First Principles Evolutionary Search for New Electrides along the Dimensionality of Anionic Electrons

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We propose a unique strategy based on the dimensionality of anionic electrons for new inorganic electride search. We adopted strontium phosphide as the initiator for the evolutionary search, and our evolutionary calculations combined with experimental synthesis found the Sr_5P_3 is a new one-dimensional electride.

Keywords: Electride, Evolutionary search, First principles.

1 Introduction

Electride is a unique material which serves a bare electron as anion, and we thereby expect chemical activity of electride, which was in fact already confirmed in inorganic electrides C_{12}A_7 [1] and Ca_2N [2] for ammonia synthesis [3]. What's the next electride is thus one of the most exciting issues in Inorganic chemistry. Recently, we reported a new electride strontium phosphide which was firstly predicted with first principles evolutionary search and succeeded in experimental synthesis [4]. The evolutionary search is quite a powerful tool in theoretical exploration for unknown compounds. Once we provide the elements constituting target compounds, the formula and corresponding stable structures are automatically identified with the first principles evolutionary search. The elements we selected in the previous study were Sr and P, *i.e.*, strontium phosphide, and if this selection were inappropriate, the evolutionary search would fail. That is, the preconditioning by human imagination before computational screening by artificial intelligence such as an evolutionary search is quite

an important step for unknown compounds search. In this paper, we explain how we focused on strontium phosphide as a candidate for new electride, which was done along the dimensionality of anionic electrons.

2 Method

Let us firstly categorize inorganic electride in terms of dimensions: zero-dimensional (0D), one-D (1D), two-D (2D), and three-D (3D). Figure 1 shows schematics and sample compounds in each category, although the sample for 3D electride is a hypothetical one [6]. Here we introduce a crude assumption that the stability of an inorganic electride could be related to the interactions between anionic electrons [7], although there are other types of ionic interactions in the system. When we accept the assumption, the anionic electron in 0D electrides is stable because it is almost isolated from other anionic electrons. On the other hand, for a 3D electride, anionic electron is surrounded by many anionic electrons which would destabilize the 3D electride compared with 0D

Figure 1. Schematic of the searching strategy based on the dimensionality of anionic electrons. (a) Inorganic electrides with 0D (reprinted with permission from Ref [5]. Copyright 2013 Nature Publishing Group), 1D, 2D, and 3D network of anionic electrons. The numbers with red indicate the number of neighboring anionic electrons. (b) The concept of the stability of anionic electrons by lowering the dimensionality of the network.

electrider. In this sense, the stability of anionic electrons in inorganic electrides can be written as $0D > 1D > 2D > 3D$.

Let us next consider what strategy is efficient to find new electrides. Since the stability of inorganic electrides would

follow the order of $0D > 1D > 2D > 3D$, when we identify the candidate for 3D electrider as A_nB_m , the compounds A_nB_m can also have a chance to appear as 2D, 1D, and 0D electrides even when the synthesis of 3D electrider A_nB_m is failed. In the same

Table 1. Relative stability of 2D electrides. E_{diff} indicates the relative stability of 2D electride compared with reference compounds; negative/positive number means stable/unstable.

compounds	$E_{\text{diff}}(\text{eV/atom})$	References
Ca_2N	-0.051	Ca_3N_2 , Ca
Sr_2N	-0.167	SrN, Sr
Ba_2N	-0.042	Ba_3N , BaN_2
Ca_2P	-0.083	CaP, Ca
Sr_2P	+0.053	Sr_3P_2 , Sr
Ba_2P	-0.003	Ba_3P_2 , Ba
Ca_2As	+0.185	Ca_5As_3 , Ca
Sr_2As	+0.102	Sr_5As_3 , Sr
Ba_2As	+0.032	$\text{Ba}_{20}\text{P}_{13}$, Ba
Ca_2Sb	+0.130	Ca_5Sb_3 , Ca
Sr_2Sb	+0.210	Sr_5Sb_3 , Sr
Ba_2Sb	+0.134	Ba_5Sb_3 , Ba
Ca_2Bi	+0.163	Ca_5Bi_3 , Ca
Sr_2Bi	+0.137	Sr_5Bi_3 , Sr
Ba_2Bi	+0.158	Ba_5Bi_3 , Ba

sense, the candidates for 2D electride X_nY_m would be expected to appear as 0D or 1D electride. This is our dimensional strategy for new inorganic electrides. Since we already know Ca_2N [2] and Y_2C [8] are 2D electrides, the dimensional strategy starting from 2D electride is a practical one.

To determine the elements for new electride search, we investigated the relative stability of hypothetical 2D electride of alkaline earth (A_e) pnictide (P) as listed in Table 1; only Ca_2N is a realistic 2D electride. The space group of the compounds is fixed to be R-3m which is identical to that of Ca_2N . The electronic structure calculations and structural relaxations were carried out using density functional theory (DFT) with PAW method implemented in VASP [9]. Based on the formal charges of ions, we adopted the formula of $(A_e)_2P$ to find anionic electrons in the crystals. For example, Ca_2N is composed of Ca^{2+} and N^{3-} , and thus one electron is expected to appear as a bare electron to hold the charge neutrality, that is, $\text{Ca}_2\text{N} : e^-$. In the same manner, the hypothetical formula of alkaline earth pnictides was adopted in the investigation of the relative stability. In Table 1, the most stable stoichiometric binary compounds were selected as References according to Materials Project database [10]; only when a 2D electride already appears in the database as the most stable one, we used second stable binary compounds as References.

3 Results and discussion

Calculated relative energies with respect to reference compounds listed in Table 1 show that 2D electrides of nitrides are stable, which corresponds to the fact that Ca_2N is an experimentally validated 2D electride. On the other hand, the arsenide, antimonide, and bismuth compounds are clearly unstable. The phosphides showing a slight stability could be candidates for new electride search, and we selected strontium phosphide, Sr_nP_m .

Now that we have fixed the target compounds Sr_nP_m for new electride, the next step is the first principles evolutionary search and we adopted USPEX code [11] coupled with VASP. At the beginning of the process, a first *generation* of structures is produced using a random-number generator, and structural relaxation is carried out with VASP for each structure to find stable crystal structures. After the first generation process, USPEX creates the second generation by keeping the most stable structure and by combining relatively stable structures through variation operations based on the evolutionary algorithm (such as heredity, permutation, mutation, soft mutation...). In this manner, the generation is updated based on the previous generation, and the update is finished when the most stable structure is unchanged over the course of 40 generations.

Since much more details of this process are written in our paper [4], we summarize the findings in the evolutionary study on Sr_nP_m : 1) 2D electride Sr_2P with R-3m structure is a *meta* stable structure from the ambient pressure to 15 GPa, 2) 1D electride Sr_5P_3 with C2/m structure is the most stable structure at the ambient pressure, and the structure is transformed to a higher symmetry P63/mcm above 10 GPa keeping the one-dimensional network of anionic electrons (*i.e.*, 1D electride), 3) Experimentally synthesized strontium phosphide is Sr_5P_3 with C2/m structure, 4) A discrepancy on the band gap between the experimental and DFT results is found; insulator by experiment but metal by calculation (DFT), and the discrepancy is rationalized as the evidence of Mott insulator of Sr_5P_3 1D electride, and 5) 0D electride Sr_8P_5 with I-4 structure, a competing phase against the 1D electride Sr_5P_3 , can appear at the ambient pressure. These results indicate the powerfulness of the evolutionary search along the dimensional point of anionic electrons, combined with experimental synthesis.

4 Summary

A unique strategy based on the dimensionality of anionic electrons was adopted in an evolutionary search for new electrifieds. According to the strategy, we adopted strontium phosphide as the initiator for the evolutionary search, and we found 1D electrified Sr_5P_3 and 0D electrified Sr_8P_5 . The dimensional strategy will be useful for searching for other unknown inorganic electrifieds.

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- [7] There is no clear validation for the assumption that the stability of inorganic electrified could be represented in terms of the interactions between anionic electrons, and it's rather a concept which has to be validated in experimental and computational study. Although we don't have such a validation, we can roughly consider as follows. The spatial distribution of anionic electron in inorganic electrified is determined by the positions of cations and anions, that is, the shape of anionic electron is modulated by the cations and anions easily. Bearing in mind that anionic electron might be captured by orbitals of cations in some systems, once we find anionic electrons in a system, we can recognize that the anionic electrons in the system show a slightly larger stability at the interstitial position than captured by orbitals of cations. Since the competition between the two situation is so naive, finding electrified is not so easy. In other words, the local situation of anionic electrons embedded in ionic crystals could be similar, regardless of the local crystal structures. If this is true, the remaining interactions related to the stability are the interactions between anionic electrons.
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