Title:Design of new sulfides and selenides using topology analysis and DFT calculations.

Vladimir A. Saleev,Vladislav A. Blatov,Inna V. Medrish,
Samara Center for Theoretical Materials Science,
Samara National Research University,Samara,443086, Russia
E-mail: blatov@gmail.com, saleev@samsu.ru, imedrish@mail.ru

Using the ToposPro package [1] we have investigated the structures of salts containing tetrahedral oxoanion: simple anhydrous sulfates and selenates $M_y(XO_4)_z$ (X = S, Se). We have performed topological analysis based on quasi-binary representationto find new polymorphs of CaS and CaSe. This representation ignores the internal structure of the complex groups $[XO_4]$ and the ternary compound is represented as a binary $M_y[X]_z$. Experimentally known structures of CaS and CaSe,denoted as B1 and B2, have **pcu-b** (NaCl) and **bcu** (CsCl) topologies. The CaS and CaSe structures B3 (**dia**, zinc-blende) and B4 (**lon,** wurtzite) have been theoretically predicted [2], but not synthesized yet. We have found new CaS and CaSe polymorphs with the **bnn**, **nia (**NiAs) and **sma** topologies, and space groups $P6_3/mc$ (186), $P6_3/mmc$ (194) and $P6_222$(180), respectively.

The energetic, electronic, vibration and mechanical properties of the proposed compounds have been calculated at the GGA level of DFT theory as implemented in the CRYSTAL14 package [3] with exchange-correlation functional PBESOL [4]. We have optimized the structures by using the conjugate-gradient method until the Hellmann–Feynman forces on the atoms became less than 0.003 eV/*Å* and the stress on the cells less than 0.01GPa. In the calculations all electrons were treated explicitly and described by the triple-ζ valence basis set with polarization quality (TZVP) as developed by Peintingeret al. [5] that reproduced the lattice parameters and the position of irreducible atoms in the experimentally known structuresB1 and B2 in the best way. In the Table: B is the bulk modulus, G_H is the shear modulus, E_H is the Young modulus and ν_H is the Poisson ratio according to Hill prescription, E-E(B1) is the cohesive energy difference per atom relative to the ground state B1.

CaS	GS	CN	CP (Å)	B (GPa) and B’	G_H(GPa),E_H(GPa), ν_H	E-E(B1), eV/atom	ρ, g/cm^3
bnn	186	5	4.75, 5.62	51.37, 4.30	21.25, 56.06, 0.32	0.168	2.18
nia	194	6	3.94, 6.84	63.14, 4.28	48.46, 115.83, 0.20	0.103	2.60
sma	180	6	5.69, 5.54	43.19, 4.66	21.56, 56.23, 0.30	0.679	2.31
CaSe							
bnn	186	5	5.06, 5.95	37.90, 4.12	10.25, 28.20, 0.38	0.272	3.03
nia	194	6	4.09, 7.27	51.17, 4.50	33.81, 83.19, 0.23	0.100	3.78
sma	180	6	5.80, 5.94	44.77, 4.42	27.90, 69.82, 0.25	0.511	3.45

Bibliography

1. V. A. Blatov, A. P. Shevchenko, D. M. Proserpio, *Cryst. Growth Des.*,**14**, 3576 – 3586 (2014); http://topospro.com.
2. S. Boucenna, Y. Medkour, L. Louail, M. Boucenna, A. Hachemi, A. Roumili. *Comp. Materials Science*, **68,** 325-334(2013).
3. R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, P. D’Arco, M. Llunell, M. Causà and Y. Noël, CRYSTAL14, (2014) CRYSTAL14 User's Manual. University of Torino, Torino.
4. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*,**77**,3865 (1996).
5. M. F. Peintinger, D. V. Oliveira and T. Bredow, *J. Comput. Chem.*,**34**, 451 (2013).