Supplementary Information

Defect formation and carrier compensation in layered oxychalcogenide $La_2CdO_2Se_2$: an insight from first principles

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Computational details for zb-CdSe

The bulk and defect calculations for zb-CdSe were conducted using the HSE06 hybrid functional. The PAW cut-off radii were set to 1.22 and 1.11 Å for Cd and Se, respectively; Cd 4d and 5s and Se 4s and 4p were treated as valence electrons. The lattice constant of the zb-CdSe primitive unit cell was relaxed until the residual stress was convergence to 0.005 GPa. A Γ-centered 6×6×6 *k*-point mesh and a plane-wave cut-off energy of 520 eV were used for the structural optimization. The band structure and DOS were evaluated using a cut-off energy of 400 eV under the optimized structure. For the DOS calculation, a Γ-centered *k*-point mesh of 12×12×12 was employed with a reduced mesh by a factor of 2 for the Fock exchange potential. For the calculation of the band-averaged effective mass tensor, the carrier concentration and temperature were set to 10^{16} cm^{-3} and 300 K, respectively, and a Γ-centered *k*-point mesh of 24×24×24 was taken with a reduced mesh by a factor of 4 for the Fock exchange potential.

The Cd vacancy and interstitial were modeled using a supercell that is a 2×2×2 enlargement of the conventional cell. The vacant tetrahedral site in the zinc-blende structure, similar to the interstitial of $La_2CdO_2Se_2$, was employed as the interstitial site. The initial structure of each defect supercell was subjected to random displacements of up to 0.2 Å in the atoms adjacent to the defects, eliminating symmetry-induced relaxation constraints. The internal atomic coordinates were relaxed under fixed lattice vectors until the atomic force became smaller than 0.03 eV Å^{-1}. A 2×2×2 non-Γ-centered *k*-point mesh with a plane-wave cutoff of 400 eV was used, and spin polarization was considered in all defect supercell calculations. The static dielectric tensor was calculated by the finite-electric-field approach using a Γ-centered 12×12×12 *k*-point mesh and a cut-off energy of 400 eV, where the *k*-point mesh was reduced by a factor of 2 for the Fock exchange potential. The components of the obtained dielectric tensor were $\varepsilon_{xx}^{\mathrm{ele}} = 5.89$ and $\varepsilon_{xx}^{\mathrm{ion}} = 3.41$. For the chemical potential, we considered the conditions of equilibrium with the Cd crystal [cation-rich conditions: $\Delta\mu_{\mathrm{Cd}} = 0$ (eV)] and the conditions of the minimum chemical potential of Cd in $La_2CdO_2Se_2$ [anion-rich conditions: $\Delta\mu_{\mathrm{Cd}} = -1.09$ (eV)].

Selection of dopants

As explained in Section 3.3 of the main text, it is too computationally expensive to use the HSE06 hybrid functional for the screening of all the candidate dopants. Therefore, we performed a series of calculations with the PBEsol-GGA+*U*, which underestimates the band gap but can reduce the computational cost. The Hubbard *U* parameter of 5.0 eV was applied to the Cd 4d-orbitals. The *k*-points mesh, the cut-off energies, and the conditions and criteria required to draw the chemical potential diagram are set to the same as in the HSE06 calculation (Section 2). The PAW radial cutoffs were set to 1.08, 1.64, 1.32, 1.06, 1.59, 1.48, 1.48, 1.59, 1.22, and 1.64 Å for Li, K, Rb, Mg, Ca, Ba, Ti, Hf, Ga, and In, respectively. Li 2s, K 3p and 4s, Rb 4s, 4p, and 5s, Mg 3s, Ca 3p and 4s, Ba 5s, 5p, and 6s, Ti 4s and 3d, Hf 6s and 5d, Ga 3d, 4s, and 4p, and In 5s and 5p were treated as valence electrons. To correct the band edges, we adopted the non-self-consistent HSE06 (nsc-HSE06) approach. Using the self-consistent wave function and charge density obtained from the PBEsol-GGA+*U* calculation as the input, we diagonalized the Hamiltonian once with the HSE06 to obtain the nsc-HSE06 single-particle levels. The band gap of $La_2CdO_2Se_2$ obtained by combining the PBEsol-GGA+*U* and nsc-HSE06 calculations is 3.27 eV, which is 0.24 eV larger than that obtained by the self-consistent HSE06 calculation and coincidentally closer to the experimental value (∼3.3 eV). Possible reasons for the difference in the calculated band gaps include differences in equilibrium lattice constants and errors in non-self-consistent calculation.

Figure S1 shows the formation energy diagrams of the dopants in $La_2CdO_2Se_2$ at the cation-rich and anion-rich conditions. The range of the Fermi level is extended from the band edges obtained by the PBEsol-GGA+*U* calculation to those obtained by the nsc-HSE06 calculation using the primitive unit cell. The chemical potential conditions and competing phases are given in Tables S3-S16. As mentioned in the main text, all the donor dopants form deep donor levels associated with localized states even at the PBEsol-GGA+*U* level. Zr and Al, which have the shallowest donor levels at each cation site, were selected for the subsequent HSE06 calculations. For the acceptor dopants, all the candidates considered are shallow acceptors with PBEsol-GGA+*U*. Sr and Na, which have a good balance of the formation energies between the substitution and interstitial sites, were selected for the HSE06 calculations.

Table S1 Limits of the chemical potentials at which $La_2CdO_2Se_2$ exists in the single phase in the La-Cd-O-Se quaternary system and the competing phases at respective limits. The unit of the chemical potential is eV.

Conditions	$\Delta\mu_{La}$	$\Delta\mu_{Cd}$	$\Delta\mu_{O}$	$\Delta\mu_{Se}$	Competing phases
A (Anion rich)	–6.23	–1.09	–1.84	–0.42	CdSe, La_2O_3, $La_4Se_3O_4$
B	–6.19	–1.08	–1.87	–0.44	La_2O_3, La_2SeO_2, $La_4Se_3O_4$
C	–4.60	0	–2.93	–1.51	CdSe, La_2O_3, Cd
D	–4.57	0	–2.95	–1.52	La_2O_3, La_2SeO_2, Cd
E	–5.08	–1.08	–2.99	–0.44	$La_{10}Se_{14}O$, La_2SeO_2, $La_4Se_3O_4$
F	–5.10	–1.09	–2.97	–0.42	CdSe, $La_{10}Se_{14}O$, $La_4Se_3O_4$
G (Cation rich)	–3.45	0	–4.07	–1.52	$La_{10}Se_{14}O$, La_2SeO_2, Cd
H	–3.47	0	–4.06	–1.51	CdSe, $La_{10}Se_{14}O$, Cd

Table S2 Thermodynamic transition levels $\varepsilon(q/q')$ of the native defects and dopants with respect to the VBM. Note that hydrogenic effective-mass states are not included here.

Native defects	$\varepsilon(q/q')$	(eV)	Dopants	$\varepsilon(q/q')$	(eV)
V_{La}	$\varepsilon(0/-1)$	0.26	Na_{Cd}	$\varepsilon(0/-1)$	0.04
	$\varepsilon(-1/-2)$	0.36	Sr_{La}	$\varepsilon(0/-1)$	0.06
	$\varepsilon(-2/-3)$	0.59	Al_{Cd}	$\varepsilon(+1/-1)$	3.00
V_{Cd}	$\varepsilon(0/-2)$	0.17	Zr_{La}	$\varepsilon(+1/0)$	2.60
V_{O}	$\varepsilon(+2/+1)$	1.66	Na_i	$\varepsilon(+1/0)$	2.94
	$\varepsilon(+1/0)$	2.67	Sr_i	$\varepsilon(+2/+1)$	2.34
V_{Se}	$\varepsilon(+2/0)$	1.31		$\varepsilon(+1/0)$	2.66
	$\varepsilon(0/-1)$	2.62		$\varepsilon(0/-1)$	2.91
La_{Cd}	$\varepsilon(+1/0)$	2.68	Al_i	$\varepsilon(+3/+1)$	2.09
	$\varepsilon(0/-1)$	2.85		$\varepsilon(+1/0)$	2.62
Cd_{La}	$\varepsilon(0/-1)$	0.15		$\varepsilon(0/-1)$	2.96
La_i	$\varepsilon(+3/+2)$	1.79	Zr_i	$\varepsilon(+4/+3)$	1.28
	$\varepsilon(+2/+1)$	2.21		$\varepsilon(+3/+2)$	1.73
	$\varepsilon(+1/0)$	2.44		$\varepsilon(+2/+1)$	2.09
	$\varepsilon(0/-1)$	2.74		$\varepsilon(+1/0)$	2.32
Cd_i	$\varepsilon(+2/0)$	2.34		$\varepsilon(0/-1)$	2.52
	$\varepsilon(0/-1)$	2.76			
O_i	$\varepsilon(0/-1)$	0.65			
	$\varepsilon(-1/-2)$	1.03			
Se_i	$\varepsilon(0/-2)$	2.33			

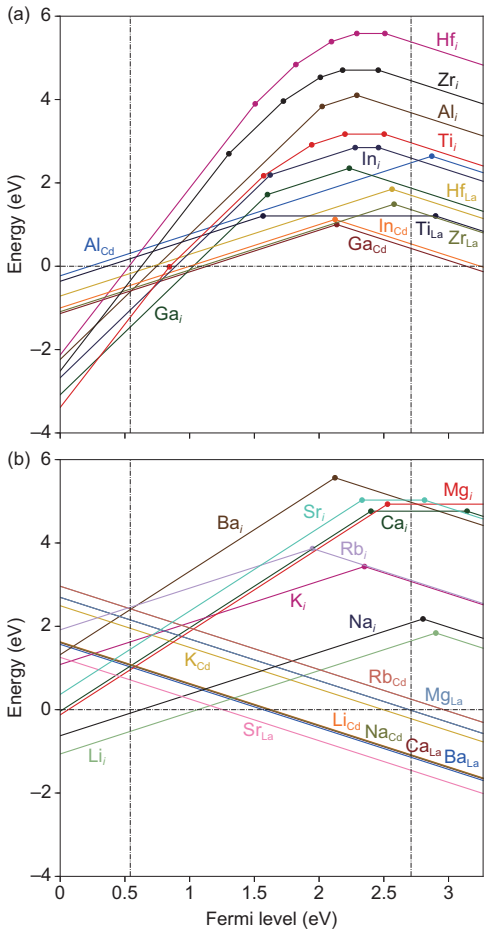

Fig. S1 (a) Formation energies of Ti, Zr, Hf, Al, Ga, and In dopants in $La_2CdO_2Se_2$ at the cation-rich conditions, and (b) formation energies of Mg, Ca, Sr, Ba, Li Na, K, and Rb dopants in $La_2CdO_2Se_2$ at the anion-rich conditions, calculated by PBEsol-GGA+U. The range of the Fermi level is extended from the band edges obtained by the PBEsol-GGA+U calculation (vertical dashed dotted lines) to those obtained by the nsc-HSE06 calculation.

Table S3 Limits of the chemical potentials at which $La_2CdO_2Se_2$ exists in the single phase in the La-Cd-O-Se-Ti quinary system and the competing phases at respective limits, calculated by PBEsol-GGA+U. The unit of the chemical potential is eV.

Conditions	$\Delta\mu_{La}$	$\Delta\mu_{Cd}$	$\Delta\mu_{O}$	$\Delta\mu_{Se}$	$\Delta\mu_{Ti}$	Competing phases
A	–4.36	–0.85	–3.32	–0.56	–2.71	$La_{10}Se_{14}O$, $La_{10}Se_{19}$, $La_2Ti_2O_7$, $La_4Se_3O_4$
B	–4.32	–0.83	–3.34	–0.59	–2.68	$La_{10}Se_{14}O$, La_2SeO_2, $La_2Ti_2O_7$, $La_4Se_3O_4$
C	–3.82	–0.50	–3.68	–0.93	–2.00	$La_{10}Se_{14}O$, La_2SeO_2, $La_2Ti_2O_7$, $La_5Ti_5O_{17}$
D	–4.35	–0.79	–3.36	–0.57	–2.59	CdSe, $La_{10}Se_{14}O$, $La_{10}Se_{19}$, $La_2Ti_2O_7$
E (Cation rich)	–3.07	0	–4.17	–1.42	–1.20	$La_{10}Se_{14}O$, La_2SeO_2, TiO, Cd
F	–3.23	–0.11	–4.07	–1.32	–1.31	$La_{10}Se_{14}O$, La_2SeO_2, Ti_2O_3, TiO
G	–3.17	0	–4.14	–1.35	–1.23	CdSe, $La_{10}Se_{14}O$, TiO, Cd
H	–3.28	–0.07	–4.07	–1.28	–1.31	CdSe, $La_{10}Se_{14}O$, Ti_2O_3, TiO
I	–3.56	–0.26	–3.89	–1.10	–1.58	CdSe, $La_{10}Se_{14}O$, $La_6Ti_3Se_9O_5$, Ti_2O_3
J	–3.41	–0.22	–3.95	–1.20	–1.49	$La_{10}Se_{14}O$, La_2SeO_2, $La_5Ti_5O_{17}$, Ti_2O_3
K	–3.56	–0.29	–3.87	–1.09	–1.61	$La_{10}Se_{14}O$, $La_5Ti_5O_{17}$, $La_6Ti_3Se_9O_5$, Ti_2O_3
L	–3.87	–0.46	–3.68	–0.89	–1.95	CdSe, $La_{10}Se_{14}O$, $La_2Ti_2O_7$, $La_5Ti_5O_{17}$
M	–3.74	–0.38	–3.76	–0.97	–1.79	CdSe, $La_{10}Se_{14}O$, $La_5Ti_5O_{17}$, $La_6Ti_3Se_9O_5$
N	–4.57	–0.90	–3.19	–0.45	–2.94	CdSe, $La_{10}Se_{19}$, $La_2Ti_2O_7$, $La_4Se_3O_4$
O (Anion rich)	–5.72	–0.90	–2.05	–0.45	–6.02	CdSe, La_2O_3, La_2TiO_5, $La_4Se_3O_4$
P	–5.41	–0.83	–2.25	–0.59	–5.60	La_2O_3, La_2SeO_2, La_2TiO_5, $La_4Se_3O_4$
Q	–5.32	–0.90	–2.45	–0.45	–4.80	CdSe, $La_2Ti_2O_7$, La_2TiO_5, $La_4Se_3O_4$
R	–5.01	–0.83	–2.66	–0.59	–4.39	La_2SeO_2, $La_2Ti_2O_7$, La_2TiO_5, $La_4Se_3O_4$
S	–4.37	0	–2.95	–1.35	–4.21	CdSe, La_2O_3, La_2TiO_5, Cd
T	–4.16	0	–3.09	–1.42	–3.93	La_2O_3, La_2SeO_2, La_2TiO_5, Cd
U	–3.96	0	–3.35	–1.35	–3.00	CdSe, $La_2Ti_2O_7$, La_2TiO_5, Cd
V	–3.76	0	–3.49	–1.42	–2.72	La_2SeO_2, $La_2Ti_2O_7$, La_2TiO_5, Cd
W	–3.25	0	–4.07	–1.35	–1.31	CdSe, Ti_2O_3, TiO, Cd
X	–3.64	0	–3.68	–1.35	–2.18	CdSe, $La_2Ti_2O_7$, $La_5Ti_5O_{17}$, Cd
Y	–3.57	0	–3.68	–1.42	–2.25	La_2SeO_2, $La_2Ti_2O_7$, $La_5Ti_5O_{17}$, Cd
Z	–3.32	0	–4.00	–1.35	–1.42	CdSe, $La_5Ti_5O_{17}$, Ti_2O_3, Cd
AA	–3.18	0	–4.07	–1.42	–1.31	La_2SeO_2, $La_5Ti_5O_{17}$, Ti_2O_3, TiO, Cd
AB	–3.17	0	–4.07	–1.42	–1.31	La_2SeO_2, $La_5Ti_5O_{17}$, Ti_2O_3, TiO, Cd
AC	–3.18	–0.01	–4.07	–1.41	–1.31	La_2SeO_2, $La_5Ti_5O_{17}$, Ti_2O_3, TiO
AD	–3.65	–0.32	–3.82	–1.04	–1.68	CdSe, $La_5Ti_5O_{17}$, $La_6Ti_3Se_9O_5$, Ti_2O_3

Table S4 Limits of the chemical potentials at which $La_2CdO_2Se_2$ exists in the single phase in the La-Cd-O-Se-Zr quinary system and the competing phases at respective limits, calculated by PBEsol-GGA+U. The unit of the chemical potential is eV.

Conditions	$\Delta\mu_{La}$	$\Delta\mu_{Cd}$	$\Delta\mu_{O}$	$\Delta\mu_{Se}$	$\Delta\mu_{Zr}$	Competing phases
A	–4.57	–0.90	–3.19	–0.45	–4.32	CdSe, $La_{10}Se_{19}$, $La_4Se_3O_4$, ZrO_2
B	–4.35	–0.79	–3.36	–0.57	–3.99	CdSe, $La_{10}Se_{14}O$, $La_{10}Se_{19}$, ZrO_2
C	–4.36	–0.85	–3.32	–0.56	–4.07	$La_{10}Se_{14}O$, $La_{10}Se_{19}$, $La_4Se_3O_4$, ZrO_2
D	–4.32	–0.83	–3.34	–0.59	–4.02	$La_{10}Se_{14}O$, La_2SeO_2, $La_4Se_3O_4$, ZrO_2
E	–4.93	–0.90	–2.84	–0.45	–5.04	CdSe, $La_2Zr_2O_7$, $La_4Se_3O_4$, ZrO_2
F	–4.62	–0.83	–3.04	–0.59	–4.62	La_2SeO_2, $La_2Zr_2O_7$, $La_4Se_3O_4$, ZrO_2
G	–3.17	0	–4.14	–1.35	–2.42	CdSe, $La_{10}Se_{14}O$, ZrO_2, Cd
H (Anion rich)	–3.07	0	–4.17	–1.42	–2.36	$La_{10}Se_{14}O$, La_2SeO_2, ZrO_2, Cd
I	–3.58	0	–3.74	–1.35	–3.23	CdSe, $La_2Zr_2O_7$, ZrO_2, Cd
J	–3.37	0	–3.88	–1.42	–2.95	La_2SeO_2, $La_2Zr_2O_7$, ZrO_2, Cd
K (Cation rich)	–5.72	–0.90	–2.05	–0.45	–7.01	CdSe, La_2O_3, $La_2Zr_2O_7$, $La_4Se_3O_4$
L	–5.41	–0.83	–2.25	–0.59	–6.59	La_2O_3, La_2SeO_2, $La_2Zr_2O_7$, $La_4Se_3O_4$
M	–4.37	0	–2.95	–1.35	–5.20	CdSe, La_2O_3, $La_2Zr_2O_7$, Cd
N	–4.16	0	–3.09	–1.42	–4.93	La_2O_3, La_2SeO_2, $La_2Zr_2O_7$, Cd

Table S5 Limits of the chemical potentials at which $La_2CdO_2Se_2$ exists in the single phase in the La-Cd-O-Se-Hf quinary system and the competing phases at respective limits, calculated by PBEsol-GGA+U. The unit of the chemical potential is eV.

Conditions	$\Delta\mu_{La}$	$\Delta\mu_{Cd}$	$\Delta\mu_{O}$	$\Delta\mu_{Se}$	$\Delta\mu_{Hf}$	Competing phases
A	–4.57	–0.90	–3.19	–0.45	–4.69	CdSe, HfO_2, $La_{10}Se_{19}$, $La_4Se_3O_4$
B	–4.35	–0.79	–3.36	–0.57	–4.37	CdSe, HfO_2, $La_{10}Se_{14}O$, $La_{10}Se_{19}$
C	–4.36	–0.85	–3.32	–0.56	–4.44	HfO_2, $La_{10}Se_{14}O$, $La_{10}Se_{19}$, $La_4Se_3O_4$
D	–4.32	–0.83	–3.34	–0.59	–4.40	HfO_2, $La_{10}Se_{14}O$, La_2SeO_2, $La_4Se_3O_4$
E	–4.82	–0.90	–2.95	–0.45	–5.19	CdSe, HfO_2, $La_2Hf_2O_7$, $La_4Se_3O_4$
F	–4.51	–0.83	–3.15	–0.59	–4.78	HfO_2, $La_2Hf_2O_7$, La_2SeO_2, $La_4Se_3O_4$
G	–3.17	0	–4.14	–1.35	–2.79	CdSe, HfO_2, $La_{10}Se_{14}O$, Cd
H (Cation rich)	–3.07	0	–4.17	–1.42	–2.73	HfO_2, $La_{10}Se_{14}O$, La_2SeO_2, Cd
I	–3.47	0	–3.85	–1.35	–3.39	CdSe, HfO_2, $La_2Hf_2O_7$, Cd
J	–3.26	0	–3.99	–1.42	–3.11	HfO_2, $La_2Hf_2O_7$, La_2SeO_2, Cd
K (Anion rich)	–5.72	–0.90	–2.05	–0.45	–7.44	CdSe, $La_2Hf_2O_7$, La_2O_3, $La_4Se_3O_4$
L	–5.41	–0.83	–2.25	–0.59	–7.03	$La_2Hf_2O_7$, La_2O_3, La_2SeO_2, $La_4Se_3O_4$
M	–4.37	0	–2.95	–1.35	–5.63	CdSe, $La_2Hf_2O_7$, La_2O_3, Cd
N	–4.16	0	–3.09	–1.42	–5.36	$La_2Hf_2O_7$, La_2O_3, La_2SeO_2, Cd

Table S6 Limits of the chemical potentials at which $La_2CdO_2Se_2$ exists in the single phase in the La-Cd-O-Se-Al quinary system and the competing phases at respective limits, calculated by PBEsol-GGA+U. The unit of the chemical potential is eV.

Conditions	$\Delta\mu_{La}$	$\Delta\mu_{Cd}$	$\Delta\mu_{O}$	$\Delta\mu_{Se}$	$\Delta\mu_{Al}$	Competing phases
A	–4.57	–0.90	–3.19	–0.45	–3.11	CdSe, $La_{10}Se_{19}$, $La_4Se_3O_4$, $LaAlO_3$
B	–4.35	–0.79	–3.36	–0.57	–2.84	CdSe, $La_{10}Se_{14}O$, $La_{10}Se_{19}$, $LaAlO_3$
C	–4.36	–0.85	–3.32	–0.56	–2.94	$La_{10}Se_{14}O$, $La_{10}Se_{19}$, $La_4Se_3O_4$, $LaAlO_3$
D	–4.32	–0.83	–3.34	–0.59	–2.92	$La_{10}Se_{14}O$, La_2SeO_2, $La_4Se_3O_4$, $LaAlO_3$
E (Cation rich)	–5.72	–0.90	–2.05	–0.45	–5.41	CdSe, La_2O_3, $La_4Se_3O_4$, $LaAlO_3$
F	–5.41	–0.83	–2.25	–0.59	–5.10	La_2O_3, La_2SeO_2, $La_4Se_3O_4$, $LaAlO_3$
G	–3.17	0	–4.14	–1.35	–1.66	CdSe, $La_{10}Se_{14}O$, $LaAlO_3$, Cd
H (Anion rich)	–3.07	0	–4.17	–1.42	–1.67	$La_{10}Se_{14}O$, La_2SeO_2, $LaAlO_3$, Cd
I	–4.37	0	–2.95	–1.35	–4.05	CdSe, La_2O_3, $LaAlO_3$, Cd
J	–4.16	0	–3.09	–1.42	–3.85	La_2O_3, La_2SeO_2, $LaAlO_3$, Cd

Table S7 Limits of the chemical potentials at which $La_2CdO_2Se_2$ exists in the single phase in the La-Cd-O-Se-Ga quinary system and the competing phases at respective limits, calculated by PBEsol-GGA+U. The unit of the chemical potential is eV.

Conditions	$\Delta\mu_{La}$	$\Delta\mu_{Cd}$	$\Delta\mu_{O}$	$\Delta\mu_{Se}$	$\Delta\mu_{Ga}$	Competing phases
A	–4.36	–0.85	–3.32	–0.56	–0.69	$Cd(GaSe_2)_2$, $La_{10}Se_{14}O$, $La_{10}Se_{19}$, $La_4Se_3O_4$
B (Cation rich)	–3.07	0	–4.17	–1.42	0	$La_{10}Se_{14}O$, La_2SeO_2, Cd, Ga
C	–4.35	–0.79	–3.36	–0.57	–0.71	$Cd(GaSe_2)_2$, CdSe, $La_{10}Se_{14}O$, $La_{10}Se_{19}$
D	–4.09	–0.68	–3.50	–0.75	–0.41	$Cd(GaSe_2)_2$, GaSe, $La_{10}Se_{14}O$, La_2SeO_2
E	–3.48	–0.27	–3.91	–1.15	0	GaSe, $La_{10}Se_{14}O$, La_2SeO_2, Ga
F	–3.17	0	–4.14	–1.35	0	CdSe, $La_{10}Se_{14}O$, Cd, Ga
G	–3.98	–0.54	–3.61	–0.82	–0.34	$Cd(GaSe_2)_2$, CdSe, GaSe, $La_{10}Se_{14}O$
H	–3.47	–0.20	–3.94	–1.15	0	CdSe, GaSe, $La_{10}Se_{14}O$, Ga
I (Anion rich)	–5.72	–0.90	–2.05	–0.45	–2.30	CdSe, La_2O_3, $La_4Ga_2O_9$, $La_4Se_3O_4$
J	–5.41	–0.83	–2.25	–0.59	–1.99	La_2O_3, La_2SeO_2, $La_4Ga_2O_9$, $La_4Se_3O_4$
K	–4.37	0	–2.95	–1.35	–0.95	CdSe, La_2O_3, $La_4Ga_2O_9$, Cd
L	–4.16	0	–3.09	–1.42	–0.74	La_2O_3, La_2SeO_2, $La_4Ga_2O_9$, Cd
M	–4.57	–0.90	–3.19	–0.45	–0.89	$Cd(GaSe_2)_2$, CdSe, $La_{10}Se_{19}$, $La_4Se_3O_4$
N	–5.41	–0.90	–2.35	–0.45	–1.53	CdSe, $La_3Ga_5O_{12}$, $La_4Ga_2O_9$, $La_4Se_3O_4$
O	–5.10	–0.83	–2.56	–0.59	–1.22	La_2SeO_2, $La_3Ga_5O_{12}$, $La_4Ga_2O_9$, $La_4Se_3O_4$
P	–4.06	0	–3.26	–1.35	–0.18	CdSe, $La_3Ga_5O_{12}$, $La_4Ga_2O_9$, Cd
Q	–5.05	–0.90	–2.71	–0.45	–0.89	$Cd(GaSe_2)_2$, CdSe, $La_3Ga_5O_{12}$, $La_4Se_3O_4$
R	–4.78	–0.83	–2.88	–0.59	–0.64	$Cd(GaSe_2)_2$, La_2SeO_2, $La_3Ga_5O_{12}$, $La_4Se_3O_4$
S	–3.96	0	–3.36	–1.35	0	CdSe, $La_3Ga_5O_{12}$, Cd, Ga
T	–3.88	0	–3.37	–1.41	0	$La_3Ga_5O_{12}$, $La_4Ga_2O_9$, Cd, Ga
U	–3.86	0	–3.38	–1.42	0	La_2SeO_2, $La_4Ga_2O_9$, Cd, Ga
V	–3.88	–0.02	–3.37	–1.40	0	La_2SeO_2, $La_3Ga_5O_{12}$, $La_4Ga_2O_9$, Ga
W	–4.51	–0.54	–3.08	–0.82	–0.34	$Cd(GaSe_2)_2$, CdSe, GaSe, $La_3Ga_5O_{12}$
X	–4.54	–0.68	–3.04	–0.75	–0.41	$Cd(GaSe_2)_2$, GaSe, La_2SeO_2, $La_3Ga_5O_{12}$
Y	–4.09	–0.20	–3.32	–1.15	0	CdSe, GaSe, $La_3Ga_5O_{12}$, Ga
Z	–4.05	–0.27	–3.33	–1.15	0	GaSe, La_2SeO_2, $La_3Ga_5O_{12}$, Ga
AA	–4.32	–0.83	–3.34	–0.59	–0.64	$Cd(GaSe_2)_2$, $La_{10}Se_{14}O$, La_2SeO_2, $La_4Se_3O_4$

Table S8 Limits of the chemical potentials at which $La_2CdO_2Se_2$ exists in the single phase in the La-Cd-O-Se-In quinary system and the competing phases at respective limits, calculated by PBEsol-GGA+U. The unit of the chemical potential is eV.

Conditions	$\Delta\mu_{La}$	$\Delta\mu_{Cd}$	$\Delta\mu_{O}$	$\Delta\mu_{Se}$	$\Delta\mu_{In}$	Competing phases
A (Cation rich)	–3.07	0	–4.17	–1.42	0	$La_{10}Se_{14}O$, La_2SeO_2, Cd, In
B	–4.35	–0.79	–3.36	–0.57	–0.52	$Cd(InSe_2)_2$, CdSe, $La_{10}Se_{14}O$, $La_{10}Se_{19}$
C	–3.69	–0.35	–3.80	–1.01	0	CdSe, InSe, $La_{10}Se_{14}O$, In
D	–4.12	–0.63	–3.51	–0.72	–0.28	$Cd(InSe_2)_2$, CdSe, InSe, $La_{10}Se_{14}O$
E	–3.17	0	–4.14	–1.35	0	CdSe, $La_{10}Se_{14}O$, Cd, In
F (Anion rich)	–5.72	–0.90	–2.05	–0.45	–1.21	CdSe, In_2O_3, La_2O_3, $La_4Se_3O_4$
G	–5.41	–0.83	–2.25	–0.59	–0.90	In_2O_3, La_2O_3, La_2SeO_2, $La_4Se_3O_4$
H	–4.37	0	–2.95	–1.35	0	CdSe, La_2O_3, Cd, In
I	–4.16	0	–3.09	–1.42	0	La_2O_3, La_2SeO_2, Cd, In
J	–4.57	–0.90	–3.19	–0.45	–0.69	$Cd(InSe_2)_2$, CdSe, $La_{10}Se_{19}$, $La_4Se_3O_4$
K	–4.52	–0.10	–2.85	–1.25	0	CdSe, In_2O_3, La_2O_3, In
L	–4.52	–0.24	–2.85	–1.18	0	In_2O_3, La_2O_3, La_2SeO_2, In
M	–5.38	–0.90	–2.39	–0.45	–0.69	$Cd(InSe_2)_2$, CdSe, In_2O_3, $La_4Se_3O_4$
N	–5.12	–0.83	–2.55	–0.59	–0.45	$Cd(InSe_2)_2$, In_2O_3, La_2SeO_2, $La_4Se_3O_4$
O	–4.64	–0.35	–2.85	–1.01	0	CdSe, In_2O_3, InSe, In
P	–4.60	–0.41	–2.85	–1.01	0	In_2O_3, InSe, La_2SeO_2, In
Q	–4.97	–0.63	–2.66	–0.72	–0.28	$Cd(InSe_2)_2$, CdSe, In_2O_3, InSe
R	–5.02	–0.77	–2.61	–0.65	–0.35	$Cd(InSe_2)_2$, In_2O_3, InSe, La_2SeO_2
S	–4.32	–0.83	–3.34	–0.59	–0.45	$Cd(InSe_2)_2$, $La_{10}Se_{14}O$, La_2SeO_2, $La_4Se_3O_4$
T	–4.36	–0.85	–3.32	–0.56	–0.50	$Cd(InSe_2)_2$, $La_{10}Se_{14}O$, $La_{10}Se_{19}$, $La_4Se_3O_4$
U	–3.69	–0.41	–3.76	–1.01	0	InSe, $La_{10}Se_{14}O$, La_2SeO_2, In
V	–4.22	–0.77	–3.41	–0.65	–0.35	$Cd(InSe_2)_2$, InSe, $La_{10}Se_{14}O$, La_2SeO_2

Table S9 Limits of the chemical potentials at which $La_2CdO_2Se_2$ exists in the single phase in the La-Cd-O-Se-Mg quinary system and the competing phases at respective limits, calculated by PBEsol-GGA+U. The unit of the chemical potential is eV.

Conditions	$\Delta\mu_{La}$	$\Delta\mu_{Cd}$	$\Delta\mu_{O}$	$\Delta\mu_{Se}$	$\Delta\mu_{Mg}$	Competing phases
A	–4.32	–0.83	–3.34	–0.59	–2.32	$La_{10}Se_{14}O$, La_2SeO_2, $La_4Se_3O_4$, MgO
B (Anion rich)	–5.72	–0.90	–2.05	–0.45	–3.62	CdSe, La_2O_3, $La_4Se_3O_4$, MgO
C	–5.41	–0.83	–2.25	–0.59	–3.41	La_2O_3, La_2SeO_2, $La_4Se_3O_4$, MgO
D	–3.17	0	–4.14	–1.35	–1.52	CdSe, $La_{10}Se_{14}O$, MgO, Cd
E (Cation rich)	–3.07	0	–4.17	–1.42	–1.49	$La_{10}Se_{14}O$, La_2SeO_2, MgO, Cd
F	–4.57	–0.90	–3.19	–0.45	–2.47	CdSe, $La_{10}Se_{19}$, $La_4Se_3O_4$, MgO
G	–4.35	–0.79	–3.36	–0.57	–2.30	CdSe, $La_{10}Se_{14}O$, $La_{10}Se_{19}$, MgO
H	–4.36	–0.85	–3.32	–0.56	–2.34	$La_{10}Se_{14}O$, $La_{10}Se_{19}$, $La_4Se_3O_4$, MgO
I	–4.37	0	–2.95	–1.35	–2.71	CdSe, La_2O_3, MgO, Cd
J	–4.16	0	–3.09	–1.42	–2.57	La_2O_3, La_2SeO_2, MgO, Cd

Table S10 Limits of the chemical potentials at which $La_2CdO_2Se_2$ exists in the single phase in the La-Cd-O-Se-Ca quinary system and the competing phases at respective limits, calculated by PBEsol-GGA+U. The unit of the chemical potential is eV.

Conditions	$\Delta\mu_{La}$	$\Delta\mu_{Cd}$	$\Delta\mu_{O}$	$\Delta\mu_{Se}$	$\Delta\mu_{Ca}$	Competing phases
A (Anion rich)	–5.72	–0.90	–2.05	–0.45	–4.13	CaO, CdSe, La_2O_3, $La_4Se_3O_4$
B	–5.41	–0.83	–2.25	–0.59	–3.92	CaO, La_2O_3, La_2SeO_2, $La_4Se_3O_4$
C	–4.37	0	–2.95	–1.35	–3.22	CaO, CdSe, La_2O_3, Cd
D	–4.16	0	–3.09	–1.42	–3.09	CaO, La_2O_3, La_2SeO_2, Cd
E	–4.57	–0.90	–3.19	–0.45	–3.70	CaSe, CdSe, $La_{10}Se_{19}$, $La_4Se_3O_4$
F	–5.29	–0.90	–2.47	–0.45	–3.70	CaO, CaSe, CdSe, $La_4Se_3O_4$
G	–5.05	–0.83	–2.61	–0.59	–3.56	CaO, CaSe, La_2SeO_2, $La_4Se_3O_4$
H	–3.94	0	–3.38	–1.35	–2.80	CaO, CaSe, CdSe, Cd
I	–3.80	0	–3.45	–1.42	–2.73	CaO, CaSe, La_2SeO_2, Cd
J	–4.32	–0.83	–3.34	–0.59	–3.56	CaSe, $La_{10}Se_{14}O$, La_2SeO_2, $La_4Se_3O_4$
K	–4.36	–0.85	–3.32	–0.56	–3.59	CaSe, $La_{10}Se_{14}O$, $La_{10}Se_{19}$, $La_4Se_3O_4$
L (Cation rich)	–3.07	0	–4.17	–1.42	–2.73	CaSe, $La_{10}Se_{14}O$, La_2SeO_2, Cd
M	–4.35	–0.79	–3.36	–0.57	–3.58	CaSe, CdSe, $La_{10}Se_{14}O$, $La_{10}Se_{19}$
N	–3.17	0	–4.14	–1.35	–2.80	CaSe, CdSe, $La_{10}Se_{14}O$, Cd

Table S11 Limits of the chemical potentials at which $La_2CdO_2Se_2$ exists in the single phase in the La-Cd-O-Se-Sr quinary system and the competing phases at respective limits, calculated by PBEsol-GGA+U. The unit of the chemical potential is eV.

Conditions	$\Delta\mu_{La}$	$\Delta\mu_{Cd}$	$\Delta\mu_{O}$	$\Delta\mu_{Se}$	$\Delta\mu_{Sr}$	Competing phases
A	–4.32	–0.83	–3.34	–0.59	–3.72	$La_{10}Se_{14}O$, La_2SeO_2, $La_4Se_3O_4$, $Sr(LaSe_2)_2$
B	–3.17	0	–4.14	–1.35	–2.96	CdSe, $La_{10}Se_{14}O$, $Sr(LaSe_2)_2$, Cd
C (Cation rich)	–3.07	0	–4.17	–1.42	–2.89	$La_{10}Se_{14}O$, La_2SeO_2, $Sr(LaSe_2)_2$, Cd
D (Anion rich)	–5.72	–0.90	–2.05	–0.45	–3.74	CdSe, La_2O_3, $La_4Se_3O_4$, SrSe
E	–5.41	–0.83	–2.25	–0.59	–3.60	La_2O_3, La_2SeO_2, $La_4Se_3O_4$, SrSe
F	–4.35	–0.79	–3.36	–0.57	–3.75	CdSe, $La_{10}Se_{14}O$, $La_{10}Se_{19}$, $Sr(LaSe_2)_2$
G	–4.57	–0.90	–3.19	–0.45	–3.77	CdSe, $La_{10}Se_{19}$, $La_4Se_3O_4$, $Sr(LaSe_2)_2$
H	–4.36	–0.85	–3.32	–0.56	–3.75	$La_{10}Se_{14}O$, $La_{10}Se_{19}$, $La_4Se_3O_4$, $Sr(LaSe_2)_2$
I	–4.59	–0.90	–3.18	–0.45	–3.74	CdSe, $La_4Se_3O_4$, $Sr(LaSe_2)_2$, SrSe
J	–4.38	–0.83	–3.28	–0.59	–3.60	La_2SeO_2, $La_4Se_3O_4$, $Sr(LaSe_2)_2$, SrSe
K	–4.37	0	–2.95	–1.35	–2.84	CdSe, La_2O_3, SrSe, Cd
L	–4.16	0	–3.09	–1.42	–2.77	La_2O_3, La_2SeO_2, SrSe, Cd
M	–3.23	0	–4.08	–1.35	–2.84	CdSe, $Sr(LaSe_2)_2$, SrSe, Cd
N	–3.13	0	–4.12	–1.42	–2.77	La_2SeO_2, $Sr(LaSe_2)_2$, SrSe, Cd

Table S12 Limits of the chemical potentials at which $La_2CdO_2Se_2$ exists in the single phase in the La-Cd-O-Se-Ba quinary system and the competing phases at respective limits, calculated by PBEsol-GGA+U. The unit of the chemical potential is eV.

Conditions	$\Delta\mu_{La}$	$\Delta\mu_{Cd}$	$\Delta\mu_{O}$	$\Delta\mu_{Se}$	$\Delta\mu_{Ba}$	Competing phases
A (Anion rich)	–5.72	–0.90	–2.05	–0.45	–3.66	BaSe, CdSe, La_2O_3, $La_4Se_3O_4$
B	–5.41	–0.83	–2.25	–0.59	–3.52	BaSe, La_2O_3, La_2SeO_2, $La_4Se_3O_4$
C	–4.37	0	–2.95	–1.35	–2.76	BaSe, CdSe, La_2O_3, Cd
D	–4.16	0	–3.09	–1.42	–2.69	BaSe, La_2O_3, La_2SeO_2, Cd
E	–4.32	–0.83	–3.34	–0.59	–3.52	BaSe, $La_{10}Se_{14}O$, La_2SeO_2, $La_4Se_3O_4$
F	–3.17	0	–4.14	–1.35	–2.76	BaSe, CdSe, $La_{10}Se_{14}O$, Cd
G (Cation rich)	–3.07	0	–4.17	–1.42	–2.69	BaSe, $La_{10}Se_{14}O$, La_2SeO_2, Cd
H	–4.35	–0.79	–3.36	–0.57	–3.54	BaSe, CdSe, $La_{10}Se_{14}O$, $La_{10}Se_{19}$
I	–4.57	–0.90	–3.19	–0.45	–3.66	BaSe, CdSe, $La_{10}Se_{19}$, $La_4Se_3O_4$
J	–4.36	–0.85	–3.32	–0.56	–3.55	BaSe, $La_{10}Se_{14}O$, $La_{10}Se_{19}$, $La_4Se_3O_4$

Table S13 Limits of the chemical potentials at which $La_2CdO_2Se_2$ exists in the single phase in the La-Cd-O-Se-Li quinary system and the competing phases at respective limits, calculated by PBEsol-GGA+U. The unit of the chemical potential is eV.

Conditions	$\Delta\mu_{La}$	$\Delta\mu_{Cd}$	$\Delta\mu_{O}$	$\Delta\mu_{Se}$	$\Delta\mu_{Li}$	Competing phases
A	–4.32	–0.83	–3.34	–0.59	–1.61	$La_{10}Se_{14}O$, La_2SeO_2, $La_4Se_3O_4$, Li_2Se
B	–3.17	0	–4.14	–1.35	–1.23	CdSe, $La_{10}Se_{14}O$, Li_2Se, Cd
C (Cation rich)	–3.07	0	–4.17	–1.42	–1.19	$La_{10}Se_{14}O$, La_2SeO_2, Li_2Se, Cd
D (Anion rich)	–5.72	–0.90	–2.05	–0.45	–1.80	CdSe, La_2O_3, $La_4Se_3O_4$, Li_2O
E	–5.41	–0.83	–2.25	–0.59	–1.70	La_2O_3, La_2SeO_2, $La_4Se_3O_4$, Li_2O
F	–4.35	–0.79	–3.36	–0.57	–1.62	CdSe, $La_{10}Se_{14}O$, $La_{10}Se_{19}$, Li_2Se
G	–4.57	–0.90	–3.19	–0.45	–1.68	CdSe, $La_{10}Se_{19}$, $La_4Se_3O_4$, Li_2Se
H	–4.36	–0.85	–3.32	–0.56	–1.62	$La_{10}Se_{14}O$, $La_{10}Se_{19}$, $La_4Se_3O_4$, Li_2Se
I	–5.48	–0.90	–2.29	–0.45	–1.68	CdSe, $La_4Se_3O_4$, Li_2O, Li_2Se
J	–5.23	–0.83	–2.43	–0.59	–1.61	La_2SeO_2, $La_4Se_3O_4$, Li_2O, Li_2Se
K	–4.37	0	–2.95	–1.35	–1.35	CdSe, La_2O_3, Li_2O, Cd
L	–4.16	0	–3.09	–1.42	–1.28	La_2O_3, La_2SeO_2, Li_2O, Cd
M	–4.12	0	–3.19	–1.35	–1.23	CdSe, Li_2O, Li_2Se, Cd
N	–3.98	0	–3.26	–1.42	–1.19	La_2SeO_2, Li_2O, Li_2Se, Cd

Table S14 Limits of the chemical potentials at which $La_2CdO_2Se_2$ exists in the single phase in the La-Cd-O-Se-Na quinary system and the competing phases at respective limits, calculated by PBEsol-GGA+U. The unit of the chemical potential is eV.

Conditions	$\Delta\mu_{La}$	$\Delta\mu_{Cd}$	$\Delta\mu_{O}$	$\Delta\mu_{Se}$	$\Delta\mu_{Na}$	Competing phases
A	–3.26	0	–4.05	–1.35	–1.05	CdSe, $Na_4Cd_3Se_5$, $NaLaSe_2$, Cd
B	–4.37	0	–2.95	–1.35	–1.05	CdSe, La_2O_3, $Na_4Cd_3Se_5$, Cd
C	–3.21	0	–4.04	–1.42	–0.97	La_2SeO_2, $Na_4Cd_3Se_5$, $NaLaSe_2$, Cd
D	–4.16	0	–3.09	–1.42	–0.97	La_2O_3, La_2SeO_2, $Na_4Cd_3Se_5$, Cd
E (Cation rich)	–3.07	0	–4.17	–1.42	–1.11	$La_{10}Se_{14}O$, La_2SeO_2, $NaLaSe_2$, Cd
F	–4.35	–0.79	–3.36	–0.57	–1.54	CdSe, $La_{10}Se_{14}O$, $La_{10}Se_{19}$, $NaLaSe_2$
G	–3.17	0	–4.14	–1.35	–1.15	CdSe, $La_{10}Se_{14}O$, $NaLaSe_2$, Cd
H	–4.32	–0.83	–3.34	–0.59	–1.52	$La_{10}Se_{14}O$, La_2SeO_2, $La_4Se_3O_4$, $NaLaSe_2$
I	–4.36	–0.85	–3.32	–0.56	–1.54	$La_{10}Se_{14}O$, $La_{10}Se_{19}$, $La_4Se_3O_4$, $NaLaSe_2$
J	–4.46	–0.83	–3.20	–0.59	–1.38	La_2SeO_2, $La_4Se_3O_4$, $Na_4Cd_3Se_5$, $NaLaSe_2$
K	–4.57	–0.90	–3.19	–0.45	–1.55	CdSe, $La_{10}Se_{19}$, $La_4Se_3O_4$, $NaLaSe_2$
L	–4.62	–0.90	–3.15	–0.45	–1.51	CdSe, $La_4Se_3O_4$, $Na_4Cd_3Se_5$, $NaLaSe_2$
M	–5.41	–0.83	–2.25	–0.59	–1.38	La_2O_3, La_2SeO_2, $La_4Se_3O_4$, $Na_4Cd_3Se_5$
N (Anion rich)	–5.72	–0.90	–2.05	–0.45	–1.51	CdSe, La_2O_3, $La_4Se_3O_4$, $Na_4Cd_3Se_5$

Table S15 Limits of the chemical potentials at which $La_2CdO_2Se_2$ exists in the single phase in the La-Cd-O-Se-K quinary system and the competing phases at respective limits, calculated by PBEsol-GGA+U. The unit of the chemical potential is eV.

Conditions	$\Delta\mu_{La}$	$\Delta\mu_{Cd}$	$\Delta\mu_{O}$	$\Delta\mu_{Se}$	$\Delta\mu_{K}$	Competing phases
A (Anion rich)	–5.72	–0.90	–2.05	–0.45	–1.75	CdSe, $K_2Cd_3Se_4$, La_2O_3, $La_4Se_3O_4$
B	–5.41	–0.83	–2.25	–0.59	–1.57	$K_2Cd_3Se_4$, La_2O_3, La_2SeO_2, $La_4Se_3O_4$
C	–4.37	0	–2.95	–1.35	–1.29	CdSe, $K_2Cd_3Se_4$, La_2O_3, Cd
D	–4.16	0	–3.09	–1.42	–1.16	$K_2Cd_3Se_4$, La_2O_3, La_2SeO_2, Cd
E	–4.57	–0.90	–3.19	–0.45	–1.75	CdSe, $K_2Cd_3Se_4$, $La_{10}Se_{19}$, $La_4Se_3O_4$
F	–4.32	–0.83	–3.34	–0.59	–1.57	$K_2Cd_3Se_4$, $La_{10}Se_{14}O$, La_2SeO_2, $La_4Se_3O_4$
G	–4.36	–0.85	–3.32	–0.56	–1.61	$K_2Cd_3Se_4$, $La_{10}Se_{14}O$, $La_{10}Se_{19}$, $La_4Se_3O_4$
H (Cation rich)	–3.07	0	–4.17	–1.42	–1.16	$K_2Cd_3Se_4$, $La_{10}Se_{14}O$, La_2SeO_2, Cd
I	–4.35	–0.79	–3.36	–0.57	–1.69	CdSe, $K_2Cd_3Se_4$, $La_{10}Se_{14}O$, $La_{10}Se_{19}$
J	–3.17	0	–4.14	–1.35	–1.29	CdSe, $K_2Cd_3Se_4$, $La_{10}Se_{14}O$, Cd

Table S16 Limits of the chemical potentials at which $La_2CdO_2Se_2$ exists in the single phase in the La-Cd-O-Se-Rb quinary system and the competing phases at respective limits, calculated by PBEsol-GGA+U. The unit of the chemical potential is eV.

Conditions	$\Delta\mu_{La}$	$\Delta\mu_{Cd}$	$\Delta\mu_{O}$	$\Delta\mu_{Se}$	$\Delta\mu_{Rb}$	Competing phases
A	–4.36	–0.79	–3.35	–0.56	–1.74	CdSe, $La_{10}Se_{19}$, $Rb_2Cd_3Se_4$, $RbLaSe_2$
B	–3.18	0	–4.14	–1.35	–1.34	CdSe, $Rb_2Cd_3Se_4$, $RbLaSe_2$, Cd
C	–3.18	0	–4.07	–1.42	–1.20	La_2SeO_2, $Rb_2Cd_3Se_4$, $RbLaSe_2$, Cd
D	–4.37	0	–2.95	–1.35	–1.34	CdSe, La_2O_3, $Rb_2Cd_3Se_4$, Cd
E	–4.16	0	–3.09	–1.42	–1.20	La_2O_3, La_2SeO_2, $Rb_2Cd_3Se_4$, Cd
F	–4.50	–0.88	–3.24	–0.49	–1.74	$La_{10}Se_{19}$, $La_4Se_3O_4$, $Rb_2Cd_3Se_4$, $RbLaSe_2$
G	–4.43	–0.83	–3.24	–0.59	–1.62	La_2SeO_2, $La_4Se_3O_4$, $Rb_2Cd_3Se_4$, $RbLaSe_2$
H	–4.57	–0.90	–3.19	–0.45	–1.79	CdSe, $La_{10}Se_{19}$, $La_4Se_3O_4$, $Rb_2Cd_3Se_4$
I	–5.41	–0.83	–2.25	–0.59	–1.62	La_2O_3, La_2SeO_2, $La_4Se_3O_4$, $Rb_2Cd_3Se_4$
J (Anion rich)	–5.72	–0.90	–2.05	–0.45	–1.79	CdSe, La_2O_3, $La_4Se_3O_4$, $Rb_2Cd_3Se_4$
K (Cation rich)	–3.07	0	–4.17	–1.42	–1.31	$La_{10}Se_{14}O$, La_2SeO_2, $RbLaSe_2$, Cd
L	–3.17	0	–4.14	–1.35	–1.34	CdSe, $La_{10}Se_{14}O$, $Rb_2Cd_3Se_4$, $RbLaSe_2$, Cd
M	–4.35	–0.79	–3.36	–0.57	–1.74	CdSe, $La_{10}Se_{14}O$, $La_{10}Se_{19}$, $Rb_2Cd_3Se_4$, $RbLaSe_2$
N	–4.36	–0.85	–3.32	–0.56	–1.74	$La_{10}Se_{14}O$, $La_{10}Se_{19}$, $La_4Se_3O_4$, $RbLaSe_2$
O	–4.32	–0.83	–3.34	–0.59	–1.72	$La_{10}Se_{14}O$, La_2SeO_2, $La_4Se_3O_4$, $RbLaSe_2$

Table S17 Limits of the chemical potentials at which $La_2CdO_2Se_2$ exists in the single phase in the La-Cd-O-Se-Zr quinary system and the competing phases at respective limits. The unit of the chemical potential is eV.

Conditions	$\Delta\mu_{La}$	$\Delta\mu_{Cd}$	$\Delta\mu_{O}$	$\Delta\mu_{Se}$	$\Delta\mu_{Zr}$	Competing phases
A	–3.47	0	–4.06	–1.51	–2.84	CdSe, $La_{10}Se_{14}O$, ZrO_2, Cd
B (Cation rich)	–3.45	0	–4.07	–1.52	–2.83	$La_{10}Se_{14}O$, La_2SeO_2, ZrO_2, Cd
C	–3.66	0	–3.87	–1.52	–3.23	La_2SeO_2, $La_2Zr_2O_7$, ZrO_2, Cd
D	–4.57	0	–2.95	–1.52	–5.53	La_2O_3, La_2SeO_2, $La_2Zr_2O_7$, Cd
E	–3.68	0	–3.85	–1.51	–3.27	CdSe, $La_2Zr_2O_7$, ZrO_2, Cd
F	–4.60	0	–2.93	–1.51	–5.56	CdSe, La_2O_3, $La_2Zr_2O_7$, Cd
G	–5.08	–1.08	–2.99	–0.44	–4.99	$La_{10}Se_{14}O$, La_2SeO_2, $La_4Se_3O_4$, ZrO_2
H	–5.28	–1.08	–2.78	–0.44	–5.40	La_2SeO_2, $La_2Zr_2O_7$, $La_4Se_3O_4$, ZrO_2
I	–5.10	–1.09	–2.97	–0.42	–5.02	CdSe, $La_{10}Se_{14}O$, $La_4Se_3O_4$, ZrO_2
J	–5.32	–1.09	–2.76	–0.42	–5.45	CdSe, $La_2Zr_2O_7$, $La_4Se_3O_4$, ZrO_2
K	–6.19	–1.08	–1.87	–0.44	–7.69	La_2O_3, La_2SeO_2, $La_2Zr_2O_7$, $La_4Se_3O_4$
L (Anion rich)	–6.23	–1.09	–1.84	–0.42	–7.74	CdSe, La_2O_3, $La_2Zr_2O_7$, $La_4Se_3O_4$

Table S18 Limits of the chemical potentials at which $La_2CdO_2Se_2$ exists in the single phase in the La-Cd-O-Se-Al quinary system and the competing phases at respective limits. The unit of the chemical potential is eV.

Conditions	$\Delta\mu_{La}$	$\Delta\mu_{Cd}$	$\Delta\mu_{O}$	$\Delta\mu_{Se}$	$\Delta\mu_{Al}$	Competing phases
A	–3.62	0	–3.91	–1.51	–2.13	Al_2O_3, CdSe, $LaAlO_3$, Cd
B	–3.59	0	–3.93	–1.52	–2.10	Al_2O_3, La_2SeO_2, $LaAlO_3$, Cd
C	–4.60	0	–2.93	–1.51	–4.12	CdSe, La_2O_3, $La_4Al_2O_9$, Cd
D	–4.57	0	–2.95	–1.52	–4.09	La_2O_3, La_2SeO_2, $La_4Al_2O_9$, Cd
E	–4.54	0	–2.99	–1.51	–3.96	CdSe, $La_4Al_2O_9$, $LaAlO_3$, Cd
F	–4.51	0	–3.01	–1.52	–3.94	La_2SeO_2, $La_4Al_2O_9$, $LaAlO_3$, Cd
G	–3.47	0	–4.06	–1.51	–1.90	Al_2O_3, CdSe, $La_{10}Se_{14}O$, Cd
H (Cation rich)	–3.45	0	–4.07	–1.52	–1.89	Al_2O_3, $La_{10}Se_{14}O$, La_2SeO_2, Cd
I	–5.08	–1.08	–2.99	–0.44	–3.52	Al_2O_3, $La_{10}Se_{14}O$, La_2SeO_2, $La_4Se_3O_4$
J	–5.22	–1.08	–2.85	–0.44	–3.73	Al_2O_3, La_2SeO_2, $La_4Se_3O_4$, $LaAlO_3$
K	–5.10	–1.09	–2.97	–0.42	–3.53	Al_2O_3, CdSe, $La_{10}Se_{14}O$, $La_4Se_3O_4$
L	–5.25	–1.09	–2.82	–0.42	–3.76	Al_2O_3, CdSe, $La_4Se_3O_4$, $LaAlO_3$
M	–6.19	–1.08	–1.87	–0.44	–5.71	La_2O_3, La_2SeO_2, $La_4Al_2O_9$, $La_4Se_3O_4$
N	–6.13	–1.08	–1.93	–0.44	–5.56	La_2SeO_2, $La_4Al_2O_9$, $La_4Se_3O_4$, $LaAlO_3$
O (Anion rich)	–6.23	–1.09	–1.84	–0.42	–5.75	CdSe, La_2O_3, $La_4Al_2O_9$, $La_4Se_3O_4$
P	–6.17	–1.09	–1.90	–0.42	–5.60	CdSe, $La_4Al_2O_9$, $La_4Se_3O_4$, $LaAlO_3$

Table S19 Limits of the chemical potentials at which $La_2CdO_2Se_2$ exists in the single phase in the La-Cd-O-Se-Sr quinary system and the competing phases at respective limits. The unit of the chemical potential is eV.

Conditions	$\Delta\mu_{La}$	$\Delta\mu_{Cd}$	$\Delta\mu_{O}$	$\Delta\mu_{Se}$	$\Delta\mu_{Sr}$	Competing phases
A (Anion rich)	–6.23	–1.09	–1.84	–0.42	–4.10	CdSe, La_2O_3, $La_4Se_3O_4$, SrSe
B	–6.19	–1.08	–1.87	–0.44	–4.08	La_2O_3, La_2SeO_2, $La_4Se_3O_4$, SrSe
C	–4.60	0	–2.93	–1.51	–3.01	CdSe, La_2O_3, SrSe, Cd
D	–4.57	0	–2.95	–1.52	–3.00	La_2O_3, La_2SeO_2, SrSe, Cd
E	–5.11	–1.09	–2.96	–0.42	–4.10	CdSe, $La_4Se_3O_4$, $Sr(LaSe_2)_2$, SrSe
F	–5.09	–1.08	–2.97	–0.44	–4.08	La_2SeO_2, $La_4Se_3O_4$, $Sr(LaSe_2)_2$, SrSe
G	–3.48	0	–4.05	–1.51	–3.01	CdSe, $Sr(LaSe_2)_2$, SrSe, Cd
H	–3.47	0	–4.05	–1.52	–3.00	La_2SeO_2, $Sr(LaSe_2)_2$, SrSe, Cd
I	–5.08	–1.08	–2.99	–0.44	–4.11	$La_{10}Se_{14}O$, La_2SeO_2, $La_4Se_3O_4$, $Sr(LaSe_2)_2$
J	–5.10	–1.09	–2.97	–0.42	–4.12	CdSe, $La_{10}Se_{14}O$, $La_4Se_3O_4$, $Sr(LaSe_2)_2$
K (Cation rich)	–3.45	0	–4.07	–1.52	–3.02	$La_{10}Se_{14}O$, La_2SeO_2, $Sr(LaSe_2)_2$, Cd
L	–3.47	0	–4.06	–1.51	–3.03	CdSe, $La_{10}Se_{14}O$, $Sr(LaSe_2)_2$, Cd

Table S20 Limits of the chemical potentials at which $La_2CdO_2Se_2$ exists in the single phase in the La-Cd-O-Se-Na quinary system and the competing phases at respective limits. The unit of the chemical potential is eV.

Conditions	$\Delta\mu_{La}$	$\Delta\mu_{Cd}$	$\Delta\mu_{O}$	$\Delta\mu_{Se}$	$\Delta\mu_{Na}$	Competing phases
A (Anion rich)	–6.23	–1.09	–1.84	–0.42	–1.63	CdSe, La_2O_3, $La_4Se_3O_4$, $Na_4Cd_3Se_5$
B	–6.19	–1.08	–1.87	–0.44	–1.61	La_2O_3, La_2SeO_2, $La_4Se_3O_4$, $Na_4Cd_3Se_5$
C	–4.60	0	–2.93	–1.51	–1.08	CdSe, La_2O_3, $Na_4Cd_3Se_5$, Cd
D	–4.57	0	–2.95	–1.52	–1.07	La_2O_3, La_2SeO_2, $Na_4Cd_3Se_5$, Cd
E	–5.36	–1.09	–2.71	–0.42	–1.63	CdSe, $La_4Se_3O_4$, $Na_4Cd_3Se_5$, $NaLaSe_2$
F	–5.34	–1.08	–2.72	–0.44	–1.61	La_2SeO_2, $La_4Se_3O_4$, $Na_4Cd_3Se_5$, $NaLaSe_2$
G	–3.73	0	–3.80	–1.51	–1.08	CdSe, $Na_4Cd_3Se_5$, $NaLaSe_2$, Cd
H	–3.72	0	–3.80	–1.52	–1.07	La_2SeO_2, $Na_4Cd_3Se_5$, $NaLaSe_2$, Cd
I	–5.08	–1.08	–2.99	–0.44	–1.88	$La_{10}Se_{14}O$, La_2SeO_2, $La_4Se_3O_4$, $NaLaSe_2$
J (Cation rich)	–3.45	0	–4.07	–1.52	–1.34	$La_{10}Se_{14}O$, La_2SeO_2, $NaLaSe_2$, Cd
K	–5.10	–1.09	–2.97	–0.42	–1.89	CdSe, $La_{10}Se_{14}O$, $La_4Se_3O_4$, $NaLaSe_2$
L	–3.47	0	–4.06	–1.51	–1.34	CdSe, $La_{10}Se_{14}O$, $NaLaSe_2$, Cd

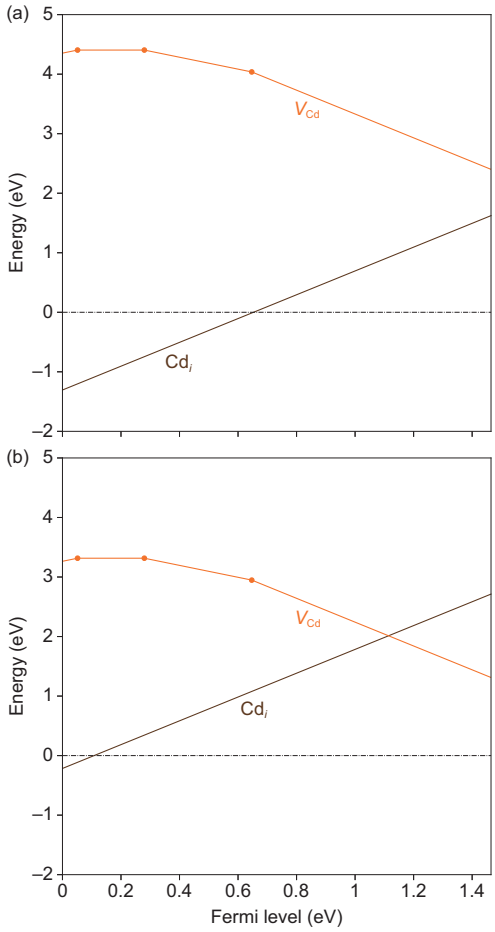

Fig. S2 Formation energies of V_{Cd} and Cd_i in zb-CdSe at (a) cation-rich ($\Delta\mu_{\mathrm{Cd}} = 0$ eV) and (b) anion-rich ($\Delta\mu_{\mathrm{Cd}} = -1.09$ eV) conditions.