



Short Communication

## Identification of promising chemical systems for the synthesis of new materials structure types: An *ab initio* minimization data mining approach

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### Abstract

In this research we performed data exploring for binary compounds with elements from groups V, IV-VI, and III-VII, with the goal to identify chemical systems where the recently proposed “5-5” structure type might be experimentally accessible. Among others, TlF, SnO, SnS, SnSe, GeS, GeSe, PbO, PbS, ZnO and ZnS, were chosen for the study. For each of these systems, a local optimization on *ab initio* level with the LDA functional was performed for the 5-5 structure type, plus other experimentally observed and theoretically proposed structure types, for comparison. Afterwards, the results were combined with earlier theoretical work involving the 5-5 structure in the earth alkaline metal oxides and the alkali metal halides. As a result, we suggest the GeSe and the ZnO systems as the most suitable ones for synthesizing the 5-5 structure type.

**Keywords:** *ab initio*, data mining, binary compounds, 5-5 structure type

### I. Introduction

The search for new crystalline compounds is one of the major issues in inorganic chemistry and material sciences. Scientists have successfully synthesized many new materials and studied their properties, but the purely experimental approach is no longer the only route to discover new compounds. The theoretical prediction of new compounds and new (meta)-stable modifications of already existing solids followed by their synthesis is fast becoming an alternative [1–8]. One of the modern approaches to address this issue is to combine data mining and quantum mechanical tools [9,10].

In previous theoretical work [11–16] and experimental studies of thin films [17,18], the so-called 5-5 structure has been observed. However, one should note that different scientific groups have rediscovered this structure in different contexts, and afterwards gave different names to this structure type. [13,17,18] This structure type can be described as a mutual fivefold coordination of cation A by anion B in a hexagonal lattice ( $P63/mmc$ , no. 194) with ABAB stacking, where A-atoms form tri-

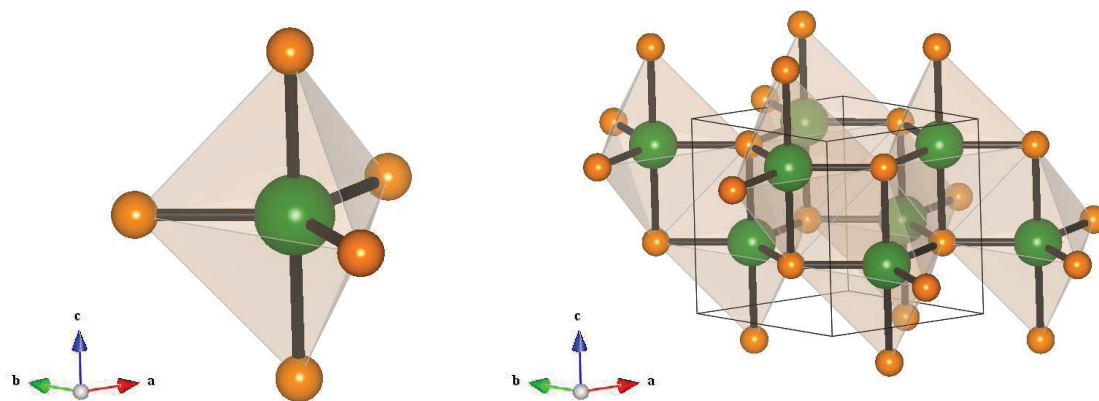
gonal bipyramids around B-atoms, and conversely (see Fig. 1) [11,19].

The 5-5 structure can be derived from the h-BN structure by requiring that the bond length in the *c*-direction must be essentially identical to the one within the planar hexagons. In order to find the best chemical system for the synthesis of a bulk modification that exhibits the 5-5 structure type, we performed data mining based explorations in group V, IV-VI, and III-VII binary compounds. In each of the investigated systems, local optimizations on *ab initio* level were performed for the 5-5 and typical AB-structure types for comparison.

### II. Theoretical Methods

In order to find suitable AB compounds for a synthesis of the 5-5 structure type, we performed a data mining based exploration in group V, IV-VI, and III-VII compounds. [20–24] The guiding idea was to find AB compounds with ten valence electrons in total per AB pair. This would formally allow the system to form AB compounds with five bonds per atom, leading in a natural way to a five-fold coordination. For such combination of elements, we first performed a local minimization of the hypothetical compound on the *ab initio* level in the 5-5 structure type. If this resulted in a stable

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**Figure 1. Visualization of the “5-5” structure type in an AB - compound: a) a 5-fold trigonal bipyramidal coordination of the A atom by B atoms; b) typical representation in a periodically repeated cell. Note the 5-fold coordination and a shorter bond length in  $c$  direction compared to the  $h$ -BN type. The darker larger spheres and smaller lighter spheres correspond to A and B atoms, respectively.**

structure, we computed the  $E(V)$  and the  $H(p)$  curves<sup>1\*</sup> for: the 5-5 modification, the experimentally observed structures, plus several important AB structure types, which had been found in previous calculations and experiments for other AB systems [15,16]. The experimentally observed structures were taken from the ICSD [25,26] and all the total energy calculations and energy minimizations were performed on the *ab initio* level using the program CRYSTAL09 [27,28]. Density functional theory (DFT) was applied for electronic structure calculations [29–32], with the Slater local exchange approximation [33,34] and Perdew-Zunger correlation functionals [35]. The all-electron basis sets (AEBS) were taken from ref. [36] and effective core potentials (ECP) were taken from ref. [37].

The symmetries and space groups of the related configurations are determined using the algorithms SFND [38] and RGS [39] as implemented in the KPLOT program [40], and the CMPZ algorithm is used to compare structures and confirm our results [41]. Visualization of the crystal structures was performed using the VESTA code [42].

### III. Results and discussion

None of the combinations among the elements of group V yielded experimental AB structures for further optimization. However, combining all the elements of the groups IV and VI and all the elements of the groups III and VII, we have found several possible candidate systems for further research. Availability of experimental data in a candidate system was one of main criteria, since in this study we performed only local optimizations, and most of the AB systems had not yet been globally explored on a theoretical level. As a result TlF, SnO, SnS, SnSe, GeS, GeSe, PbO, PbS, ZnO and ZnS were chosen as candidate systems.

Our results show that in most of the chosen systems, the 5-5 structure type appears in the negative pressure region<sup>2\*</sup> as a local minimum. The best candidate for synthesis of the 5-5 type in this pressure region appears to be germanium selenide.

In the GeSe system we performed local optimizations with LDA starting from two experimentally known structures, the GeS type, showing space group  $Pnma$  (no. 62), and the NaCl type, exhibiting space group  $Fm-3m$  (no. 225), and three so far unknown types in this system (TII type, space group  $Cmcm$  (no. 63); wurtzite, space group  $P63mc$  (no. 186); and the 5-5 type, space group  $P63/mmc$  (no. 194)). The calculations were performed also with the B3LYP functional, resulting in slight changes of the  $E(V)$  curves. However, the order of predicted minima did not change: the TII type was the high pressure phase and the 5-5 structure type was a transition structure on the route to the wurtzite type in the low-density region.

This procedure was followed in the GeS, SnS, SnSe, TlF, SnO and PbO systems. The results were similar, with the exception that the 5-5 modification was higher in energy compared to the ground state in the GeSe system (at standard pressure). In the PbS system there is a lower possibility of finding the 5-5 type, since it is only a small minimum on the way to the wurtzite modification in the negative pressure region. In contrast, for ZnO and ZnS, the 5-5 structure might be a high-pressure phase. Concerning the ZnO system, studies using the prescribed path algorithm [43,44] showed that the 5-5 type is a local minimum along the route from the wurtzite to the rock salt type of modification, and it should be accessible via solid state synthesis. Similarly, in the ZnS system the 5-5 structure type might appear at high pressure, but only as a metastable modification (after the wurtzite to the NaCl transition, and not in-between like in the ZnO system).

<sup>1\*</sup>  $E(V)$  – Energy as function of volume; and  $H(p)$  – Enthalpy as function of pressure

<sup>2\*</sup> i.e., it is most likely to be accessible as a (meta)stable compound at effective negative pressures

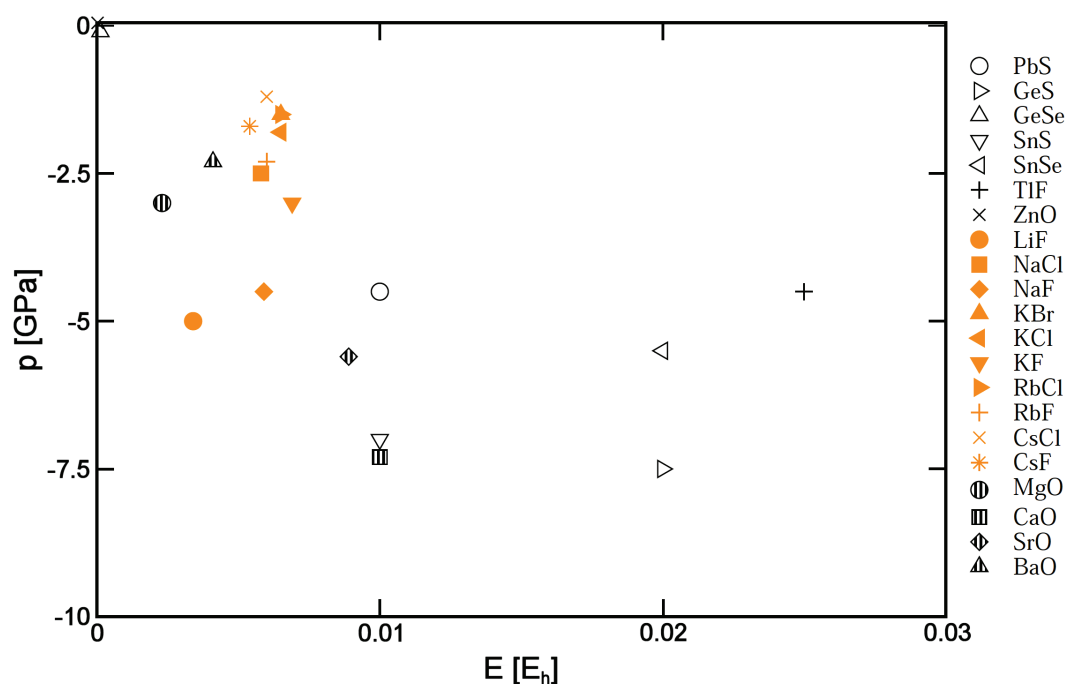
**Table 1. Thermodynamic stability and cell parameters of the 5-5 structure at various pressure ranges in different systems calculated with the LDA functional. Note that the 5-5 type has a hexagonal lattice with fixed atom positions: A ( $1/3, 2/3, 3/4$ ); B ( $1/3, 2/3, 1/4$ ) and therefore the only free parameters are the  $a$  and  $c$  cell parameter. Also note that No entry in the 3<sup>rd</sup> column mean that for all pressures the 5-5 structure is a metastable modification, and Yes entry mean that the 5-5 modifications is stable in the negative pressure region.**

System	Cell parameters	Thermodynamic stability*
SnS	$a = 4.80 \text{ \AA}, c = 5.69 \text{ \AA}$	Yes
SnSe	$a = 4.94 \text{ \AA}, c = 5.83 \text{ \AA}$	Yes
SnO	$a = 4.11 \text{ \AA}, c = 4.98 \text{ \AA}$	No
GeS	$a = 4.52 \text{ \AA}, c = 5.35 \text{ \AA}$	No
GeSe	$a = 4.61 \text{ \AA}, c = 5.58 \text{ \AA}$	Yes
PbO	$a = 4.21 \text{ \AA}, c = 5.17 \text{ \AA}$	No
PbS	$a = 4.88 \text{ \AA}, c = 5.84 \text{ \AA}$	Yes
TlF	$a = 4.51 \text{ \AA}, c = 5.38 \text{ \AA}$	No
ZnO	$a = 3.53 \text{ \AA}, c = 4.76 \text{ \AA}$	No
ZnS	$a = 4.11 \text{ \AA}, c = 5.42 \text{ \AA}$	No

\*for calculated range of pressures

The results of these calculations, performed on *ab initio* level (using LDA), are summarized in Table 1, showing the cell parameters of the 5-5 structure in different chemical systems and whether they are thermodynamically stable for some (positive or negative) pressures. We note here that the systems where the 5-5 structure type exists as a stable phase are those with a small negative pressure window between the 6-fold and the 4-fold-coordinated modifications. In systems where the 5-5 type is metastable, the 5-5 type is usually much worse regarding its energy than the other candidates, which suggests that the synthesis is less likely in these systems. Furthermore, the results can be compared with earlier theoretical work involving the 5-5 structure type in earth alkaline metal oxides [15] and alkali metal halides [16].

Next, we have investigated the correlation between the ratio of ionic radii ( $r$ ) and transition pressure ( $p$ ) for these systems. We have observed the transition to the metastable 5-5 structure in the ZnS system, which could occur at about 20 GPa. Similarly, at extreme negative pressures of about  $-20$  GPa, we have observed the 5-5 modification in PbO and SnO, which is very far from other related systems and would be very difficult to reach experimentally. Therefore, we excluded these three systems as unlikely for a synthesis of the 5-5 structure at this point of the investigation. From this analysis, we find the ZnO and the GeSe systems to be the best candidates for synthesizing the 5-5 type structure in binary compounds, and as closest other possibilities the MgO and the NaCl system.



**Figure 2. Correlation diagram for the AB systems with the 5-5 structure type, using energies and transition pressures - Note that the energies are calculated as the difference between the local minimum and the 5-5 structure in the investigated system ( $E = E_{loc} - E_{5-5}$ ). Energies per formula unit are given in hartree ( $E_h$ ).**

Similarly, we have performed a correlation investigation between the ratio of the ionic radii ( $r$ ) and the calculated energy ( $E$ ), which has been calculated as the difference between the minimum energy and the energy of the 5-5 structure in a specific system. As a result of using these criteria in the analysis, the tin oxide (SnO) system was discarded as being energetically too high. In contrast, ZnS shows a surprisingly low energy, and therefore, one could choose this system as a strong candidate for the synthesis of the 5-5 structure. However, since this type appears to be metastable, the actual synthesis might be difficult. Therefore, again the ZnO and the GeSe systems are the best choice according to these criteria for synthesizing the 5-5 type, and as the closest alternatives, we identify the MgO and the LiF system.

Finally, we investigate the correlation between the transition pressures ( $p$ ) and the calculated energies with respect to the global minimum ( $E$ ) in the various systems (see Fig. 2). In order to make such a correlation possible, we exclude the systems with extreme values of energies and transition pressures (PbO, SnO and ZnS). From this correlation we can draw similar conclusions as before, i.e. that again the ZnO and the GeSe system are the best candidates for synthesizing the 5-5 type, while this time the closest alternatives (if we exclude the ionic ratio) would be the CsCl and the CsF system.

#### IV. Conclusions

In order to find suitable AB compound for synthesis of the “5-5” structure type, we performed data exploration for binary compounds with elements from groups V, IV-VI, and III-VII, followed by local optimizations on *ab initio* level using the LDA functional. Furthermore, the results were compared with earlier theoretical work involving the 5-5 structure type in the earth alkaline metal oxides and the alkali metal halides. We suggest GeSe and ZnO as the most suitable systems for synthesizing the 5-5 structure type. In both cases, the possibility of synthesis of this 5-fold coordinated structure should exist in a small pressure range between the 6-fold coordinated NaCl and the 4-fold coordinated wurtzite structure type.

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#### References

- J.C. Schön, M. Jansen, “First step towards planning of syntheses in solid-state chemistry: Determination of promising structure candidates by global optimization”, *Angew. Chem., Int. Ed. Eng.*, **35** (1996) 1286–1304.
- P. Verwer, F.J.J. Leusen, “Computer simulation to predict possible crystal polymorphs”, *Rev. Comput. Chem.*, **12** (1998) 327–365.
- C. Mellot Draznieks, J.M. Newsam, A.M. Gorman, C.M. Freeman, G. Férey, “De Novo prediction of inorganic structures developed through automated assembly of secondary building units (AASBU method)”, *Angew. Chem. Int. Ed.*, **39** (2000) 2270–2275.
- M. Jansen, “A concept for synthesis planning in solid state chemistry”, *Angew. Chem. Int. Ed.*, **41** (2002) 3747–3766.
- S.L. Price, “From crystal structure prediction to polymorph prediction: interpreting the crystal energy landscape”, *Phys. Chem. Chem. Phys.*, **10** (2008) 1996–2009.
- S.M. Woodley, C.R.A. Catlow, “Crystal structure prediction from first principles”, *Nature Mater.*, **7** (2008) 937–946.
- M. Jansen, K. Doll, J.C. Schön, “Addressing chemical diversity by employing the energy landscape concept”, *Acta. Cryst. A*, **66** (2010) 518–534.
- A.R. Oganov, *Modern Methods of Crystal Structure Prediction*, Wiley, Weinheim, 2011.
- G. Ceder, D. Morgan, C. Fischer, K. Tibbetts, S. Curtarolo, “Data Mining Driven Quantum Mechanics for the Prediction of Structure”, *MRS Bull.*, **31** (2006) 981–985.
- S. Curtarolo, G.L. W. Hart, M.B. Nardelli, N. Mingo, S. Sanvito, O. Levy, “The high-throughput highway to computational materials design”, *Nature Mater.*, **12** (2013) 191–201.
- J.C. Schön, M. Jansen, “Determination of candidate structures for simple ionic compounds through cell optimisation”, *Comp. Mater. Sci.*, **4** (1995) 43–58.
- C.R.A. Catlow, S.A. French, A.A. Sokol, A.A. Al-Sunaidi, S.M. Woodley, “Zinc oxide: A case study in contemporary computational solid state chemistry”, *J. Comput. Chem.*, **29** (2008) 2234–2249.
- A.J. Kulkarni, M. Zhou, K. Sarasamak, S. Limpijumnong, “Novel phase transformation in ZnO nanowires under tensile loading”, *Phys. Rev. Lett.*, **97** (2006) 105502.
- J.E. Jaffe, J.A. Snyder, Z. Lin, A.C. Hess, “LDA and GGA calculations for high-pressure phase transitions in ZnO and MgO”, *Phys. Rev. B*, **62** (2000) 1660–1665.
- J.C. Schön, “Enthalpy landscapes of the earth alkaline metal oxides”, *Z. Anorg. Allg. Chem.*, **630** (2004) 2354–2366.
- Ž. Cancarevic, J. C. Schön, M. Jansen, “Stability of alkali metal halide polymorphs as a function of pressure”, *Chem. Asian J.*, **3** (2008) 561–572.
- C.L. Pueyo, S. Siroky, S. Landsmann, M.W.E. van den Berg, M.R. Wagner, J.S. Reparaz, A. Hoffmann, S. Polarz, “Molecular precursor route to a metastable form of zinc oxide”, *Chem. Mater.*, **22** (2010) 4263–4270.
- C. Tusche, H.L. Meyerheim, J. Kirschner, “Observation of depolarized ZnO (0001) monolayers: Formation of unreconstructed planar sheets”, *Phys. Rev. Lett.*, **99** (2007) 026102–026106.



19. D. Zagorac, J. C. Schön, I. Pentin, M. Jansen, “Structure prediction and energy landscape exploration in the zinc oxide system”, *Process. Appl. Ceram.*, **5** (2011) 73–78.
20. J. Han, M. Kamber, *Data Mining: Concepts and Techniques, 2<sup>nd</sup> Edition*, Ed. J. Gray, The Morgan Kaufmann Series in Data Management Systems, 2006.
21. M.M. Gaber, *Scientific data mining and knowledge discovery: Principles and Foundation*, Springer, Berlin, Heidelberg, 2010.
22. P. Villars, “A three-dimensional structural stability diagram for 998 binary AB intermetallic compounds”, *J. Less Common Metals*, **92** (1983) 215–238.
23. D.G. Pettifor, “The structures of binary compounds. II. Theory of the pd-bonded AB compounds”, *J. Phys. C: Solid State Phys.*, **19** (1986) 315–330.
24. G.L.W. Hart, “Where are nature’s missing structures?”, *Nature Mater.*, **6** (2007) 941–945.
25. G. Bergerhoff, R. Hundt, R. Sievers, I.D. Brown, *J. Chem. Inf. Comput. Sci.*, **23**, 66 (1983).
26. FIZ-Karlsruhe, *ICSD - Inorganic Crystal Structure Database*, <http://icsd.fizkarlsruhe.de/>, 2012.
27. 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’Arc o, M. Llunell, *CRYSTAL09 User’s Manual*, University Torino, Torino, 2009.
28. R. Dovesi, R. Orlando, B. Civalleri, C. Roetti, V. R. Saunders, C.M. Zicovich-Wilson, “CRYSTAL: a computational tool for the *ab initio* study of the electronic properties of crystals”, *Z. Kristallogr.*, **220** (2005) 571–573.
29. L.H. Thomas, “The calculation of atomic fields”, *Proc. Camb. Philos. Soc.*, **23** (1927) 542–548.
30. E. Fermi, “Eine statistische Methode zur Bestimmung einiger Eigenschaften des Atoms und ihre Anwendung auf die Theorie des periodischen Systems der Elemente”, *Z. Phys.*, **48** (1928) 73–79.
31. P. Hohenberg, W. Kohn, “Inhomogeneous electron gas”, *Phys. Rev.*, **136** (1964) 864–871.
32. W. Kohn, L.J. Sham, “Self-consistent equations including exchange and correlation effects”, *Phys. Rev.*, **140** (1965) 1133–1138.
33. J. Slater, H. C. Verma, “The theory of complex spectra”, *Phys. Rev.*, **34** (1929) 1293–1322.
34. J.C. Slater, *The Self-Consistent Field for Molecular and Solids, Quantum Theory of Molecular and Solids, Vol. 4*, McGraw-Hill, New York, 1974.
35. J.P. Perdew, A. Zunger, “Self-interaction correction to density-functional approximations for many-electron systems”, *Phys. Rev. B*, **23** (1981) 5048–5079.
36. R. Dovesi, et al., *Basis sets*. University Torino, [http://www.crystal.unito.it/Basis\\_Sets/Ptable.html](http://www.crystal.unito.it/Basis_Sets/Ptable.html), 2013.
37. M. Dolg, K.A. Peterson, P. Schwerdtfeger, H. Stoll, *Stuttgart/Köln (ab initio) Pseudopotentiale für Wellenfunktions- und Dichtefunktionalrechnungen. Theoretical Chemistry*. University of Stuttgart and University of Cologne, <http://www.tc.unikoeln.de/PP/index.de.html>, 2012.
38. R. Hundt, J.C. Schön, A. Hannemann, M. Jansen, “Determination of symmetries and idealized cell parameters for simulated structures”, *J. Appl. Crystallogr.*, **32** (1999) 413–416.
39. A. Hannemann, R. Hundt, J.C. Schön, M. Jansen, “A new algorithm for space-group determination”, *J. Appl. Crystallogr.*, **31** (1998) 922–928.
40. R. Hundt, *KPLOT: A Program for Plotting and Investigation of Crystal Structures*, University of Bonn, Bonn <http://www.crystalimpact.com/download/kplot.htm>, 2012.
41. R. Hundt, J.C. Schön, M. Jansen, “CMPZ - an algorithm for the efficient comparison of periodic structures”, *J. Appl. Crystallogr.*, **39** (2006) 6–16.
42. K. Momma, F. Izumi, “VESTA: a three-dimensional visualization system for electronic and structural analysis”, *J. Appl. Crystallogr.*, **41** (2008) 653–658.
43. D. Zagorac, J.C. Schön, K. Doll, M. Jansen, “Structure prediction for PbS and ZnO at different pressures and visualization of the energy landscapes”, *Acta Phys. Pol. A*, **120** (2011) 215–220.
44. D. Zagorac, J.C. Schön, M. Jansen, “Energy landscape investigations using the prescribed path method in the ZnO system”, *J. Phys. Chem. C*, **116** (2012) 16726–16739.

