Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Prediction of stable silver selenide-based energy materials sustained by rubidium selenide alloying

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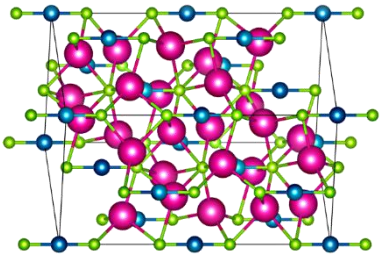
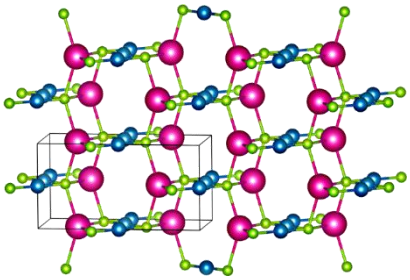
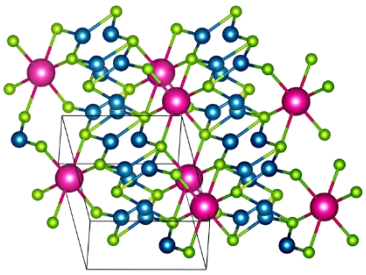
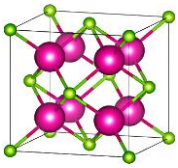
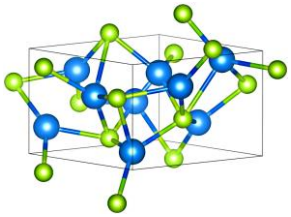
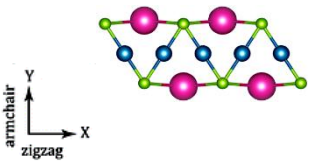
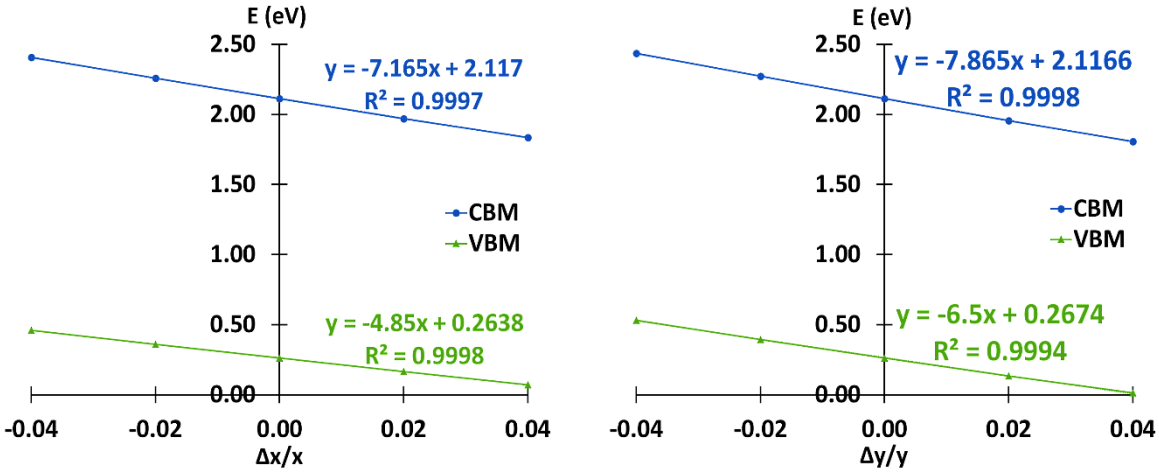
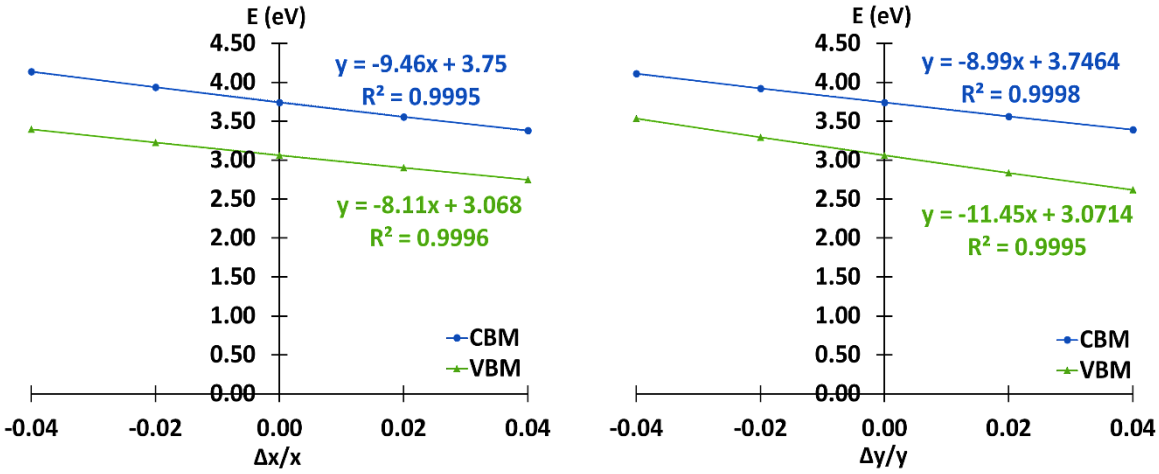
S1 Crystallographic data and space group (SG) for Rb_2Se-Ag_2Se phases. Red, blue and green spheres represent Rb, Ag and Se atoms, respectively.

Space group	Unit cell	Lattice constants / Å	Atomic Wyckoff positions
Bulk $Rb_6Ag_2Se_4$ $R\bar{3}c$ (SG 167)		a = 9.409 c = 19.126	Rb1 18e (0.28270, 0.00000, 0.25000) Ag1 6b (0.00000, 0.00000, 0.00000) Se1 12c (0.00000, 0.00000, -0.37077)
Bulk $Rb_2Ag_2Se_2$ $Cmcm$ (SG 63)		a = 6.653 b = 12.802 c = 6.266	Rb1 4c (0.00000, 0.22767, 0.25000) Ag1 4b (0.00000, 0.50000, 0.00000) Se1 4c (0.00000, -0.34886, 0.25000)

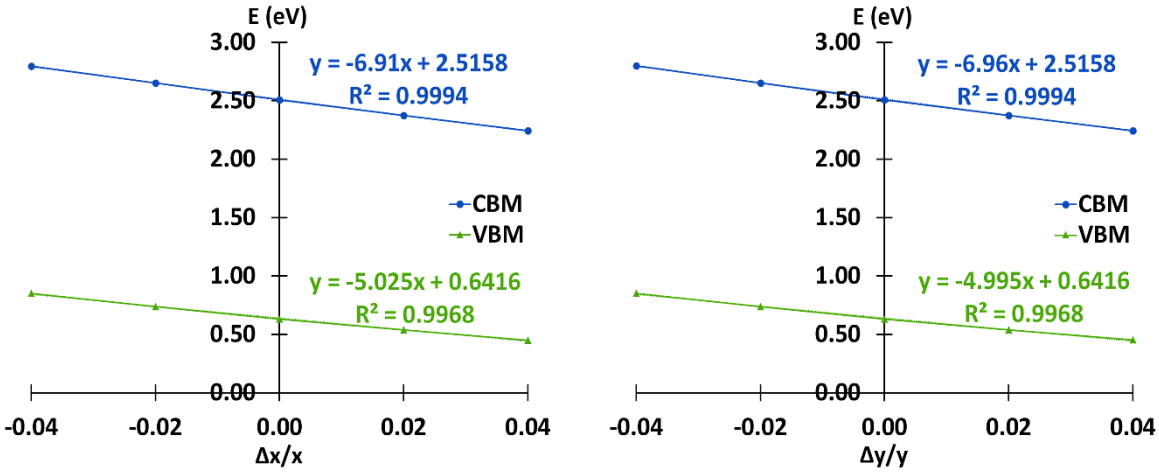
Bulk $Rb_2Ag_6Se_4$ $P1$ (SG 1)		a = 8.887 b = 8.481 c = 5.473	Rb1 1a (-0.00191, 0.17494, -0.08372) Rb2 1a (0.00281, -0.32311, 0.40799) Ag1 1a (0.41240, -0.03285, -0.46218) Ag2 1a (0.49613, 0.16157, -0.07138) Ag3 1a (-0.38305, -0.13610, -0.19985) Ag4 1a (-0.43488, 0.34633, 0.33661) Ag5 1a (0.40166, 0.47962, 0.02478) Ag6 1a (0.49788, -0.33740, 0.42362) Se1 1a (0.24382, 0.13063, 0.32368) Se2 1a (0.23545, -0.37551, -0.18996) Se3 1a (-0.24970, 0.20336, -0.47508) Se4 1a (-0.24668, -0.30765, 0.03254)
Bulk Rb_2Se $Fm\bar{3}m$ (SG 225)		a = 8.098	Rb1 8c (0.25000, 0.25000, 0.25000) Se1 4a (0.00000, 0.00000, 0.00000)
Bulk Ag_8Se_4 $P2_12_12_1$ (SG 19)		a = 7.358 b = 7.024 c = 4.645	Ag1 4a (-0.38258, -0.02138, -0.25905) Ag2 4a (-0.29060, -0.36886, 0.07677) Se1 4a (0.08355, 0.24681, -0.13060)
2D $Rb_2Ag_2Se_2$ $P2_1\bar{m}$ (SG 11)		a = 5.036 b = 5.478 c = 19.490 β = 91.87°	Rb1 2e (-0.48738, 0.25000, -0.37995) Ag1 2c (0.00000, 0.00000, 0.50000) Se1 2e (-0.01578, 0.25000, 0.39193)


E (eV)
y = -7.165x + 2.117
R² = 0.9997
CBM
VBM
y = -4.85x + 0.2638
R² = 0.9998
Δx/x
E (eV)
y = -7.865x + 2.1166
R² = 0.9998
CBM
VBM
y = -6.5x + 0.2674
R² = 0.9994
Δy/y

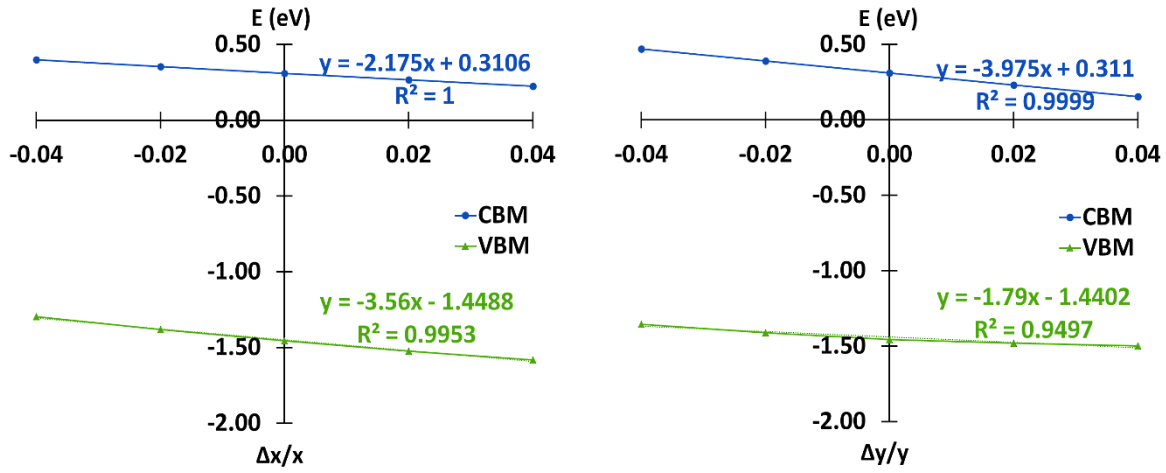
(a)


E (eV)
y = -9.46x + 3.75
R² = 0.9995
CBM
VBM
y = -8.11x + 3.068
R² = 0.9996
Δx/x
E (eV)
y = -8.99x + 3.7464
R² = 0.9998
CBM
VBM
y = -11.45x + 3.0714
R² = 0.9995
Δy/y

(b)


E (eV)
y = -6.91x + 2.5158
R² = 0.9994
CBM
VBM
y = -5.025x + 0.6416
R² = 0.9968
Δx/x
E (eV)
y = -6.96x + 2.5158
R² = 0.9994
CBM
VBM
y = -4.995x + 0.6416
R² = 0.9968
Δy/y

(c)



(d)

S2 Band energies of the CBM and VBM for bulk (a) $Rb_2Ag_2Se_2$, (b) $Rb_2Ag_6Se_4$, (c) $Rb_6Ag_2Se_4$ and (d) monolayer $Rb_2Ag_2Se_2$ phases as a function of lattice dilation along *x* and *y* directions. The fitted slopes show the E_D in eV.

S3 Elastic properties, Debye temperature, sound velocities and Gruneisen parameter

Based on the Voigt-Reuss-Hill approximation [1], elastic moduli such as shear modulus *G* (GPa), bulk modulus *B* (GPa), Young's modulus *E* (GPa) and Poisson's ratio *v* were calculated. Relevant equations for these computations are stated as follows.

$$B = \frac{1}{2}\left(B_{\text{Voigt}} + B_{\text{Reuss}}\right) \tag{1}$$

$$G = \frac{1}{2}\left(G_{\text{Voigt}} + G_{\text{Reuss}}\right) \tag{2}$$

in which *B* and *G* are the mean of Voigt [2] and Reuss [3] approximations.

$$E = \frac{9BG}{3B + G} \tag{3}$$

$$v = \frac{3B - 2G}{6B + 2G} \tag{4}$$

Another crucial parameter which has a strong influence on the physical properties of the solid is the Debye temperature Θ_D, calculated by means of the sound velocity [4], as follows:

$$\Theta_D = \frac{h}{k_B}\left[\frac{3n}{4\pi}\left(\frac{N_A\rho}{M}\right)\right]v_m \tag{5}$$

where k_B, h, N_A, ρ, M and n are the Boltzmann's constant, Planck's constant, Avogadro's constant, density, molecular weight and number of atoms per unit cell, respectively. The longitudinal sound velocity, transverse sound velocity and mean sound velocity are represented by v_l, v_t and v_m, respectively. v_m is quantifiable by v_l and vt [4] using the following:

$$v_l = \left[\frac{\left(B + {}^4/_3\, G\right)}{\rho}\right]^{\frac{1}{2}} \tag{6}$$

$$v_t = \left(\frac{G}{\rho}\right)^{\frac{1}{2}} \tag{7}$$

$$v_m = \left[\frac{1}{3}\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)\right]^{-\frac{1}{3}} \tag{8}$$

Finally, these velocities can also be applied onto the formulation below to determine the Gruneisen parameter γ.

$$\gamma = \frac{9\left(v_l^2 - {}^4/_3\, v_t^2\right)}{2(v_l^2 + 2v_t^2)} \tag{9}$$

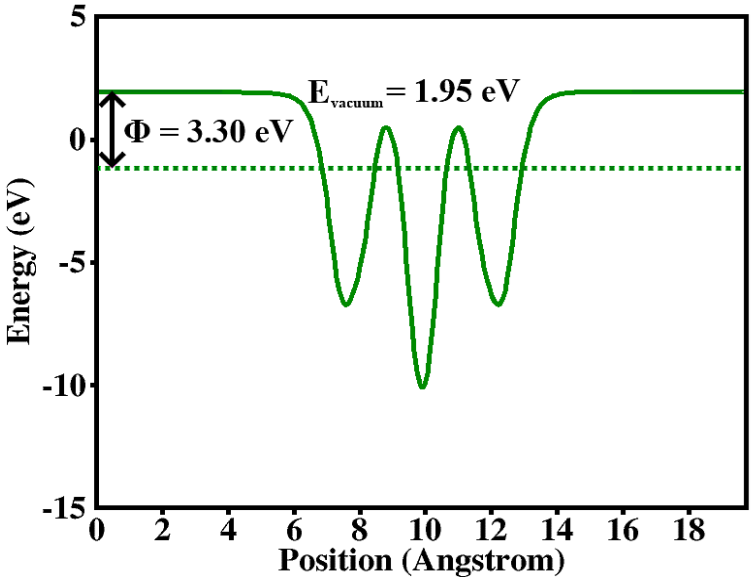
[1] R. Hill (1952). The elastic behavior of a crystalline aggregate. Proc. Phys. Soc. A, 65, 349-354.

[2] W. Voigt (1928). Lehrbuch der Kristallohysic Teubner, Leipzig, Germany.

[3] A. Reuss (1929). Berechnung der Fliebgrenze von Mischkristallen auf Grundder Plastizittsbedingung fur Einkristalle. Z. Angew. Math. Mech., 9, 49-58.

[4] O.L. Anderson (1963). A Simplified Method For Calculating The Debye Temperature From Elastic Constants. J. Phys. Chem. Solids, 24, 909-917.

S4 Surface calculations for 2D $Rb_2Ag_2Se_2$



Electrostatic potential in z-direction for 2D $Rb_2Ag_2Se_2$

S5 Detailed operation of scissor factor

For dielectric function calculations using VASP, the scissor shift value was added to the "SCISSOR" tag, following the method described in

https://www.vasp.at/wiki/index.php/Improving_the_dielectric_function#Model-BSE

while for transport calculations, it was set in one of the BoltzTraP input file lines (0 0 0 0.0 # iskip idebug setgap shiftgap), under the "shiftgap" tag.