Japan

[5]Graduate School of Human and Environmental Studies, Kyoto University, Nihonmatsu-cho, Yoshida, Sakyo-ku, Kyoto, Kyoto 606-8317, Japan

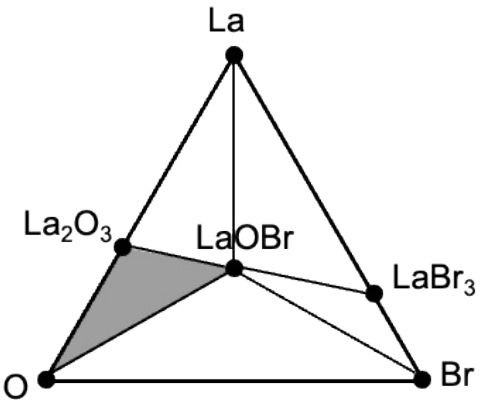

Figure S1 A schematic phase diagram of the La-O-Br ternary system. Grey area means the assumed equilibrium condition in this study.

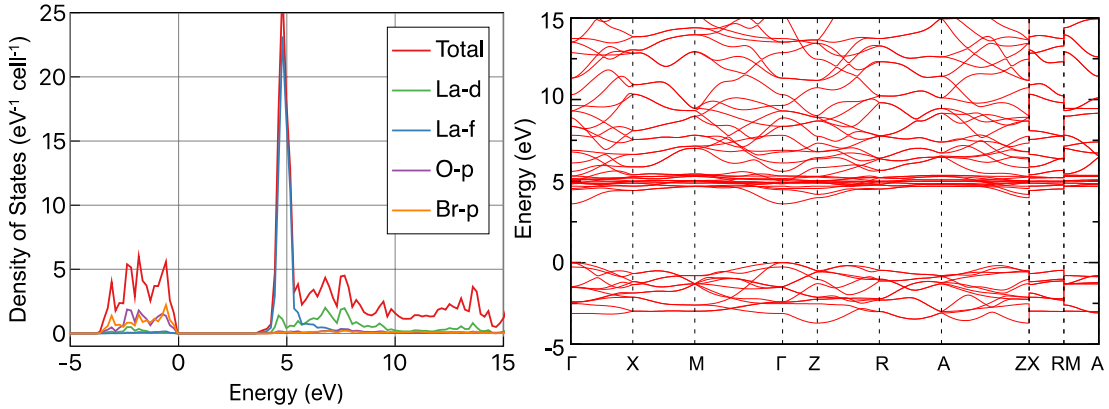

Figure S2 Calculated density of states (DOS) and band structure of pure LaOBr.

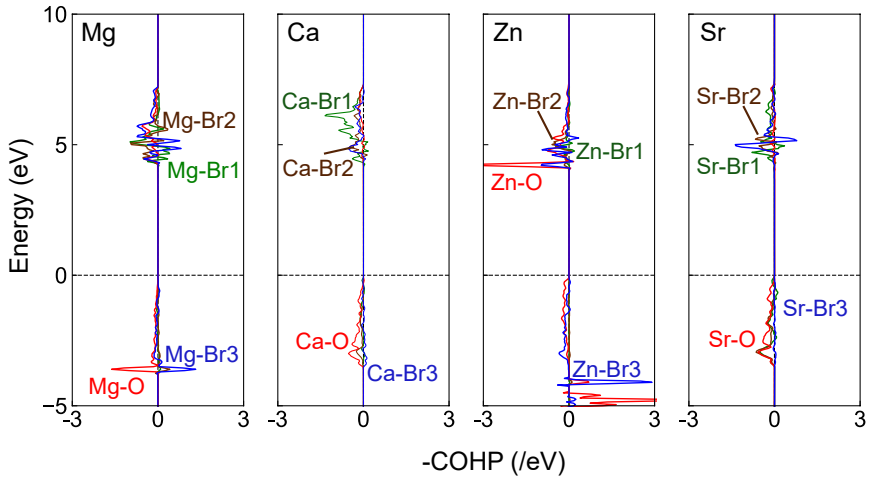

Figure S3 Calculated COHP of M^{2+}-doped LaOBr models. It is noted that negative COHP was plotted. Br1, Br2, and Br3 correspond to Br ions bonded to substitutional *M* (*M*: Mg, Ca, Zn, Sr) ions in Fig. 3(b-e).

We applied crystal orbital Hamilton population (COHP) analysis[1] to the M^{2+}-doped models to confirm these interactions. Figure 4 shows the calculated negative COHP (−COHP) values. The Fermi level was set to 0 eV. Positive and negative −COHP values indicate bonding and antibonding orbitals, respectively. Bonding states between substitutional *M* and Br at the B r3 site were found to be approximately −4 eV for the doped Mg and Zn, suggesting strong bonding interactions between these atoms. Less −COHP values were observed for Ca and Sr.

1 S. Maintz, V. L. Deringer, A. L. Tchougréeff and R. Dronskowski, *Journal of Computational Chemistry*, 2016, **37**, 1030–1035.

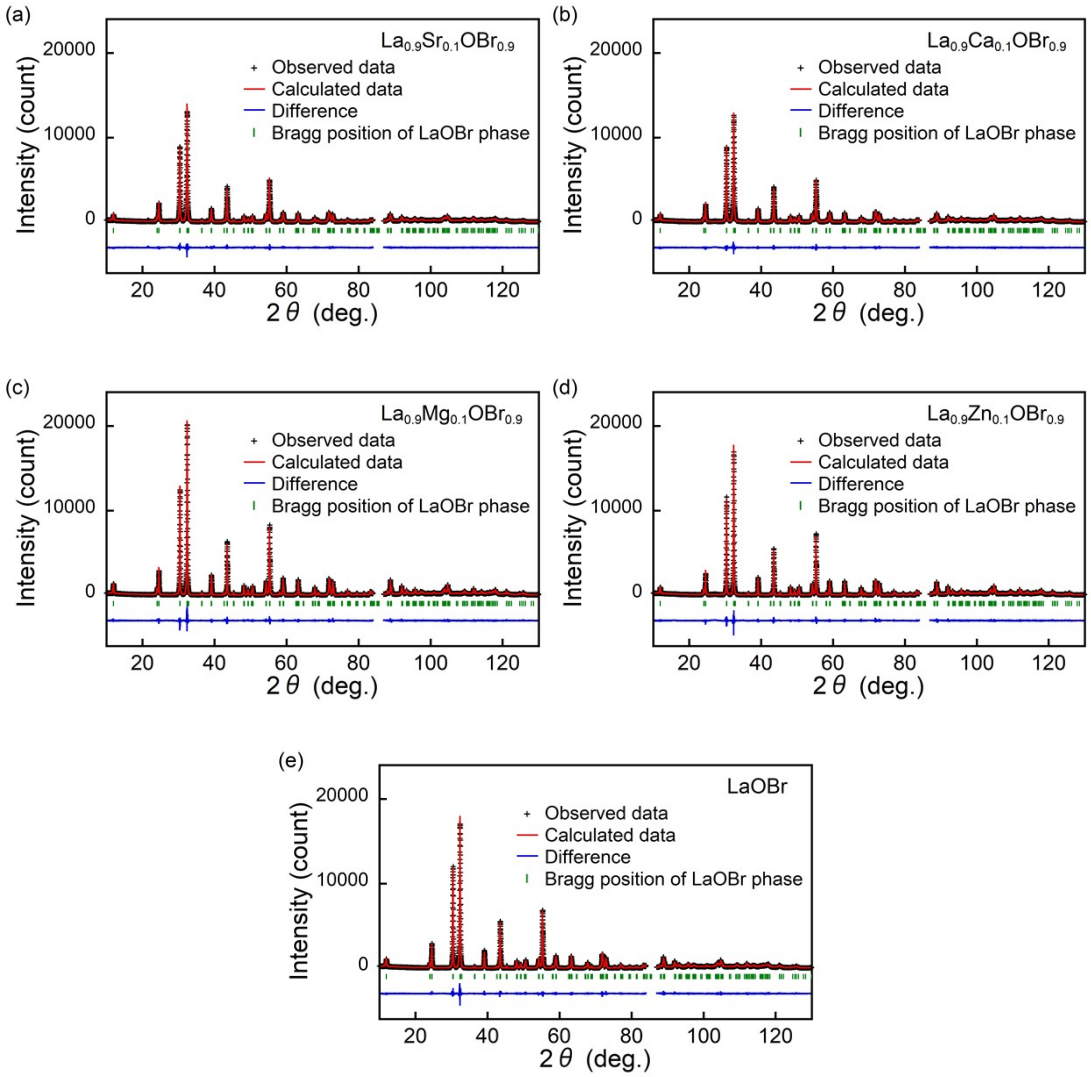

Figure S4 Results of the Rietveld refinements for $La_{0.9}M_{0.1}OBr_{0.9}$ (*M*: Sr, Ca, Mg, Zn) and LaOBr.

Table S1 Structural parameters determined by Rietveld refinements for $La_{0.9}M_{0.1}OBr_{0.9}$ (*M*: Sr, Ca, Mg, Zn) and LaOBr.

Sample	Atom	Wyckoff position	*g*	*x*	*y*	*z*	*B* (Å^2)
$La_{0.9}Sr_{0.1}OBr_{0.9}$	La	2*c*	0.9	0	1/2	0.1623(1)	0.50(1)
	Sr	2*c*	0.1	0	1/2	= *z*(La)	= *B*(La)
	O	2*a*	1	0	0	0	1.02(11)
	Br	2*c*	0.9	0	1/2	0.6365(1)	0.40(2)
Space group: *P*4/*nmm*, *a* = 4.1581(1) Å, *c* = 7.3823(1) Å, *V* = 127.637(2) Å^3, R_{wp} = 9.05%, *S* = 1.52							
$La_{0.9}Ca_{0.1}OBr_{0.9}$	La	2*c*	0.9	0	1/2	0.1619(1)	0.40(1)
	Ca	2*c*	0.1	0	1/2	= *z*(La)	= *B*(La)
	O	2*a*	1	0	0	0	1.28(10)
	Br	2*c*	0.9	0	1/2	0.6364(1)	0.66(2)
Space group: *P*4/*nmm*, *a* = 4.1557(1) Å, *c* = 7.3879(1) Å, *V* = 127.589(2) Å^3, R_{wp} = 8.83%, *S* = 1.45							
$La_{0.9}Mg_{0.1}OBr_{0.9}$	La	2*c*	0.9	0	1/2	0.1617(1)	0.42(1)
	Mg	2*c*	0.1	0	1/2	= *z*(La)	= *B*(La)
	O	2*a*	1	0	0	0	1.25(9)
	Br	2*c*	0.9	0	1/2	0.6363(1)	0.71(2)
Space group: *P*4/*nmm*, *a* = 4.1553(1) Å, *c* = 7.3855(1) Å, *V* = 127.520(1) Å^3, R_{wp} = 9.26%, *S* = 1.58							
$La_{0.9}Zn_{0.1}OBr_{0.9}$	La	2*c*	0.9	0	1/2	0.1615(1)	0.44(1)
	Zn	2*c*	0.1	0	1/2	= *z*(La)	= *B*(La)
	O	2*a*	1	0	0	0	1.23(11)
	Br	2*c*	0.9	0	1/2	0.6368(1)	0.51(2)
Space group: *P*4/*nmm*, *a* = 4.1551(1) Å, *c* = 7.3866(1) Å, *V* = 127.529(1) Å^3, R_{wp} = 10.10%, *S* = 1.64							
LaOBr	La	2*c*	1	0	1/2	0.1618(1)	0.31(1)
	O	2*a*	1	0	0	0	0.42(9)
	Br	2*c*	1	0	1/2	0.6366(1)	0.73(2)
Space group: *P*4/*nmm*, *a* = 4.1534(1) Å, *c* = 7.3979(1) Å,*V* = 127.619(2) Å^3, R_{wp} = 9.48%, *S* = 1.59							

Table S2 Average bond lengths of La/*M*-Br1, La/*M*-Br2, La/*M*-Br3, and La/*M* -O, where the Br1, Br2, Br3, and O sites are corresponding to those in Fig. 3(b-e). The ratio of La/*M*-Br3 to La/*M*-Br1 and that of La/*M*-O to La/*M*-Br2 were estimated from these average lengths.

Sample	La/*M*-Br1 (Å)	La/*M*-Br2 (Å)	La/*M*-Br3 (Å)	La/*M*-O (Å)	$\frac{\text{La/M - Br3}}{\text{La/M - Br1}}$	$\frac{\text{La/M - O}}{\text{La/M - Br2}}$
$La_{0.9}Sr_{0.1}OBr_{0.9}$	3.5007(1)	3.2944(4)	3.8816(10)	2.3994(3)	1.1088(4)	0.7283(1)
$La_{0.9}Ca_{0.1}OBr_{0.9}$	3.5057(9)	3.2946(4)	3.8822(9)	2.3976(2)	1.1074(4)	0.7277(1)
$La_{0.9}Mg_{0.1}OBr_{0.9}$	3.5062(8)	3.2951(4)	3.8793(8)	2.3962(2)	1.1064(3)	0.7272(1)
$La_{0.9}Zn_{0.1}OBr_{0.9}$	3.5112(9)	3.2943(4)	3.8754(9)	2.3956(2)	1.1037(4)	0.7272(1)
LaOBr	3.5127(9)	3.2939(4)	3.8852(9)	2.3969(2)	1.1060(4)	0.7277(1)