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Structural diversity among multinary pnictide oxides: a minireview focused on semiconducting and superconducting heteroanionic materials

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Abstract: Incorporating different anions with varied ionic sizes and charges is a rapidly growing approach to bring out unusual physical properties among various classes of solid-state materials, pnictides and chalcogenides in particular. This minireview is focused on hetero-anionic materials based on the pnictogens, which have been demonstrated to offer an impressive diversity of crystal chemistry and electronic structures. In addition, many pnictide oxides or oxypnictides, over the course of the last decade, have been shown to exhibit a broad spectrum of superconducting, magnetic, and semiconducting properties. However, the structural diversity of the mixed-anion materials is far greater than the several known structure types, or their variants, of the well-known layered superconductive materials. Therefore, with this treatise, we aim to provide a comprehensive overview of the crystal chemistry of pnictide oxides by recounting almost 40 different structures of such ternary and multinary compounds. In addition to the structural aspects, we also highlight some of the challenges associated with the synthesis, and briefly summarize reported, to date, physical properties of this remarkable class of solids.

Keywords: crystal structure; pnictide oxides; semiconductors; superconductors.

1 Introduction

The simultaneous presence of oxygen and pnictogen (Pn), i.e., electronegative element of group 15 ($Pn = P, As, Sb, Bi$), occurs in numerous ternary and multinary compounds.

The vast majority of these are classic inorganic salts, such as phosphates, phosphonates, arsenates, etc. These compounds can be understood by recognizing the formation of distinct oxoanions with $Pn-O$ bonding; the character of the bonding is largely polar covalent, with the polarity being associated with the partial electron transfer from the less electronegative pnictogen to the more electronegative oxygen. Therefore, in most simple terms, the pnictogen atoms are characterized as cations in such salts, with typical oxidation states of +3 or +5. Less-common positive oxidation states are also possible, for example the +4 in the hypophosphate $P_2O_6^{4-}$ ion featuring homoatomic P–P bonding. From a solid-state chemistry point of view, rationalizing the bonding in such compounds with the concepts of pnictide cations and oxide anions is supported, since the electronic band structures are typically characterized by distinct energy separation between the occupied O^{2-} p states and empty Pn states; therefore, such materials are usually wide-bandgap semiconductors (or rather, insulators).

In contrast to these single-anion oxide-based pnictate phases, compounds with electropositive elements such as metals (yet with no distinct $Pn-O$ bonding) contain another type of anion, Pn^{3-} , which is found in pnictides [1]. Such solid-state phases with pnictogen and oxygen as anions are referred to as *pnictide oxides* or *oxypnictides*. This class of compounds is a part of the intensively developing large family of heteroanionic materials, such as pnictide chalcogenides, pnictide halides, and chalcogenide halides, to name a few [2]. A unique mixed-anion composition results in the formation of structures different from those typical for pnictides or oxides, synergizing structural arrangements from both classes. Consequently, a structural uniqueness results in interesting physical properties, making mixed-anion compounds favorable candidates for catalysis, energy conversion, and electronic materials, including those with infrared nonlinear optical properties, semiconducting properties, and superconductivity [3–6].

The comprehensive investigation of oxypnictide materials by the solid-state chemistry community began in recent years only. The first comprehensive review on pnictide oxides was published in 1995 by *Kauzlarich* and co-authors [7], summarizing the data available at that time

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for around 30 known compounds. The 2008 discovery of superconductivity in the iron-arsenides and related pnictide oxides noticeably increased the interest in this field [8–12]. Over the last years, many other oxypnictide phases have been reported, including many crystallizing in their own structure types; there have been a number of detailed studies describing structures and physical properties as well.

Structural and compositional diversity in pnictide oxides materials can be traced to the semiconducting Zintl pnictides [13, 14], many of which are compositionally akin to various oxypnictides. Whereas a coordination environment of the oxide O^{2-} anion is usually different than for the Pn^{3-} anion, the simultaneous presence of both noticeably enriches the structural diversity. Interestingly, the $Pn:O$ ratio in the typical pnictide oxides usually exceeds 1, as highlighted in this minireview (with a few exceptions). Commonly, oxygen-rich compounds are derivatives of the oxyacids, and the oxoanions, as mentioned already feature $Pn-O$ bonding characteristics which do not belong to the realm of the mixed-anion compounds discussed herein.

On this note, here, we need to bring the attention to the fact that in oxypnictides, the consideration of both oxide O^{2-} and pnictide Pn^{3-} anions implies an increased average charge transfer level (i.e., high degree of ionicity of the bonding). This also suggests that the valence electrons from the electropositive element(s) will be “fully” donated to the electropositive pnictogen and oxygen atoms, which will use them to form anionic or polyanionic species, satisfying the octet rule. Of course, the relatively small amount of oxygen atoms in the structure also means that the degree of polarity of the bonding will only be slightly higher than in related pnictide materials’ structures. Thus, the main features of the bonding within the structures of the oxypnictides, in analogy to the Zintl phases [13, 14], can be described by the Zintl–Klemm concept [15]; oxypnictides can therefore be considered as charge-balanced narrow bandgap semiconductors or semimetals.

In the following paragraphs, we recount the structural chemistry and properties of many known ternary and multinary pnictide oxides. This minireview is not exhaustive, although it covers nearly two dozen well-studied layered structures, *vide infra*, as well as several unique examples that crystallize in their own structure types. Novel heteroanionic solid-state materials are being discovered and studied at a very fast pace and by summarizing and highlighting the recent advances and trends, we hope that this article will serve the scientific community and will promote additional theoretical and experimental research in this field.

2 Synthesis

The synthetic approaches, methodologies, and conditions for preparing oxypnictide phases are similar to the techniques used for the synthesis of other Zintl pnictides. A more elaborate overview of the typical synthetic methods and their applicability for the synthesis of Zintl pnictides (and oxypnictides) can be found elsewhere [13, 14, 16]. Herein, only several aspects of the synthetic work of particular relevance to oxypnictides will be outlined.

Since compounds of interest to the condensed matter community generally need to be prepared in bulk form, we discuss only reactions aimed at obtaining single-crystalline or polycrystalline samples in gram-quantities. Such experiments usually require a combination of high temperatures and inert atmosphere. Oxygen often becomes an inadvertent reagent at such conditions, and in fact, many oxypnictides have originally been detected as side products of reactions targeting the synthesis of pnictide phases. While it is complicated to unambiguously determine the source of the latter, partial oxidation of air-sensitive starting materials, such as alkaline-earth or rare-earth metals, or outgassing of silica tubes were believed to be culprits. Alumina crucibles used for flux reaction should also be considered as a possible source of oxygen. It was recently shown that the reaction between the crucible and specific fluxes might even promote tuning the oxygen content in the melt [17].

The limited content and unadvertised origin of oxygen in many known pnictide oxide materials complicated its detection in the crystal structures. Several early works had misidentified ternary oxypnictides as binary pnictides primarily because of the weak scattering origin of oxygen atoms and limited sensitivity of instruments. An excellent example was the discovery of Ca_2Pn ($Pn = Sb, Bi$) phases with the tetragonal La_2Sb structure type [18], which later had to be revised and reformulated to be Ca_4Pn_2O with the *anti*- K_2NiF_4 structure [19, 20]. It is also well established that some intermetallic phases, such as Mn_5Si_3 -type, Th_2Zn_{17} -type or Ti_8Bi_9 -type can be stabilized by non-metal impurities, such as boron, carbon, nitrogen, and oxygen which are reasonably considered as anionic species [21–24]. Such compositions can also be considered as oxypnictides in cases where oxygen served as a “stabilizing agent”. In the case of Ca_4Pn_2O [19, 20], electronic structure calculations readily provide clues pointing at the electronic instability of Ca_2Pn , suggesting that modern computational chemistry might become a powerful tool for screening the structural databases for potential omissions.

The unadvertised origin of oxygen in the initial discoveries usually resulted in low yields of pnictide oxides. Therefore the formation of phase-pure ternary and multinary oxypnictide materials in quantitative amounts often requires a direct reaction between the stoichiometric amounts of metals and metal/pnictogen oxides, peroxides, or superoxides. Such reactions also require an inert atmosphere in order to exclude unmetereed oxygen, although conditions for the synthesis vary depending on the studied system and are often unique for different compounds. In some cases, reactions have to be performed in Nb and Ta tubes, yet the reactivity of several pnictogens, such as As and P with Nb and Ta tubes, has to be considered [25–27]. Therefore, using bound pnictogens, such as binary metal pnictides or sesquioxides of pnictogens as less-reactive intermediate products, is one of the possible solutions. Proper choice of starting materials benefits reaction kinetics and phase purity. For instance, solid-state metathesis reaction between LaOCl and NaFeAs ternary phases yields in the synthesis of LaFeAsO pnictide oxide with noticeably improved phase purity [28].

The synthesis of oxypnictides usually requires relatively high temperatures, as high as 1000 °C or above. However, the formation of single crystals has been detected even at relatively low temperatures of ca. 650 °C, as was shown for the ternary Ba₃Sb₄O phase [29]. Proper homogenization, phase purity, and densification can be achieved by grinding together manually or using a ball-mill followed by pressing pellets and annealing or by spark-plasma sintering (SPS) [30].

The discovery of pnictide oxides with novel structures remains mostly of serendipitous nature. Recent advances in computational materials discovery are often limited by predicting compounds within known structure types. However, further development of machine-learning-driven screening techniques and approaches may lead to the discovery of new mixed-anion semiconducting materials [31]. While structural reports reviewed herein often lack property characterization, further first-principle calculations will benefit comprehensive characterization and potentially reveal promising properties and applications. A good illustration of this approach is the recent prediction of thermoelectric properties of Ca₄Pn₂O (*Pn* = Sb, Bi) phases [32], which for decades have remained as a laboratory curiosity.

3 Crystal chemistry and properties of the oxypnictide compounds

The main section of this review describes crystal structures and properties for known ternary and multinary

heteroanionic pnictide oxides. Basic crystallographic data, i.e., the structure type, the space group symbol, and lattice parameters, are summarized in Tables 1 and 2. Data are arranged in the order of compositional complexity, starting from ternary compounds, and grouped by structure types. Several compounds of the same structure type are organized in the order of increasing atomic masses of pnictogen.

Crystal structures of the discussed pnictide oxides have been comprehensively studied with the aid of single-crystal X-ray diffraction or neutron powder diffraction in most cases. With the growing demand for data accessibility, we suggested that ICSD collection codes (where possible) will be helpful for readers by providing convenient access to the structure of interest for further investigation. Atomic coordinates and unit cell parameters used for the figures were taken from the ICSD entries.

3.1 Coordination environments and building blocks

Apparent similarities in chemistries of the pnictide oxides and Zintl pnictides imply the existence of common structural features for both classes of compounds with regard to the *Pn*^{3−} anion. Indeed, numerous Zintl (poly)anions, such as dimers (Figure 1a), square nets (Figure 1b), or chains (Figure 1c) made of pnictide atoms, exist for both families. More complex anions, such as [*MPn*₃] with trigonal planar coordination (Figure 1d), [*MPn*₄] with tetrahedral or square-planar coordination (Figure 1e and f), [*MPn*₅] with square-pyramidal coordination (Figure 1g) (*M* = transition metal; *Pn* = pnictogen), are also well-known building blocks for both pnictide and pnictides oxides. Structural chemistry of the oxide part in oxypnictides is abundant and represented by the O-centered trigonal planes [*OAE*₃] (Figure 1d), tetrahedra or square-planes [*OAE*₄], [*OM*₄] (Figure 1e and f), square pyramids [*OAE*₅] (Figure 1g), and octahedra [*OAE*₆] (Figure 1h) (*AE* = alkaline-earth or rare-earth metal; *M* = transition metal).

The listed structural polyhedra serve as primary building blocks, which can be merged with three main types of connectivity: corner-sharing, edge-sharing, and face-sharing. Resulting arrangements form infinite 1D, 2D, and 3D substructures, while compounds with layers are the most studied among pnictide oxides. A distinct separation of the oxidic and pnictide substructures of different dimensionalities greatly extends the number of adopted structure types through the different altering of common building blocks. This is especially true for the layered oxypnictides, where different stacking of several layers is

Table 1: Crystallographic data for ternary pnictide oxides.

Compound	Structure type	Space group	Pearson symbol	<i>a</i> , Å	<i>b</i> , Å/ <i>β</i> (°)	<i>c</i> , Å	ICSD collection code	References
Ca ₄ P ₂ O	K ₂ NiF ₄	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 14	4.497(1)	<i>a</i>	15.103(5)	402952	[33]
Ca ₄ As ₂ O	K ₂ NiF ₄	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 14	4.537(1)	<i>a</i>	15.449(4)	68203	[34]
Ca ₄ Sb ₂ O	K ₂ NiF ₄	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 14	4.677(2)	<i>a</i>	16.342(7)	16353	[19]
Ca ₄ Bi ₂ O	K ₂ NiF ₄	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 14	4.7192(16)	<i>a</i>	16.505(9)	416137	[20]
Sr ₄ P ₂ O	K ₂ NiF ₄	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 14	4.794(1)	<i>a</i>	15.985(4)	33903	[35]
Sr ₄ As ₂ O	K ₂ NiF ₄	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 14	4.831(1)	<i>a</i>	16.364(4)	33904	[35]
Sr ₄ Bi ₂ O	K ₂ NiF ₄	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 14	4.9948(7)	<i>a</i>	17.548(4)	710070	[36]
Ba ₄ As ₂ O	K ₂ NiF ₄	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 14	5.1246(4)	<i>a</i>	17.336(1)	33905	[35]
Ba ₄ Sb ₂ O	K ₂ NiF ₄	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 14	5.116(10)	<i>a</i>	17.946(32)	402284	[37]
Ba ₄ Bi ₂ O	K ₂ NiF ₄	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 14	5.2662(7)	<i>a</i>	18.625(4)	710071	[36]
Eu ₄ As ₂ O	K ₂ NiF ₄	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 14	4.7924(4)	<i>a</i>	16.1933(9)	1222	[38]
Eu ₄ Sb ₂ O	K ₂ NiF ₄	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 14	4.919(1)	<i>a</i>	17.124(4)	402953	[39]
Eu ₄ Bi ₂ O	K ₂ NiF ₄	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 14	4.9540(3)	<i>a</i>	17.367(3)	402954	[40]
Sm ₄ Bi ₂ O	K ₂ NiF ₄	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 14	4.9228(4)	<i>a</i>	17.558(2)	423294	[41]
Yb ₄ As ₂ O	K ₂ NiF ₄	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 14	4.562(4)	<i>a</i>	15.44(1)	402951	[42]
Ba ₄ P ₂ O	La ₂ CuO ₄	<i>Cmca</i>	<i>oS</i> 28	7.335(1)	7.164(1)	16.732(3)	33906	[35]
La ₂ SbO ₂	<i>anti</i> -ThCr ₂ Si ₂	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 10	4.0674(6)	<i>a</i>	13.705(3)	262301	[43]
Ce ₂ SbO ₂	<i>anti</i> -ThCr ₂ Si ₂	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 10	4.0167(3)	<i>a</i>	13.710(2)	419608	[44]
Pr ₂ SbO ₂	<i>anti</i> -ThCr ₂ Si ₂	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 10	3.9957(3)	<i>a</i>	13.580(2)	419607	[44]
Nd ₂ SbO ₂	<i>anti</i> -ThCr ₂ Si ₂	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 10	3.9648(6)	<i>a</i>	13.555(3)	262302	[43]
Sm ₂ SbO ₂	<i>anti</i> -ThCr ₂ Si ₂	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 10	3.9220(6)	<i>a</i>	13.323(2)	262303	[43]
Gd ₂ SbO ₂	<i>anti</i> -ThCr ₂ Si ₂	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 10	3.8900(6)	<i>a</i>	13.277(3)	262304	[43]
Ho ₂ SbO ₂	<i>anti</i> -ThCr ₂ Si ₂	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 10	3.8279(5)	<i>a</i>	13.039(3)	262305	[43]
Er ₂ SbO ₂	<i>anti</i> -ThCr ₂ Si ₂	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 10	3.8151(5)	<i>a</i>	13.007(3)	262306	[43]
Y ₂ BiO ₂	<i>anti</i> -ThCr ₂ Si ₂	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 10	3.8734(1)	<i>a</i>	13.2469(5)	261432	[45]
La ₂ BiO ₂	<i>anti</i> -ThCr ₂ Si ₂	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 10	4.08483(6)	<i>a</i>	13.9866(2)	422645	[45]
Ce ₂ BiO ₂	<i>anti</i> -ThCr ₂ Si ₂	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 10	4.0369(5)	<i>a</i>	13.746(2)	419606	[44]
Pr ₂ BiO ₂	<i>anti</i> -ThCr ₂ Si ₂	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 10	4.0149(1)	<i>a</i>	13.7017(6)	419609	[44]
Nd ₂ BiO ₂	<i>anti</i> -ThCr ₂ Si ₂	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 10	3.99258(5)	<i>a</i>	13.6663(2)	422646	[45]
Sm ₂ BiO ₂	<i>anti</i> -ThCr ₂ Si ₂	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 10	3.95296(6)	<i>a</i>	13.5083(3)	261433	[45]
Gd ₂ BiO ₂	<i>anti</i> -ThCr ₂ Si ₂	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 10	3.9181(1)	<i>a</i>	13.4246(5)	261435	[45]
Tb ₂ O ₂ Bi	<i>anti</i> -ThCr ₂ Si ₂	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 10	3.8962(6)	<i>a</i>	13.317(3)	423916	[46]
Dy ₂ BiO ₂	<i>anti</i> -ThCr ₂ Si ₂	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 10	3.8761(3)	<i>a</i>	13.233(2)	423915	[46]
Ho ₂ BiO ₂	<i>anti</i> -ThCr ₂ Si ₂	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 10	3.86212(9)	<i>a</i>	13.2262(4)	261434	[45]
Er ₂ BiO ₂	<i>anti</i> -ThCr ₂ Si ₂	<i>I</i> 4/ <i>mmm</i>	<i>t</i> 10	3.84531(1)	<i>a</i>	13.1513(4)	422647	[45]
La ₃ SbO ₃	Own	<i>C</i> 2/ <i>m</i>	<i>mS</i> 28	13.856(3)	4.1050(8)/118.55(3)	12.343(3)	380456	[47]
Sm ₃ SbO ₃	La ₃ SbO ₃	<i>C</i> 2/ <i>m</i>	<i>mS</i> 28	13.332(2)	3.9501(4)/118.310(11)	11.9187(18)	380455	[47]
Gd ₃ SbO ₃	La ₃ SbO ₃	<i>C</i> 2/ <i>m</i>	<i>mS</i> 28	13.272(3)	3.8971(2)/118.40(3)	11.878(2)	380460	[47]
Ho ₃ SbO ₃	La ₃ SbO ₃	<i>C</i> 2/ <i>m</i>	<i>mS</i> 28	13.014(3)	3.8218(7)/118.213(14)	11.679(2)	380458	[47]
Gd ₃ BiO ₃	La ₃ SbO ₃	<i>C</i> 2/ <i>m</i>	<i>mS</i> 28	13.444(3)	3.8449(8)/118.31(3)	12.033(2)	429459	[48]
Sm ₈ Sb ₃ O ₈	Own	<i>C</i> 2/ <i>m</i>	<i>mS</i> 38	13.462(3)	3.8929(8)/106.77(3)	15.230(3)	380454	[47]
Gd ₈ Sb ₃ O ₈	Sm ₈ Sb ₃ O ₈	<i>C</i> 2/ <i>m</i>	<i>mS</i> 38	13.394(3)	3.8191(8)/107.05(3)	15.104(3)	380459	[47]
Ho ₈ Sb ₃ O ₈	Sm ₈ Sb ₃ O ₈	<i>C</i> 2/ <i>m</i>	<i>mS</i> 38	13.1368(11)	3.7609(2)/106.958(7)	14.8700(13)	380457	[47]
Gd ₈ Bi ₃ O ₈	Sm ₈ Sb ₃ O ₈	<i>C</i> 2/ <i>m</i>	<i>mS</i> 38	13.3939(3)	3.87360(10)/107.031(2)	15.1160(3)	428036	[48]
La ₉ Sb ₅ O ₅	Own	<i>P</i> 4/ <i>n</i>	<i>tP</i> 38	10.415(1)	<i>a</i>	9.340(1)	414019	[49]
Ce ₉ Sb ₅ O ₅	La ₉ Sb ₅ O ₅	<i>P</i> 4/ <i>n</i>	<i>tP</i> 38	10.297(1)	<i>a</i>	9.228(1)	414018	[49]
Pr ₉ Sb ₅ O ₅	La ₉ Sb ₅ O ₅	<i>P</i> 4/ <i>n</i>	<i>tP</i> 38	10.2203(3)	<i>a</i>	9.1508(3)	241209	[50]
Sm ₉ Sb ₅ O ₅	La ₉ Sb ₅ O ₅	<i>P</i> 4/ <i>n</i>	<i>tP</i> 38	10.0341(4)	<i>a</i>	8.9839(3)	241207	[50]
Tb ₉ Sb ₅ O ₅	La ₉ Sb ₅ O ₅	<i>P</i> 4/ <i>n</i>	<i>tP</i> 38	9.8618(12)	<i>a</i>	8.838(2)	409978	[51]
Dy ₉ Sb ₅ O ₅	La ₉ Sb ₅ O ₅	<i>P</i> 4/ <i>n</i>	<i>tP</i> 38	9.8389(3)	<i>a</i>	8.7986(3)	241208	[50]
Ba ₃ Sb ₂ O	Own	<i>Pbam</i>	<i>oP</i> 24	12.4228(11)	12.630(3)	5.101(3)	280592	[52]
Ba ₃ Sb ₄ O	Own	<i>P</i> 2/ <i>c</i>	<i>mP</i> 32	6.9342(17)	12.807(3)/112.385(10)	12.941(3)	415032	[29]
Ti ₈ BiO ₇	Own	<i>Cmmm</i>	<i>oS</i> 32	7.8473(4)	16.8295(10)	3.0256(2)	239415	[53]

Figure 1: Selected building blocks and structural fragments typical for pnictide oxide phases. (a) $[\text{Sb-Sb}]^{4-}$ dimers observed in the $\text{Ba}_3\text{Sb}_2\text{O}$ and $\text{Ba}_5\text{Cd}_2\text{Sb}_5\text{O}$ structures; (b) polypnictide square nets $^2[\text{As}]_n$ observed the $\text{U}_2\text{Cu}_2\text{As}_3\text{O}$ structure; (c) polypnictide chains $^1[\text{Sb}]_n$ observed in the $\text{Ba}_3\text{Sb}_4\text{O}$ structure; (d) trigonal-planar coordination typical for oxygen $[\text{OAE}_3]$ and coinage metals $[\text{MAN}_3]$ ($M = \text{Cu, Ag, Au}$); (e) square-planar coordination observed for oxygen $[\text{OAE}_4]$, $[\text{OM}_4]$ and transition metals $[\text{MAN}_4]$ ($M = \text{Ti, Ni, Pd, Au}$); (f) O-centered $[\text{OAE}_4]$ and M-centered $[\text{MAN}_4]$ tetrahedron – the most common structural fragment in oxypnictides ($M = \text{transition metal}$); (g) pyramidal coordination typical for oxygen $[\text{OAE}_5]$ and early transition metals $[\text{MAN}_5]$ ($M = \text{Sc, Ti, V}$); (h) octahedral coordination typical for oxygen $[\text{OAE}_6]$ and titanium $[\text{TiAn}_6]$; (i) fluorite type $[\text{M}_2\text{Pn}_2]$ layers ($M = \text{divalent transition metals, such as } M = \text{Ti, Cr, Mn, Fe, Co, Ni, Zn, Cd}$); $\text{AE} = \text{alkali, alkaline-earth, rare-earth metal}$; $\text{An} = \text{O, P, As, Sb Bi}$. Here and after AE , M , Pn , and O atoms are represented by the same size spheres regardless of their chemical identities and bonds drawn between them.

responsible for structural intricacies. Such a modular approach also helps tuning transport properties through selective stacking of layers or modifying interlayer spacing by selecting interlayer cations.

Among the oxypnictide layers, of specific interest are fluorite-type $[\text{M}_2\text{Pn}_2]$ and *anti*-fluorite-type $[\text{AE}_2\text{O}_2]$ layers, which are formed by fused edge-sharing $[\text{MPn}_4]$ or $[\text{OAE}_4]$ tetrahedra, respectively (Figure 1i). The presence of the fluorite-type $[\text{M}_2\text{Pn}_2]$ layers was shown to be an excellent criterion for the classification of oxypnictides and was implemented in one of the prior reviews on pnictide oxides with *d*-metals [9]. We acknowledge such approach and partially use it in the current work, yet a range of oxypnictide structures also include structural fragments of different dimensionalities which complicates classification criteria.

3.2 Ternary compounds

Ternary pnictide oxides are usually made of electropositive metallic elements, such as alkaline-earth metals or rare-earth metals coordinated by oxygen and pnictogens. An obvious electronegativity difference between metal cations and non-metal anions results in a noticeable bond polarity and, therefore, charge-balanced compositions, similar to those in Zintl pnictides [13, 14]. A compositional

uniqueness of compounds with both O^{2-} and Pn^{3-} anions often leads to the formation of structure types which are unique for oxypnictides. A list of known ternary pnictide oxides is provided in Table 1.

3.2.1 Ternary “4–2–1” structures with K_2NiF_4 -type

Probably the most abundant and well-studied class of ternary oxypnictide compounds are the “4–2–1” phases with general formula $\text{AE}_4\text{Pn}_2\text{O}$ ($\text{AE} = \text{Ca, Sr, Ba}$, $\text{Pn} = \text{P, As, Sb, Bi}$) [19, 20, 33–42]. Most of the known compositions crystallize in the tetragonal crystal system with the body-centered space group $I4/mmm$, Pearson symbol $tI14$. Its structure is isopointal with the *anti*-perovskite-related K_2NiF_4 structure (*anti*-Ruddlesden–Popper) and can be described as corner-sharing oxygen-centered distorted octahedra of AE, forming infinite layers stacked in ABAB-fashion along the *c*-axis (Figure 2a). Pnictogen coordination resembles a tri-capped trigonal prism polyhedron with nine AE atoms in vertexes (Figure 2b). Several structures, such as $\text{Sr}_4\text{Bi}_2\text{O}$, exhibit a noticeable anisotropy of the atomic displacement of the O atoms, indicating the preference for the lower coordination number of 5 instead of 6 for oxygen. Thus, the coordination environment of oxygen can also be viewed as square pyramidal (Figure 2c). Alternatively, the structure can be

Figure 2: (a) Crystal structure of tetragonal AE_4Pn_2O phase; (b) coordination environment of Pn atoms; (c) square-pyramidal coordination of distorted O atoms in Sr_4Bi_2O . O atoms are shown as split site with SOF of 0.5; (d) crystal structure of the orthorhombic Ba_4P_2O phase. AE atoms are dark gray, Pn atoms are orange, and O atoms are red. Unit cells are outlined.

described as AE-centered octahedrons, where four Pn^{3-} anions and two O^{2-} anions coordinate one AE site, while another is coordinated by five Pn^{3-} anions and O^{2-} anion.

The Ba_4P_2O phase has similar composition and the chemical bonding can be rationalized in an analogous way, although it crystallizes in a different structure, which resembles *anti*- La_2CuO_4 structure type, space group $Cmca$, Pearson symbol $oS28$. $[OBa_6]$ elongated octahedra are linked via corners to form layers and tilted towards the *ab*-plane (Figure 2d). All “4–2–1” phases appear to be electron-balanced according to the notation $(AE^{2+})_4(Pn^{3-})_2(O^{2-})$ regardless of the adopted structure type.

In recent years, AE_4Pn_2O phases attracted much attention beyond structural studies. This family of compounds shows promising ferroelectric and antiferroelectric behavior, while some compounds can polarize even under open-circuit boundary conditions [54]. “4–2–1”-type compounds were predicted to be candidates for photovoltaic materials, although with heavy holes and layered connectivity [55, 56]. Testing for the presence of superconductivity was also performed, yet, was unsuccessful due to the semiconducting nature of these phases [57]. A recent study predicted excellent thermoelectric properties for Ca_4Bi_2O and Ca_4Sb_2O semiconductors [32].

3.2.2 Ternary $RE_mPn_nO_m$ phases

A family of ternary $RE_mPn_nO_m$ and quaternary $(RE, Ca)_mPn_nO_m$ derivatives (RE = rare-earth metal; Pn = Sb, Bi) rare-earth-based oxypnictides is constituted by numerous structures with different stacking sequences of rare-earth oxide substructures [43–48, 58–63]. A combination of semimetallic binary rare-earth pnictides $REPn$ and insulating rare-earth oxides RE_2O_3 was shown to be a potential approach to produce narrow-bandgap semiconducting

materials. Ternary and quaternary phases can be synthesized by the direct reactions of rare-earth pnictide, calcium pnictide, or pnictogen with rare-earth oxide in different ratios at relatively high temperatures (Figure 3), which results in a variety of phases with different structural features, bandgaps, and properties.

These compounds are considered as rare examples of oxygen-rich oxypnictides, and the synthesis, structures, and properties of this family of compounds have recently been reviewed [62]. Here, we will only briefly discuss known subclasses within this large family of compounds. Their crystal structures are very similar and consist of O-centered $[ORE_4]$ edge- and corner-sharing tetrahedra of different arrangements (Figure 4).

The simplest composition can be described with the formula RE_2PnO_2 (RE = Y, La, Nd Sm, Gd, Ho, Er; Pn = Sb, Bi), which adopt a disordered *anti*- $ThCr_2Si_2$ structure type (space group $I4/mmm$, Pearson symbol $tI10$) [43–46, 59–61]. The crystal structure can be described as a square net layer made of Pn^{2-} anions sandwiched between $[RE_2O_2]^{2+}$ *anti*-fluorite-type layers, which also can be considered as $(REO)^+$ PbO-like slabs (Figure 4). Pnictogens occupy distorted positions, thus making possible Zintl-

Figure 3: Schematic representation of the synthetic conditions for the selected $(RE,Ca)-Pn-O$ phases. Adapted with permission from [62]. Copyright © 2017 American Chemical Society.

Figure 4: Structural sequences in the $(RE,Ca)_mPn_nO_m$ phases. Reprinted with permission from [62]. Copyright ©2017 American Chemical Society.

type $[Pn^{2-}-Pn^{2-}]$ bonding (Figure 1a), which results in the charge-balanced formula $(RE^{3+})_2(Pn^{2-})(O^{2-})_2$. A more appropriate crystallographic description of this class of materials was provided for the Pr_2SbO_2 phase, which has a commensurately modulated orthorhombic crystal structure with the superspace group $Immm(0\beta 0)000$ [64]. RE_2BiO_2 phases undergo an insulator-to-metal transition as early rare-earth elements are replaced by late rare-earth metals [45]. Thermoelectric properties of RE_2SbO_2 phases were also reported, yet dimensionless thermoelectric figure-of-merit values do not exceed 0.02 at 400 K [43]. Several “2–1–2” bismuthides were reported to be superconducting with T_c values below 3 K [65–67].

RE_3PnO_3 ($RE = La, Sm, Gd, Ho$; $Pn = Sb, Bi$) phases crystallize in their own structure type (space group $C2/m$, Pearson symbol $mS28$) [47, 48, 63]. Oxygen-centered corner- and edge-sharing $[ORE_4]$ tetrahedra build up a three-dimensional framework, which hosts Pn atoms inside extended voids formed by two distinct blocks of two and four units (Figure 4). The charge balance is achieved according to the notation $(RE^{3+})_3(Pn^{3-})(O^{2-})_3$. First-principle calculations and electrical resistivity measurements suggest semiconducting behavior [47, 48]. Higher tetragonal symmetry (space group $P4_2/mmm$, Pearson symbol $tP28$) is observed for the corresponding quaternary phases with two different rare-earth metals of different atomic radii [63] synthesized at the temperatures of 1550 °C or greater (Figure 3). The structural framework in $(RE^I RE^{II})_3SbO_3$ is similar to that of RE_3SbO_3 , yet, it is formed by units with a different number of edge-sharing $[ORE_4]$ tetrahedra (Figure 4).

$RE_8Pn_{3-x}O_8$ ($RE = Sm, Gd, Ho$; $Pn = Sb, Bi$) pnictide oxides also adopt novel crystal structure with the space group $C2/m$, Pearson symbol $mS38$ [47, 48]. In analogy with RE_3PnO_3 , the “8–3–8” crystal structure is formed by REO frameworks built of the O-centered $[ORE_4]$ edge-sharing tetrahedra with empty channels filled with Sb atoms (Figure 4). In addition, an unusual trigonal planar coordination of the oxygen atom was observed in $RE_8Pn_{3-x}O_8$ phases. Electronic structure calculations predicted metallic behavior for the idealized $RE_8Pn_3O_8$ structure, which is one-electron short according to the notation $(RE^{3+})_8(Pn^{3-})_3(O^{2-})_8(h^+)$. In fact, a deficiency on the Pn site is readily observed for all reported structures, which improves an electron count and results in the experimentally observed semiconducting behavior for $RE_8Sb_{3-x}O_8$ phases [47].

3.2.3 Ternary $RE_9Pn_5O_5$ phases

$RE_9Sb_5O_5$ ($RE = La-Pr, Sm, Tb, Dy$) were synthesized from Sb_2O_3 , antimony, and the rare earth metals [49–51]. These compounds represent their own structure type, space group $P4/n$, Pearson symbol $tP38$. The crystal structure can be considered as a defect variant of the Sc_2Sb structure filled up with oxygen atoms. The structure can also be characterized by 2D fragments of the $LaSb$ structure (NaCl-structure type), where ${}^2[LaSb_{5/5}]$ layers alter with layers formed by O-centered $[ORE_4]$ tetrahedra and $[ORE_5]$ pyramids (Figure 5). Two additional electrons per formula unit are necessary to satisfy the formal charge balance according to the notation $(RE^{3+})_9(Sb^{3-})_5(O^{2-})_5(2e^-)$. As a result, $La_9Sb_5O_5$ behaves like a bad metal with reported room-

Figure 5: Crystal structure of the tetragonal $AE_9Pn_5O_5$ phases (AE denotes rare-earth metals of rare-earth/alkaline-earth mixed occupied sites). Unit cell is outlined. AE atoms are dark-gray, Pn atoms are orange, and O atoms are red.

temperature electrical conductivity of 6.7 mΩ cm. $RE_9Sb_5O_5$ phases can be doped by divalent Ca atom, which results in the formation of quaternary $Ca_2RE_7Pn_5O_5$ series ($RE = Pr, Sm, Gd, Dy$; $Pn = Sb, Bi$) (Table 2) with semiconducting behavior, which corroborates well with the electron-balanced formula $(Ca^{2+})_2(RE^{3+})_7(Pn^{3-})_5(O^{2-})_5$ [68].

3.2.4 Other ternary structures

Ba_3Sb_2O crystallizes with the space group $Pbam$, Pearson symbol $oP24$ with its own structure type [52]. Its anionic substructure can be described with two types of anions – $[Sb_2]^{4-}$ dimers and O^{2-} anions separated by Ba^{2+} counter cations (Figure 6a). The coordination environment of oxygen resembles slightly distorted tetrahedra connected via corners to form chains running along the c -axis. This phase is charge-balanced according to the notation $(Ba^{2+})_3[Sb_2]^{4-}(O^{2-})$ and can be considered as a Zintl phase.

Another barium antimonide oxide Ba_3Sb_4O was synthesized from respective metals and pnictide sesquioxides in alumina crucibles at a temperature as low as 650 °C with the presence of $RbSb$ as additional starting material. It crystallizes in the monoclinic crystal system with the space group $P2_1/c$ with its own structure [29]. The structural hallmark of this phase are chiral chains $^1[Sb_n]^{n-}$ running along a -axis (Figure 1c). O^{2-} anions are tetrahedrally coordinated by Ba^{2+} cations (Figure 6b) thus forming a unit formed by two edge-sharing $[OBa_4]$ tetrahedra. Ba_3Sb_4O is

Figure 6: Crystal structures of Ba_3Sb_2O (a) and Ba_3Sb_4O (b). Unit cells are outlined. Ba atoms are dark-gray, Sb atoms are orange, and O atoms are red.

an electron-precise phase with isolated $[Sb_4]^{4-}$ Zintl anion and can be described according to the following breakdown as $(Ba^{2+})_3([Sb_4]^{4-})(O^{2-})$.

Metallic ternary bismuthide oxide phase Ti_8BiO_7 was prepared by a high-temperature reaction between Ti and Bi_2O_3 in inert conditions [53]. It crystallizes in its own structure type (space group $Cmmm$, Pearson symbol $oS32$). A noticeable structural feature of the crystal structure is the plethora of different coordinations for O atom, such as square-planar, tetrahedral, and orthogonal pyramidal of Ti (Figure 7). Three Ti sites exhibit three different types of coordination: isosceles-triangle threefold and rectangular fourfold coordination of O atoms and octahedral sixfold

Figure 7: (a) Crystal structure of orthorhombic Ti_8BiO_7 ; (b) close-up view of coordination polyhedra and linear Bi chains occurred in the Ti_8BiO_7 structure. Unit cell is outlined. Ti atoms are blue, Bi atoms are orange, and O atoms are red.

coordination of four O and two Bi atoms. Bi atoms form infinite linear chains along the c -axis. With the absence of direct Bi–O bonds, Ti_8BiO_7 is considered as a heteroanionic one-electron-short system according to the notation $(\text{Ti}^{2+})_8(\text{Bi}^-)(\text{O}^{2-})_7(\text{h}^+)$ [53].

3.3 Multinary compounds

Incorporation of additional positively charged species, such as alkali, alkaline-earth, rare-earth or d-metal ions, noticeably expands the number and structural variety of the multinary pnictide oxides compared to the ternary phases [9, 62]. In some instances, quaternary phases are considered as solid-state solutions within the ternary structure types, similar to the previously discussed $\text{RE}_9\text{Sb}_5\text{O}_5$ compounds and their Ca-bearing quaternary derivatives [68]. Another example, which unifies ternary and quaternary compounds is the *anti*-perovskite K_4NiF_4 structure type, which is observed for “4–2–1” ternary and several quaternary compounds, such as $\text{Na}_2\text{Ti}_2\text{Pn}_2\text{O}$ ($\text{Pn} = \text{As}, \text{Sb}$), which are considered as ordered derivatives of “4–2–1” phases [69]. However, the vast majority of the quaternary phases crystallize in their own structure types, although at least 12 of them share identical fluorite-type $[\text{M}_2\text{Pn}_2]$ layers (M = transition metal; Pn = pnictogen), responsible for superconducting behavior. Several structure types also feature *anti*-fluorite $[\text{AE}_2\text{O}_2]$ (AE = alkaline-earth or rare-earth metals) layers typical for ternary phases with *anti*- ThCr_2Si_2 structure. The list of known multinary phases is presented in Table 2.

Table 2: Crystallographic data for multinary pnictide oxides.

Compound	Structure type	Space group	Pearson symbol	a , Å	b , Å/ β (°)	c , Å	ICSD collection code	Reference
$(\text{Ca}, \text{Pr})_9\text{Sb}_5\text{O}_5$	$\text{La}_9\text{Sb}_5\text{O}_5$	$P4/n$	$tP38$	10.2234(14)	a	9.1379(18)	429690	[68]
$(\text{Ca}, \text{Sm})_9\text{Sb}_5\text{O}_5$	$\text{La}_9\text{Sb}_5\text{O}_5$	$P4/n$	$tP38$	10.0668(14)	a	9.0111(18)	429691	[68]
$(\text{Ca}, \text{Gd})_9\text{Sb}_5\text{O}_5$	$\text{La}_9\text{Sb}_5\text{O}_5$	$P4/n$	$tP38$	9.9921(14)	a	8.9758(18)	429692	[68]
$(\text{Ca}, \text{Gd})_9\text{Bi}_5\text{O}_5$	$\text{La}_9\text{Sb}_5\text{O}_5$	$P4/n$	$tP38$	10.1018(14)	a	9.0270(18)	429693	[68]
$(\text{Ca}, \text{Dy})_9\text{Bi}_5\text{O}_5$	$\text{La}_9\text{Sb}_5\text{O}_5$	$P4/n$	$tP38$	9.99960(10)	a	8.9341(2)	492694	[68]
$(\text{La}, \text{Dy})_3\text{SbO}_3$	Li_3AuO_3	$P4_2/mnm$	$tP28$	11.9473(17)	a	3.9263(8)	425139	[63]
$(\text{La}, \text{Ho})_3\text{SbO}_3$	Li_3AuO_3	$P4_2/mnm$	$tP28$	11.9203(17)	a	3.9057(8)	425140	[63]
$(\text{Ce}, \text{Ho})_3\text{SbO}_3$	Li_3AuO_3	$P4_2/mnm$	$tP28$	11.8802(17)	a	3.8906(8)	425138	[63]
$\text{CaCe}_3\text{SbO}_4$	Ti_5Te_4	$I4/m$	$tI18$	9.6084(14)	a	4.0148(8)	426810	[58]
$\text{CaPr}_3\text{SbO}_4$	Ti_5Te_4	$I4/m$	$tI18$	9.5632(14)	a	3.9754(8)	426811	[58]
$\text{CaNd}_3\text{SbO}_4$	Ti_5Te_4	$I4/m$	$tI18$	9.5541(14)	a	3.9507(8)	426812	[58]
$\text{CaSm}_3\text{SbO}_4$	Ti_5Te_4	$I4/m$	$tI18$	9.4414(130)	a	3.8960(8)	426813	[58]
$\text{CaGd}_3\text{SbO}_4$	Ti_5Te_4	$I4/m$	$tI18$	9.4205(13)	a	3.8388(8)	426814	[58]
$\text{Ca}_2\text{Pr}_8\text{Sb}_3\text{O}_{10}$	$\text{In}_6\text{Sn}_8\text{S}_{19}$	$C2/m$	$mS46$	13.651(3)	3.9229(8)/93.54(3)	17.628(4)	427079	[58]
$\text{Ca}_2\text{Nd}_8\text{Sb}_3\text{O}_{10}$	$\text{In}_6\text{Sn}_8\text{S}_{19}$	$C2/m$	$mS46$	13.605(3)	3.8884(8)/93.47(3)	17.594(4)	426815	[58]
$\text{Ca}_2\text{Sm}_8\text{Sb}_3\text{O}_{10}$	$\text{In}_6\text{Sn}_8\text{S}_{19}$	$C2/m$	$mS46$	13.462(3)	3.8429(8)/93.62(3)	17.458(4)	426816	[58]
$\text{Ca}_2\text{Gd}_8\text{Sb}_3\text{O}_{10}$	$\text{In}_6\text{Sn}_8\text{S}_{19}$	$C2/m$	$mS46$	13.386(3)	3.7985(8)/93.59(3)	17.368(4)	426817	[58]
$\text{Ca}_2\text{Tb}_8\text{Sb}_3\text{O}_{10}$	$\text{In}_6\text{Sn}_8\text{S}_{19}$	$C2/m$	$mS46$	13.307(3)	3.7791(8)/93.67(3)	17.271(4)	426818	[58]
$\text{KBa}_{11}\text{P}_7\text{O}_2$	Own	$Fddd$	$oF168$	10.699(1)	15.143(2)	31.646(4)	85421	[70]
$\text{KBa}_{11}\text{As}_7\text{O}_2$	$\text{KBa}_{11}\text{P}_7\text{O}_2$	$Fddd$	$oF168$	10.878(2)	15.423(2)	32.324(4)	85422	[70]
$\text{KBa}_4\text{Sb}_3\text{O}$	$\text{Sr}_5\text{Pb}_3\text{F}$	$I4/mcm$	$tI36$	8.824(1)	a	16.5936(16)	410747	[71]
$\text{RbBa}_4\text{Sb}_3\text{O}$	$\text{Sr}_5\text{Pb}_3\text{F}$	$I4/mcm$	$tI36$	8.937(4)	a	16.427(9)	415036	[29]

Table 2: (continued)

Compound	Structure type	Space group	Pearson symbol	<i>a</i> , Å	<i>b</i> , Å/ <i>β</i> (°)	<i>c</i> , Å	ICSD collection code	Reference
KBa ₄ Bi ₃ O	Sr ₅ Pb ₃ F	<i>I4/mcm</i>	<i>tI36</i>	8.9675(14)	<i>a</i>	16.664(3)	409487	[72]
α-CeZnPO	ZrCuSiAs	<i>P4/nmm</i>	<i>tP8</i>	4.038(1)	<i>a</i>	8.896(1)	85777	[73]
β-CeZnPO	NdZnPO	<i>R$\bar{3}m$</i>	<i>hR8</i>	4.012(4)	<i>a</i>	31.21(3)	416475	[74]
β-PrZnPO	NdZnPO	<i>R$\bar{3}m$</i>	<i>hR8</i>	3.990(2)	<i>a</i>	31.08(1)	416476	[74]
β-NdZnPO	Own	<i>R$\bar{3}m$</i>	<i>hR8</i>	3.976(1)	<i>a</i>	30.955(5)	85776	[73]
β-SmZnPO	NdZnPO	<i>R$\bar{3}m$</i>	<i>hR8</i>	3.946(2)	<i>a</i>	30.71(1)	418525	[75]
β-GdZnPO	NdZnPO	<i>R$\bar{3}m$</i>	<i>hR8</i>	3.922(2)	<i>a</i>	30.56(1)	418524	[75]
β-DyZnPO	NdZnPO	<i>R$\bar{3}m$</i>	<i>hR8</i>	3.8933(6)	<i>a</i>	30.305(4)	418526	[75]
β-YZnPO	NdZnPO	<i>R$\bar{3}m$</i>	<i>hR8</i>	3.885(2)	<i>a</i>	30.32(1)	418523	[75]
RbSm ₂ Fe ₄ As ₄ O ₂	KCa ₂ Fe ₄ As ₄ F ₂	<i>I4/mmm</i>	<i>tI26</i>	3.9209(2)	<i>a</i>	31.381(2)	— ^a	[76]
Ba ₂ Cd _{3-x} Bi ₃ O	Own	<i>I4/mmm</i>	<i>tI36</i>	4.7396(4)	<i>a</i>	43.601(7)	261122	[77]
Th ₂ Ni _{3-x} P ₃ O	Own	<i>P4/nmm</i>	<i>tP18</i>	3.9462(4)	<i>a</i>	17.232(3)	83373	[78]
U ₂ Cu ₂ As ₃ O	Own	<i>P4/nmm</i>	<i>tP16</i>	3.9111(2)	<i>a</i>	17.916(4)	75132	[79]
Sm ₂ CuAs ₃ O	Hf ₂ CuGe ₄	<i>Pnma</i>	<i>oP28</i>	34.469(1)	3.948(1)	3.984(1)	174368	[80]
La ₃ Cu ₄ P ₄ O ₂	Own	<i>I4/mmm</i>	<i>tI26</i>	4.033(1)	<i>a</i>	26.765(8)	84699	[81]
Pr ₃ Cu ₄ P ₄ O _{2-x}	La ₃ Cu ₄ P ₄ O ₂	<i>I4/mmm</i>	<i>tI26</i>	3.978(1)	<i>a</i>	26.587(5)	412191	[82]
Sm ₃ Cu ₄ P ₄ O _{2-x}	La ₃ Cu ₄ P ₄ O ₂	<i>I4/mmm</i>	<i>tI26</i>	3.928(1)	<i>a</i>	26.436(5)	412192	[82]
La ₃ Cu ₄ As ₄ O ₂	La ₃ Cu ₄ P ₄ O ₂	<i>I4/mmm</i>	<i>tI26</i>	4.130(1)	<i>a</i>	27.486(1)	— ^a	[83]
Ce ₃ Cu ₄ As ₄ O ₂	La ₃ Cu ₄ P ₄ O ₂	<i>I4/mmm</i>	<i>tI26</i>	4.07733(10)	<i>a</i>	27.4146(9)	259394	[84]
La ₅ Cu ₄ P ₄ O ₄ Cl ₂	La ₅ Cu ₄ As ₄ O ₄ Cl ₂	<i>I4/mmm</i>	<i>tI36</i>	4.0752(5)	<i>a</i>	40.568(7)	430390	[85]
La ₅ Cu ₄ As ₄ O ₄ Cl ₂	Own	<i>I4/mmm</i>	<i>tI36</i>	4.1346(7)	<i>a</i>	41.44(1)	421137	[83]
Ba ₂ Mn ₃ P ₂ O ₂	Sr ₂ Mn ₃ As ₂ O ₂	<i>I4/mmm</i>	<i>tI18</i>	4.202(1)	<i>a</i>	19.406	— ^a	[86]
Sr ₂ Mn ₃ As ₂ O ₂	Own	<i>I4/mmm</i>	<i>tI18</i>	4.16(1)	<i>a</i>	18.84(4)	32010	[87]
Ba ₂ Mn ₃ As ₂ O ₂	Sr ₂ Mn ₃ As ₂ O ₂	<i>I4/mmm</i>	<i>tI18</i>	4.248(5)	<i>a</i>	19.77(3)	32011	[87]
Sr ₂ Mn ₃ Sb ₂ O ₂	Sr ₂ Mn ₃ As ₂ O ₂	<i>I4/mmm</i>	<i>tI18</i>	4.262(4)	<i>a</i>	20.11(2)	32012	[87]
Ba ₂ Mn ₃ Sb ₂ O ₂	Sr ₂ Mn ₃ As ₂ O ₂	<i>I4/mmm</i>	<i>tI18</i>	4.367(5)	<i>a</i>	20.78(2)	32013	[87]
Sr ₂ Mn ₃ Bi ₂ O ₂	Sr ₂ Mn ₃ As ₂ O ₂	<i>I4/mmm</i>	<i>tI18</i>	4.28(1)	<i>a</i>	20.55(5)	32014	[87]
Ba ₂ Zn ₃ As ₂ O ₂	Sr ₂ Mn ₃ As ₂ O ₂	<i>I4/mmm</i>	<i>tI18</i>	4.206(1)	<i>a</i>	19.665(6)	67998	[88]
Sr ₂ Cr ₃ As ₂ O ₂	Sr ₂ Mn ₃ As ₂ O ₂	<i>I4/mmm</i>	<i>tI18</i>	4.00800(2)	<i>a</i>	18.8214(1)	28102	[89]
Ba ₂ Cr ₃ As ₂ O ₂	Sr ₂ Mn ₃ As ₂ O ₂	<i>I4/mmm</i>	<i>tI18</i>	4.05506(2)	<i>a</i>	20.5637(1)	— ^a	[89]
Ba ₂ MnZn ₂ As ₂ O ₂	Sr ₂ Mn ₃ As ₂ O ₂	<i>I4/mmm</i>	<i>tI18</i>	4.24257(8)	<i>a</i>	19.5087(7)	85659	[90]
Sr ₂ MnZn ₂ As ₂ O ₂	Sr ₂ Mn ₃ As ₂ O ₂	<i>I4/mmm</i>	<i>tI18</i>	4.12298(3)	<i>a</i>	18.6587(2)	92875	[91]
Sr ₂ Mn ₂ CuAs ₂ O ₂	Sr ₂ Mn ₃ As ₂ O ₂	<i>I4/mmm</i>	<i>tI18</i>	4.0833(2)	<i>a</i>	18.5919(9)	169513	[92]
Sr ₂ Mn ₂ CrAs ₂ O ₂	Sr ₂ Mn ₃ As ₂ O ₂	<i>I4/mmm</i>	<i>tI18</i>	4.09354(10)	<i>a</i>	19.0646(6)	13782	[93]
Sr ₂ VFeAsO ₃	Sr ₂ CuGaSO ₃	<i>P4/nmm</i>	<i>tP16</i>	3.9296	<i>a</i>	15.6732	165984	[94]
Ba ₂ ScFeAsO ₃	Sr ₂ CuGaSO ₃	<i>P4/nmm</i>	<i>tP16</i>	4.1266(5)	<i>a</i>	16.8001(15)	420654	[95]
Sr ₂ CrFeAsO ₃	Sr ₂ CuGaSO ₃	<i>P4/nmm</i>	<i>tP16</i>	3.91122(4)	<i>a</i>	15.7905(3)	420653	[95]
Sr ₃ Sc ₂ Fe ₂ As ₂ O ₅	Sr ₃ Fe ₂ O ₅ Cu ₂ S ₂	<i>I4/mmm</i>	<i>tI28</i>	4.0781(1)	<i>a</i>	26.8386(5)	260449	[96]
Eu ₃ Sc ₂ Fe ₂ As ₂ O ₅	Sr ₃ Fe ₂ O ₅ Cu ₂ S ₂	<i>I4/mmm</i>	<i>tI28</i>	4.06400(6)	<i>a</i>	26.4694(7)	429704	[97]
Na ₂ Ti ₂ As ₂ O	Own	<i>I4/mmm</i>	<i>tI14</i>	4.070(2)	<i>a</i>	15.288(4)	— ^a	[98]
Na ₂ Ti ₂ Sb ₂ O	Na ₂ Ti ₂ As ₂ O	<i>I4/mmm</i>	<i>tI14</i>	4.144(1)	<i>a</i>	16.5610(10)	69648	[98]
Sc ₄ Yb ₄ Sb ₄ O	Na ₂ Ti ₂ As ₂ O	<i>I4/mmm</i>	<i>tI14</i>	4.2721(3)	<i>a</i>	16.0869(15)	427132	[99]
BaTi ₂ As ₂ O	Own	<i>P4/mmm</i>	<i>tP6</i>	4.047(3)	<i>a</i>	7.275(4)	169074	[100]
BaTi ₂ Sb ₂ O	BaTi ₂ As ₂ O	<i>P4/mmm</i>	<i>tP6</i>	4.1055(2)	<i>a</i>	8.0712(4)	430061	[101]
BaTi ₂ Bi ₂ O	BaTi ₂ As ₂ O	<i>P4/mmm</i>	<i>tP6</i>	4.12316(4)	<i>a</i>	8.3447(1)	430063	[102]
Ba ₂ Ti ₂ Fe ₂ As ₄ O	Own	<i>I4/mmm</i>	<i>tI22</i>	4.0276(1)	<i>a</i>	27.3441(4)	263018	[103]
Ba ₂ Ti ₂ Cr ₂ As ₄ O	Ba ₂ Ti ₂ Fe ₂ As ₄ O	<i>I4/mmm</i>	<i>tI22</i>	4.0391(1)	<i>a</i>	27.8474(3)	257022	[104]
Ba ₂ Mn ₂ As ₂ O	Own	<i>C2/m</i>	<i>mS14</i>	7.493(4)	4.196(1)/96.17(3)	10.352(3)	75454	[105]
Ba ₂ Mn ₂ Sb ₂ O	Own	<i>P6₃/mmc</i>	<i>hP14</i>	4.71(1)	<i>a</i>	20.04(2)	16360	[106]
Ba ₂ Mn ₂ Bi ₂ O	Ba ₂ Mn ₂ Sb ₂ O	<i>P6₃/mmc</i>	<i>hP14</i>	4.803(5)	<i>a</i>	20.097(10)	16361	[106]
Ba ₅ Cd ₂ Sb ₄ O ₂	Own	<i>C2/m</i>	<i>mS26</i>	17.247(7)	4.9279(18)/132.558(4)	12.240(5)	423458	[107]
Nd ₁₀ Au ₃ As ₈ O ₁₀	Own	<i>I4/m</i>	<i>tI62</i>	9.1503(14)	<i>a</i>	14.579(3)	428964	[108]
Sm ₁₀ Au ₃ As ₈ O ₁₀	Nd ₁₀ Au ₃ As ₈ O ₁₀	<i>I4/m</i>	<i>tI62</i>	9.0836(10)	<i>a</i>	14.352(2)	428962	[108]

Table 2: (continued)

Compound	Structure type	Space group	Pearson symbol	a , Å	b , Å/ β (°)	c , Å	ICSD collection code	Reference
LT-Nd ₁₀ Pd ₃ As ₈ O ₁₀	Own	$C2/c$	$mS124$	12.709(1)	14.690(1)/135	17.973(1)	— ^a	[109]
HT-Nd ₁₀ Pd ₃ As ₈ O ₁₀	Nd ₁₀ Au ₃ As ₈ O ₁₀	$I4/m$	$tI62$	9.005(1)	a	14.735(2)	— ^a	[109]
Sm ₁₀ Pd ₃ As ₈ O ₁₀	Nd ₁₀ Au ₃ As ₈ O ₁₀	$I4/m$	$tI62$	8.948(1)	a	14.523(4)	— ^a	[109]
Eu ₅ Zn ₂ As ₅ O	Eu ₅ Cd ₂ Sb ₅ F	$Cmcm$	$oS52$	4.3457(11)	20.897(5)	13.571(3)	2004823	[110]
Eu ₅ Cd ₂ As ₅ O	Eu ₅ Cd ₂ Sb ₅ F	$Cmcm$	$oS52$	4.4597(9)	21.112(4)	13.848(3)	2004824	[110]
Ba ₅ Cd ₂ Sb ₅ O _{1-x}	Eu ₅ Cd ₂ Sb ₅ F	$Cmcm$	$oS52$	4.9582(5)	23.346(2)	15.2796(14)	421814	[111]
Eu ₅ Cd ₂ Sb ₅ O	Eu ₅ Cd ₂ Sb ₅ F	$Cmcm$	$oS52$	4.7088(5)	21.965(2)	14.5982(15)	261244	[112]
La ₂ AuP ₂ O	La ₂ AuP ₂ O	$C2/m$	$mS24$	15.373(3)	4.2739(8)/131.02(1)	10.092(2)	423802	[113]
Ce ₂ AuP ₂ O	La ₂ AuP ₂ O	$C2/m$	$mS24$	15.152(4)	4.2463(8)/130.90(2)	9.992(2)	425401	[114]
Pr ₂ AuP ₂ O	La ₂ AuP ₂ O	$C2/m$	$mS24$	15.036(4)	4.2277(8)/130.88(2)	9.930(2)	425402	[114]
Nd ₂ AuP ₂ O	La ₂ AuP ₂ O	$C2/m$	$mS24$	15.0187(5)	4.2085(5)/131.12(1)	9.903(3)	425403	[114]
Ce ₉ Au _{5-x} As ₈ O ₆	Own	$Pnnm$	$oP116$	13.2164(6)	40.730(3)	4.2396(2)	431599	[115]
Pr ₉ Au _{5-x} As ₈ O ₆	Ce ₉ Au _{5-x} As ₈ O ₆	$Pnnm$	$oP116$	13.1501(4)	40.5287(8)	4.2068(1)	431600	[115]

^aICSD code unavailable.

3.3.1 Mixed-cation quaternary compounds

3.3.1.1 Quaternary $(RE, Ca)_mPn_nO_m$ phases

Iso- or aliovalent substitutions on the cationic sites in ternary oxypnictide phases often result in the formation of quaternary solid solutions with the same structures. The $Ca_2RE_7Pn_5O_5$ series discussed in the previous section [68] is an excellent example. These phases crystallize with $La_9Sb_5O_5$ -type, typical for the respective ternary compounds [49]. However, incorporating another cation often causes structural perturbations, although crystal structures of ternary and respective quaternary phases remain similar as was previously described for RE_3PnO_3 and $(RE^I RE^{II})_3PnO_3$ compounds.

Several other quaternary derivatives of $RE_mPn_nO_m$ (RE = rare-earth metal; Pn = pnictogen) ternary oxypnictides offer the formation of structures barely existing for ternary phases. For instance, the family of quaternary oxyantimonides $(RE, Ca)_mSb_nO_m$ with $m = 4$ adopt the tetragonal crystal system with the space group $I4/m$, Pearson symbol $tI18$ and exist as quaternary solid solutions described by the approximate composition of $CaRE_3SbO_4$ (RE = Ce–Nd, Sm, Gd) [58]. The structural framework can be described as corner-sharing $[O_2(RE, Ca)_6]$ blocks made by two edge-sharing O-centered tetrahedra (Figure 4). Ca and RE atoms share the same atomic site in ca. 3:1 ratio, thus providing a charge-balanced composition $(Ca^{2+})(RE^{3+})_3(Sb^{3-})(O^{2-})_4$, which corroborates well with experimentally confirmed semiconducting behavior.

Atomic arrangements in the quaternary $Ca_2RE_8Sb_3O_{10}$ phases (RE = Pr, Nd, Sm, Gd, Tb) are also similar to the previously described ternary and quaternary oxyantimonides,

such as $CaRE_3SbO_4$ and RE_3SbO_3 (Figure 4), although these quaternary compounds crystallize with a different space group $C2/m$, Pearson symbol $mS46$ [58]. Electrical resistivity dependence of temperature for the $Ca_2RE_8Sb_3O_{10}$ compounds also exhibits semiconducting behavior despite the unbalanced electron count for $(Ca^{2+})_2(RE^{3+})_8(Sb^{3-})_3(O^{2-})_{10}(h^+)$. The origin of such behavior was explained by the localization of Sb p-states near the Fermi level, which arises from the highly disordered Sb layers in the structure.

3.3.1.2 Other transition-metal-free quaternary $(A, AE)Pn-O$ phases

Admixing monovalent alkali metal (A) and divalent alkaline-earth metal (AE) also enhances structural diversity in pnictide oxides. For instance, two ternary Zintl oxypnictides with formula $KBa_{11}Pn_7O_2$ (Pn = P, As) were synthesized by the direct reaction between $BaPn$, Ba, K, and BaO [70]. They crystallize with the space group $Fddd$, Pearson symbol $oF168$ with own structure type. The structure contains infinite zigzag chains, $^1[Ba_4Ba_{22}O]$ of oxygen-centered corner-sharing $[O Ba_6]$ octahedra, connected by linear strings along the a -axis built of alternating isolated Pn^{3-} atoms and $[Pn_2]^{4-}$ dimers (Figure 8a). Ba and K atoms mixed-occupy both cationic atomic sites with an approximate ratio Ba:K = 11:1, which results in the charge-balanced notation $(Ba^{2+})_{11}(K^+)(Pn^{3-})_5[Pn_2]^{4-}(O^{2-})_2$ according to the Zintl–Klemm concept.

Another example of quaternary pnictide oxide phase with two highly electropositive cations is described with the formula ABa_4Pn_3O (A = K, Rb; Pn = Sb, Bi) [29, 71, 72, 116]. These compounds can be synthesized with the mixture of

Figure 8: Crystal structures of $ABa_{11}Pn_7O_2$ (a) and ABa_4Pn_3O (b). Unit cells are outlined. A atoms are pink, mixed-occupied A/AE atoms are black, AE atoms are dark-gray, Pn atoms are orange, and O atoms are red.

metals and correspondent pnictide sesquioxides in alumina crucibles, similar to the previously described Ba_3Sb_4O phase. Three known compounds (Table 2) crystallize in the tetragonal crystal system with the space group $I4/mcm$, Pearson symbol $tI36$ with Sr_5Pb_3F -type or stuffed Cr_5B_3 -type, where tetrahedral voids are filled with oxygen. The anionic substructure consists of $[Pn_2]^{4-}$ dimers and isolated Pn^{3-} and O^{2-} anions. Each atom in the $[Pn_2]^{4-}$ dimer is surrounded by six Ba^{2+} and two A^+ cations, building a twice-capped trigonal prism. Coordination polyhedron for the isolated Bi^{3-} anions resembles square antiprism of Ba^{2+} cations twice capped with K^+ , whereas O^{2-} cation is tetrahedrally coordinated by four Ba^{2+} cations (Figure 8b). Two cations are located in different sites and, unlike the previous family, are examples of daltonides, i.e., stoichiometric compounds. ABa_4Pn_3O compositions are charge-balanced Zintl phases according to the notation $(A^+)(Ba^{2+})_4[Pn_2]^{4-}(Pn^{3-})(O^{2-})$.

3.3.2 Layered multinary pnictide oxides with fluorite-type $[M_2Pn_2]$ layers

The schematic view of the fluorite type $[M_2Pn_2]$ layer is presented in Figure 1i (M = transition metal; Pn = pnictogen). $[M_2Pn_2]$ layers, as those found in the pnictides with the $ThCr_2Si_2$ structure type [117] are considered as one of the common structural blocks for layered pnictides and pnictide oxides with superconducting properties. There are at least 12 known structure types where $[M_2Pn_2]$ layers are observed. Most of these structures have been comprehensively discussed in the previous reviews [9–12], however, some structure types are relatively recent and require additional attention.

3.3.2.1 ZrCuSiAs-type

More than 150 quaternary oxypnictides are known for the family of compounds with the general formula $REMPnO$ (RE = lanthanide or actinide; M = d-metal; Pn = pnictogen). “1–1–1–1” phases crystallize with the space group $P4/nmm$, Pearson symbol $tP8$, with ZrCuSiAs-type of structure.

A structural description for quaternary compounds with ZrCuSiAs structure can be considered as two different layers, fluorite-type $[M_2Pn_2]$ and anti-fluorite-type $[RE_2O_2]$, both with tetrahedral coordination moieties (Figure 1i). The first layer is formed by edge-sharing $[MPn_4]$ tetrahedra (M = transition metal), where M atoms form square nets with Pn atoms residing above and below. The second layer can be described with oxygen atoms filling tetrahedral voids between electropositive (usually rare-earth) metals (Figure 9a). Interaction between these layers is weak yet noticeable enough to question the distinct layering [6].

Most of the “1–1–1–1” pnictide oxides can be considered as electron-precise Zintl-like phases according to the charge-balanced notation of $(RE^{3+})(M^{2+})(Pn^{3-})(O^{2-})$ or $(RE^{4+})(M^+)(Pn^{3-})(O^{2-})$. Such charge-partitioning decently describes compounds with tetravalent cation species such as $Th^{4+}Cu^+Pn^{3-}O^{2-}$, yet, calculated charge transfer between cationic $[Th_2O_2]^{4+}$ and anionic $[Cu_2Pn_2]^{4-}$ layers were shown to be noticeably smaller compared to such fully ionic approximation [118]. On the other hand, quantitative XPS analysis for Ce-bearing phases, $CeMnSbO$ and $CeZnSbO$, suggested more complicated charge assignments described as $[Ce^{3.9+}O^{2-}][Mn^{2.8+}Sb^{3-}]$ and $[Ce^{3.3+}O^{2-}][Zn^{2+}Sb^{3-}]$, respectively [119]. Despite the formal charge balance, many “1–1–1–1” phases are multi-band metals

Figure 9: Most common families of layered pnictide oxides with fluorite-type $[M_2Pn_2]$ layers (blue) exemplified by the crystal structures of selected representatives. Anti-fluorite-type $[AE_2O_2]$ layers are depicted in red. The atom color codes are presented in the formula labels. The unit cells are outlined in black.

with observed superconducting transition, thus they can be barely described as members of the Zintl phases family.

Both direct and flux reactions, among other synthetic approaches, are known to be most successful for the synthesis of $REMPnO$ phases. Metallic Sn or a NaCl/KCl mixture can be used as a flux media, while the source of oxygen usually originates from the loaded oxides, RE_2O_3 , MO , or Pn_2O_3 . While the vast majority of the known oxypnictides within this class are thermally stable, we would like to mention two phases, $CeZnPO$ and $PrZnPO$, which exhibit high-temperature phase transition, with high-temperature modification crystallizing in $NdZnPO$ structure type, *vide infra* [74].

Tremendous interest in “1–1–1–1” oxypnictide systems emerged after the report of high-temperature superconductivity in the iron-arsenides $\text{LaFeAsO}_{1-x}\text{F}_x$ [120], LaFePO [121], and LaNiPO [122], to name a few. However, this class of compounds is also known for its interesting magnetic behavior, optical and optoelectronic properties [6]. This class also deserves a brief discussion of thermoelectric properties, which were studied for several quaternary and

quinary pnictide oxides such as $REMPnO$ [123, 124] and $RE_{1-x}AE_xZnPnO$ (RE = lanthanides; AE = Ca, Sr; M = Zn, Mn; Pn = As, Sb) [125–128]. These phases exhibit large thermopower values and low thermal conductivity values, yet high electrical resistivity values limit their applicability for thermoelectric devices.

The vast majority of $ZrCuSiAs$ -based pnictide oxides, their crystal chemistry, magnetic and superconducting properties were comprehensively discussed in previous reviews [6, 8, 129], summarizing the data available for almost all known representatives. Therefore, we prefer to avoid surplus discussion, instead referring the reader to the previously reported works [6, 129, 130], where the complete list of known “1–1–1–1” quaternaries with $ZrCuSiAs$ -type can be found. The current report provides structural parameters for a single example of this phase (Table 2) to introduce typical unit cells for $ZrCuSiAs$ -type structure.

3.3.2.2 $\text{RbSm}_2\text{Fe}_4\text{As}_4\text{O}_2$ -type

Successful block-layer structural design of the intergrowth structures requires a proper lattice match and charge

transfer between distinct block layers, as summarized in the recent report [131]. Excellent examples of such composite materials are $ARE_2Fe_4As_4O_2$ ($A = K, Rb, Cs$; $RE = Nd, Sm, Gd-Ho$) phases, or the so-called “1–2–4–4–2” family, which crystallizes with the space group $I4/mmm$, Pearson symbol $tI26$ with the $KCa_2Fe_4As_4F_2$ structure. Its structure is made of alternating blocks of AFe_2As_2 , and $2REFeAsO$ structures with different types of bonding occurring in isolating $[RE_2O_2]$ layers and double asymmetric $[Fe_2As_2]$ layers (Figure 9) [76, 132, 133]. Due to the lack of precise single-crystal X-ray diffraction or synchrotron data for the “1–2–4–4–2” structure, a single entry on $RbSm_2Fe_4As_4O_2$ in Table 2 exemplifies crystallographic information for this phase.

3.3.2.3 $Ba_2Cd_{3-x}Bi_3O$ -type

$Ba_2Cd_{3-x}Bi_3O$ is the only example of its structure and crystallizes in the tetragonal crystal system with the space group $I4/mmm$, Pearson symbol $tI36$ [77]. This phase was reported as an unadventurous product in the lead-flux reaction targeting a ternary pnictide phase performed in the alumina crucible. The layered structure is complex and can be viewed as an intergrowth of $BaCdBiO$ slab (ZrCuSiAs-type) and $BaCd_2Bi_2$ slab with the $CeMg_2Si_2$ -structure. PbO -type layers of fused $[CdBi_4]$ tetrahedra are alternately stacked along the c -axis with BaO slabs and Bi square-nets (Figure 9). Partial occupancy of one of the Cd sites results in the electron-deficient compositions according to the Zintl-Klemm notation $(Ba^{2+})_2(Cd^{2+})_{3-x}(Bi^{3-})_3(O^{2-})(h^+)_{2x}$.

3.3.2.4 $Th_2Ni_{3-x}P_3O$ -type

Ternary $Th_2Ni_{3-x}P_3O$ ($x \approx 0.5$) phase was first observed as an impurity product in samples aimed at preparing $ThNi_2P_2$ phosphide in an alumina crucible, which served as an inadvertent source of oxygen. However, this compound can also be readily synthesized from the mixture of elements and ThO_2 [78]. It crystallizes in its own structure type with the space group $P4/nmm$, Pearson symbol $tP18$. Two nickel atoms are partially occupied and tetrahedrally coordinated by phosphorus atoms, and both have four nickel neighbors forming a square. These edge-sharing tetrahedra form three fluorite-type $[Ni_2P_2]$ layers interconnected by slightly elongated P–P bonds (2.34 Å), thus forming a complex $[Ni_{3-x}P_3]$ multilayered slab (Figure 9). Oxygen atoms are located in the tetrahedral voids formed by Th atoms, thus forming an oxide *anti*-fluorite-type $[Th_2O_2]$ layer, altering a multilayered slab described above. Thus, the structure resembles $ZrCuSiAs$ -type with different stacking sequences. The charge balance in this quaternary phase has been suggested to be $(Th^{4+})_2(Ni^+)_2(Ni^0)[P_2]^{5-}(P^{3-})(O^{2-})$, where zero-charged Ni has been

considered in the middle of the triple-layer slab. An unusual formal charge of 5– for $[P-P]$ structural fragment was suggested due to the elongated interatomic distance between phosphorus atoms exceeding the sum of covalent radii.

3.3.2.5 $U_2Cu_2As_3O$ -type

$U_2Cu_2As_3O$ was also serendipitously synthesized in a reaction where the initial introduction of oxygen was not intended. The compound came into being from the slight oxidation of the starting materials in the air or from outgassing the silica tubes at high temperatures [79]. The only phase of this structure type crystallizes with the space group $P4/nmm$, Pearson symbol $tP16$. It consists of three types of layers, a fluorite-type $[Cu_2As_2]$, an *anti*-fluorite-type $[U_2O_2]$, and a covalently bonded square-planar net of $[As_4]$ layers (Figure 9). The latter has been found in several “1–1–2” pnictides [13] yet remains rare for the pnictide oxides. An electron charge-balance can be broken down to the $(U^{4+})_2(Cu^+)_2(As^{3-})_2(As^{2-})(O^{2-})$ notation. While $U_2Cu_2As_3O$ remains only the oxypnictide with this structure, a prior report on $U_4Cu_4P_7$ was later revised in favor of $U_2Cu_2P_3O$ composition, which was believed to be isostructural to the described quaternary arsenide phase [79].

3.3.2.6 Sm_2CuAs_3O -type

Crystals of Sm_2CuAs_3O were obtained as a by-product of the alkali-halide flux synthesis targeted in the $SmCuAs_2$ phase [80]. It was believed the oxygen originated from silica tubes, whereas attempts to synthesize this phase from different oxides were not successful. Sm_2CuAs_3O crystallizes in the orthorhombic crystal system with the space group $Pnma$, Pearson symbol $oP28$ and exemplifies the only pnictide oxide phase of distorted Hf_2CuGe_4 structure type. Its layered crystal structure contains fluorite-type $[Cu_2As_2]$ and *anti*-fluorite-type $[Sm_2O_2]$ layers that were described previously. However, these layers are separated by planar sheets of Sm and distorted square nets of As atoms, which have to be preferably described as planar infinite twinned zigzag chains $[As^-]_n$ running along the b -axis (Figure 9). Such chains are the hallmark of this structure and are unique for the quaternary oxypnictides with d metals. The Zintl-Klemm concept is also applicable for the discussed compound, which is believed to be electron-balanced according to the notation $(Sm^{3+})_2(Cu^+)(As^-)_2(As^{3-})(O^{2-})$. While semiconducting behavior for this compound is expected, a structural similarity with known superconductive phases hints at possible superconductivity transition.

3.3.2.7 $\text{La}_3\text{Cu}_4\text{P}_4\text{O}_2$ -type

Unlike previously described layered pnictide oxides, where one member represented one structure type, a small family of lanthanide transition metal pnictide oxides $\text{RE}_3\text{M}_4\text{Pn}_4\text{O}_2$ ($\text{RE} = \text{La-Nd, Sm}$; $\text{M} = \text{Ni, Cu}$ $\text{Pn} = \text{P, As}$) contain several compounds which crystallize with the space group $I4/mmm$, Pearson symbol $tI26$ [81–85, 134]. Compounds adopt a layered crystal structure with own structure, which resembles an ordered $\text{Zr}_3\text{Cu}_4\text{Si}_6$ -type. The structure is formed by *anti*-fluorite type $[\text{RE}_2\text{O}_2]$ (B) layers made of condensed edge-sharing $[\text{ORE}_{4/4}]$ tetrahedra stacked with fluorite-type $[\text{M}_2\text{Pn}_2]$ (A) layers tetrahedra in the sequence of $-\text{B}-\text{B}-\text{A}-$ (Figure 9). Two $[\text{M}_2\text{Pn}_2]$ layers are linked by $\text{Pn}-\text{Pn}$ bonds, similar to the previously described $\text{Th}_2\text{Ni}_{3-x}\text{P}_3\text{O}$ phase. The presence of two different $[\text{Pn}_2]^{4-}$ and Pn^{3-} units was determined by the ^{31}P solid-state NMR method on P-bearing phases. Precise structural refinement showed partial occupancy for the oxygen position resulting in ca. 1.5 oxygen atoms per formula unit. Therefore, chemical bonding can be rationalized with the charge-balance formulation $(\text{RE}^{3+})_3(\text{Cu}^+)_4[\text{Pn}_2]^{4-}(\text{Pn}^{3-})_2(\text{O}^{2-})_{1.5}$ and is expected to behave as semiconductors. However, “3–4–4–2” phases with Ni or Cu phases exhibit metallic behavior with rare examples of superconducting transition ($T_c = 2.2\text{ K}$) as was reported for $\text{La}_3\text{Ni}_4\text{P}_4\text{O}_2$ compound [81, 134, 135].

$\text{La}_5\text{Cu}_4\text{Pn}_4\text{O}_4\text{Cl}_2$ ($\text{Pn} = \text{P, As}$) can be considered a structural derivative of the “3–4–4–2” phase. These complex mixed-anion quinary compounds can be readily prepared from a cold-pressed pellet of La, Cu_2O , P, LaCl_3 (phosphide), and La, As, Cu_2O , LaOCl (arsenide) from NaCl flux [83, 85]. It adopts a new structure type with space group $I4/mmm$, Pearson symbol $tI38$. It can be described as an intergrowth of LaOCl slabs, ZrCuSiAs - and $\text{La}_3\text{Cu}_4\text{P}_4\text{O}_2$ -related slabs (*vide supra*) (Figure 9). Structural relationships between these slabs can be expressed as $2\text{LaOCl} + \text{La}_3\text{Cu}_4\text{P}_4\text{O}_2 = \text{La}_5\text{Cu}_4\text{P}_4\text{O}_4\text{Cl}_2$, which makes $\text{La}_5\text{Cu}_4\text{As}_4\text{O}_4\text{Cl}_2$ a strongly anisotropic hybrid material composed of covalently bonded metallic $[\text{CuAs}_{4/4}]$ layers located within ionic insulating oxide and chloride blocks. This phase is one-electron short according to the fully ionic partitioning notation $(\text{La}^{3+})_5(\text{Cu}^+)_4(\text{As}^{3-})_2[\text{As}_4]^{4-}(\text{O}^{2-})_4(\text{Cl}^-)_2(h^+)$.

3.3.2.8 $\text{Sr}_2\text{Mn}_3\text{As}_2\text{O}_2$ -type

Several layered quaternary oxypnictides $\text{AE}_2\text{M}_3\text{Pn}_2\text{O}_2$ ($\text{AE} = \text{Sr, Ba}$; $\text{M} = \text{Cr, Mn, Zn}$; $\text{Pn} = \text{P, As, Sb, Bi}$) were obtained by the high-temperature reaction between correspondent amounts of metals and/or metal oxides. They crystallize in their own structure type, space group $I4/mmm$, Pearson symbol $tI18$, and are considered as two-dimensional magnetic materials with high magnetic

ordering temperatures [7, 9, 86–88, 136–139]. The crystal structure of the $\text{AE}_2\text{M}_3\text{Pn}_2\text{O}_2$ family of compounds can be described as a 1:1 intergrowth of fluorite-type $[\text{M}_2\text{Pn}_2]$ layers, similar to those in BaAl_4 -type with tetrahedral coordination of M , and $[\text{M}'\text{O}_2]$ layers with square-planar coordination of metal, which occur in cuprate superconductors in the form of $[\text{CuO}_2]$ planes (Figure 9). Sr^{2+} and Ba^{2+} cations serve as countercharges and are located between anionic layers. “2–3–2–2” phases are formally charge-balanced according to the notation $(\text{AE}^{2+})_2(\text{Mn}^{2+})_3(\text{Pn}^{3-})_2(\text{O}^{2-})_2$ suggesting semiconducting behavior.

Ordered quinary variants of $\text{Sr}_2\text{Mn}_3\text{As}_2\text{O}_2$ structure were reported as well. A clear layer separation results in the formation of phases, where different 3d-metals, such as Cr, Fe, Cu, or Zn, substitute Mn atoms predominantly in $[\text{Mn}_2\text{As}_2]^{2-}$ layers. Resulting quinary compounds with formulae $\text{Sr}_2\text{Mn}_{2.23}\text{Cr}_{0.77}\text{As}_2\text{O}_2$ [93], $\text{Sr}_2\text{CrFe}_2\text{As}_2\text{O}_2$ [140], $\text{Sr}_2\text{Mn}_2\text{CuAs}_2\text{O}_2$ [92], $\text{AE}_2\text{MnZn}_2\text{As}_2\text{O}_2$ [90,91], and $\text{Sr}_2\text{CrCo}_2\text{As}_2\text{O}_2$ [141] are made up from square planar $[\text{MnO}_2]^{2-}$ or $[\text{CrO}_2]^{2-}$ layers with layers of $[\text{M}_2\text{As}_2]^{2-}$ tetrahedra interspersed by alkaline-earth cations.

3.3.2.9 $\text{Sr}_2\text{ScFeAsO}_3$ -type

The family of quinary $\text{AE}_2\text{M}'\text{M}''\text{PnO}_3$ ($\text{AE} = \text{Ca, Sr, Ba}$; $\text{M}' = \text{Al, Sc, Ti, V, Cr}$; $\text{M}'' = \text{Fe, Cr, Co}$; $\text{Pn} = \text{P, As}$) superconductive phases crystallizes in the tetragonal crystal system with the space group $P4/nmm$, Pearson symbol $tP16$ with $\text{Sr}_2\text{CuGaSO}_3$ structure [94, 95, 142–148]. These layered pnictide oxides can be readily synthesized by the solid-state reaction between metals, metal oxides, and/or binary metal pnictides. The crystal structure can be described as alternatively stacking fluorite-type $[\text{Fe}_2\text{Pn}_2]$ layers and perovskite-type $\text{AE}_4\text{M}_2\text{O}_6 (=2\text{AE}_2\text{MO}_3)$ layers as presented in sky-blue in Figure 9. Five O atoms coordinate M' atom in a square-pyramidal fashion. Therefore, their composition can also be described as $(\text{AE}_4\text{M}'_2\text{O}_6)(\text{M}''_2\text{Pn}_2)$, emphasizing the presence of constituting layers. $\text{Sr}_2\text{ScFePO}_3$ and $\text{Sr}_2\text{VFeAsO}_3$ undergo superconducting transition at $T_c \approx 17$ and 37 K respectively under ambient pressure [142, 149], whereas V-bearing samples exhibit the relatively high value of $T_c \approx 46\text{ K}$ under high pressure [150].

3.3.2.10 $\text{Sr}_3\text{Sc}_2\text{Fe}_2\text{As}_2\text{O}_5$ -type

$\text{AE}_3\text{Sc}_2\text{M}_2\text{As}_2\text{O}_5$ ($\text{AE} = \text{Sr, Ba, Eu}$; $\text{M} = \text{Cr, Fe, Co, Ni}$) layered oxide arsenides were also synthesized by high-temperature solid-state method from the mixture of metals, metal oxides and/or metal arsenides [96, 97, 144, 151–155]. These phases crystallize with space group $I4/mmm$, Pearson symbol $tI28$, with $\text{Sr}_3\text{Fe}_2\text{O}_5\text{Cu}_2\text{S}_2$ -type structure. Similar to the previously described pnictide oxide phases, the “3–2–2–2–5” family of compounds can be described as a

layered structure where fluorite-type $[M_2As_2]$ layers stack alternately with the perovskite oxide layer $(ScO_2)(AEO)$ (ScO_2) (Figure 9). Two AE atoms exhibit 12-fold (to 12 oxide anions) and 8-fold coordination (to four oxide and four arsenide anions). Scandium is surrounded by five oxide anions in square-pyramidal coordination. A homologous series was observed for the “3–2–2–2–5” family, which can be described as fluorite-type $[Fe_2As_2]$ layers separated by double or triple perovskite layers. Resulting compositions can be generally described as $(M_2As_2)[AE_{n+1}M'_nO_y]$ or $(M_2As_2)[AE_{n+2}M'_nO_y]$ ($AE = Ca, Sr, Ba; M' = Mg, Al, Sc, Ti; n = 3–5$) with reported compositions of $Ba_4Sc_2Ni_2As_2O_6$ (similar to the $Sr_2ScFeAsO_3$ -type), $Sr_4(Sc,Ti)_3Fe_2As_2O_8$, $Ba_4Sc_3Ni_2As_2O_8$, $Ca_5(Sc,Ti)_4Fe_2As_2O_{11}$, and $Ca_6(Sc,Ti)_5Fe_2As_2O_{14}$ to name a few [154–159].

Sr- and Ba-bearing samples are not superconductive and show no structural anomaly or magnetic ordering [151]. Rare examples of superconductive compounds within this family have composition $Ca_3Al_2Fe_2Pn_2O_{5-y}$ ($Pn = P, As$) with a transition temperature T_c of ca. 30 K for arsenide and 16.6 K for phosphide [153]. However, the correspondent phosphide-arsenide solid solution shows no evidence of superconductive behavior [160]. Compounds in $(Fe_2As_2)[Ca_{n+1}M'_nO_y]$ series are also superconductive with relatively high T_c values of up to 42 K [156].

3.3.3 Layered multinary pnictide oxides without fluorite-type $[M_2Pn_2]$ layers

3.3.3.1 NdZnPO-type

As was previously mentioned, several “1–1–1–1” quaternary phases, such as $CeZnPO$ and $PrZnPO$ with $ZrCuSiAs$ -type, undergo high-temperature phase transition with the formation of rhombohedral modification with $NdZnPO$ structure, space group $R\bar{3}m$, Pearson symbol $hR8$ [74]. Several $REZnPO$ compositions ($RE = Y, La-Nd, Sm, Gd, Dy, Ho$) are known for phosphides [73–75]. Despite similar compositions in “1–1–1–1” phases, the structures of the two modifications are slightly different. Both $[RE_2O_2]$ and $[M_2Pn_2]$ layers in $NdZnPO$ -type are similar to those in La_2O_3 or $CaAl_2Si_2$ structures, with the difference of $[M_2Pn_2]$ is considered as *anti*- $[La_2O_2]$ layer (Figure 10). Both layers are distinctly separated and follow $ABA'B'A''B''$ stacking sequence in opposite to the $ABAB$ sequence in the low-temperature $ZrCuSiAs$ -type modification (Figure 10). A charge-balance in the $NdZnPO$ structure is identical to those in $ZrCuSiAs$ -type pnictide oxides, and a distinct separation of rare-earth–oxygen and zinc–phosphorous layers is also observed.

Figure 10: Crystal structure of layered rhombohedral $NdZnPO$ structure. Unit cell is outlined. Nd atoms are dark-gray, Zn atoms are blue, P atoms are orange, and O atoms are red.

3.3.3.2 $Na_2Ti_2As_2O$ -type

$Na_2Ti_2Pn_2O$ phases ($Pn = As, Sb$) crystallize in their own structure type with the space group $I4/mmm$, Pearson symbol $tI14$, which can also be considered ordered *anti*- K_2NiF_4 -type [98]. The successful synthesis should start with the Na_2O/Na_2O_2 mixture, which serves as the source of oxygen [69]. An anionic substructure of this family of compounds consists of edge-sharing $\infty 2[Ti_{4/2}Pn_2O_{4/4}]^{2-}$ layers separated by double layers of Na^+ cations and resembles previously discussed “4–2–1” phases (Figure 11) [98]. $[Ti_2Pn_2O]^{2-}$ layer contains Ti_2O square-net of the *anti*-

Figure 11: Crystal structure of $\text{Na}_2\text{Ti}_2\text{As}_2\text{O}$ (top) and $\text{BaTi}_2\text{As}_2\text{O}$ (bottom). Unit cells are outlined. Na atoms are pink, Ba atoms are dark-gray, Ti atoms are blue, As atoms are orange, and O atoms are red.

CuO_2 type, similar to those in superconductive cuprates. Each Ti atom can also be considered octahedrally coordinated by two O atoms and four Pn atoms, resembling previously discussed “4–2–1” phases. O atom can be viewed as coordinated by four Ti in a square-planar fashion.

The temperature dependent electrical resistivity for these compounds exhibits an anomaly reminiscent of charge-density-wave/spin-density-wave materials. An electron balance in $\text{Na}_2\text{Ti}_2\text{Pn}_2\text{O}$ quaternary phases can be

described according to the notation $(\text{Na}^+)_2(\text{Ti}^{3+})_2(\text{Pn}^{3-})_2(\text{O}^{2-})$. The As-bearing compound shows an insulator-to-insulator transition around 135 K, whereas the Sb-bearing phase shows a metal-to-metal transition around 120 K.

$\text{Yb}_4\text{Sc}_4\text{Sb}_4\text{O}$ is a single representative in the correspondent compositional diagram, and it was synthesized in an attempt to produce the ScYbSb ternary compound [99]. However, the latter La_2Sb -type phase exists if stabilized by oxygen atom similar to the previously described $\text{RE}_4\text{Pn}_2\text{O}$ phases and $\text{Na}_2\text{Ti}_2\text{Pn}_2\text{O}$ phase, with the difference of ca. 0.5 site occupation factor assigned for the oxygen atom. Structures of $\text{Yb}_4\text{Sc}_4\text{Sb}_4\text{O}$ and $\text{Na}_2\text{Ti}_2\text{Pn}_2\text{O}$ are identical and, therefore, the former will not be discussed in depth.

3.3.3.3 $\text{BaTi}_2\text{As}_2\text{O}$ -type pnictide oxides and derivatives

$\text{BaTi}_2\text{Pn}_2\text{O}$ ($\text{Pn} = \text{As}, \text{Sb}, \text{Bi}$) phases are also structurally related to the $\text{Na}_2\text{Ti}_2\text{Pn}_2\text{O}$ compounds with the difference of single layer of Ba atoms along the c -axis (Figure 11). Compounds crystallize in the tetragonal crystal system with the space group $P4/nmm$, Pearson symbol $tP6$ with own structure type [100–102]. The resistivity studies for the As-bearing exhibit anomaly at 200 K, which was suggested to be a spin-density wave or phase transition [100]. Suppressing this anomaly by doping carriers often results in emerging of superconductivity. Indeed, the isostructural Sb-bearing phase exhibits superconducting transition at $T_c = 1.2$ K [101], whereas critical temperature T_c for its Na- and K-doped quaternary phases increases to 5.5 and 6.1 K, respectively [161, 162]. Heavier Bi-bearing analog indicates an increased T_c of 4.6 K [102]. A recent study reported pressure-induced transformation of $\text{BaTi}_2\text{Pn}_2\text{O}$ structure associated with unusual Pn-Pn bond elongation ($\text{Pn} = \text{As}, \text{Sb}$) [163], yet such structural rearrangement results in the decreased T_c values for Na-doped $\text{BaTi}_2\text{Sb}_2\text{O}$ solid solutions [164]. However, T_c for the superconducting sample of $\text{BaTi}_2\text{Bi}_2\text{O}$ monotonically increased with the pressure up to 4.0 GPa followed by saturation [165]. More insights on superconductivity in the titanium pnictide oxides can be found in the recent review [166].

The superconductive nature of $\text{BaTi}_2\text{Pn}_2\text{O}$ phases stimulated synthetic efforts to synthesize more complex layered oxypnictides based on $[\text{Ti}_2\text{Pn}_2\text{O}]^{2-}$ slabs. Beyond bare alkali and alkali-earth metal cations, complex units, such as $[(\text{SrF}_2)_2]^{2+}$ or $[(\text{SmO})_2]^{2+}$ serve as interlayered cations [167]. In addition, the previously discussed modular approach can also be applied for the superconductive systems based on $[\text{Ti}_2\text{Pn}_2\text{O}]^{2-}$. For instance, the $\text{BaTi}_2\text{As}_2\text{O}$ phase can be modified to synthesize quinary compounds with the formula $\text{Ba}_2\text{Ti}_2\text{M}_2\text{As}_4\text{O}$ ($\text{M} = \text{Fe}, \text{Cr}$), which can be viewed as an intergrowth of layered BaM_2As_2 and $\text{BaTi}_2\text{As}_2\text{O}$

phases, thus containing $[M_2As_2]$ layers and $[Ti_2O]$ sheets (Figure 9) [103, 104]. Such “2–2–2–4–1” phases crystallize with space group $I4/mmm$, Pearson symbol $tI22$ with an expected c -axis of $c_{“2-2-2-4-1”} = c_{“1-2-2”} + 2c_{“1-2-2-1”}$. While these phases contain the fluorite-type $[M_2As_2]$ layer, they also belong to the group of compounds discussed in Section 3.3.2. However, they are direct structural derivatives of the $BaTi_2Pn_2O$ phases, therefore presented herein.

3.3.3.4 $Ba_2Mn_2As_2O$ -type and $Ba_2Mn_2Sb_2O$ -type

$Ba_2Mn_2Pn_2O$ ($Pn = As, Sb, Bi$) oxypnictides were synthesized at high temperatures from the mixture of metals and Pn_2O_3 or MnO_2 powder as the source of oxygen [105, 106, 168]. Members of this family adopt two different structure types, with arsenide oxide member crystallizing in its own structure type, monoclinic crystal system, space group $C2/m$, Pearson symbol $mS14$, whereas heavier oxypnictides adopt hexagonal crystal system, space group $P6_3/mmc$, Pearson symbol $hP14$ with own structure. Both structures share similar features and are formed by the same type of distorted $[MnSb_3O]$ corner-sharing tetrahedra linked together by O atoms, thus forming linear Mn–O–Mn fragment, whereas edge-sharing connection is realized through the Sb/Bi atoms (Figure 12). However, layered anionic substructures are slightly different for both types of compounds. $Ba_2Mn_2As_2O$ phase is single-layered, composed of infinite, corner-sharing $[Mn_2O]$ and edge-sharing $[Mn_2Sb_2]$ connections (Figure 12a), whereas heavier oxypnictides form anionic double layers $[Mn_2Sb_2O]^{2-}$ oriented parallel to the ab -plane (Figure 12b). While O atoms bridge sublayers, a prolongation is achieved via edge-sharing $[Mn_2Pn_2]$ connections.

Physical properties were studied for the Sb-bearing compound. Magnetic susceptibility and specific heat show anomalies at $T_N = 60$ K, consistent with antiferromagnetic

ordering. Charge balanced notation $(Ba^{2+})_2(Mn^{2+})_2(Sb^{3-})_2(O^{2-})$ suggest a semiconducting behavior, which corroborates well with both calculations and experiment reporting energy gaps of ca. 0.686 and 0.59 eV, respectively [168].

3.3.3.5 $Ba_5Cd_2Sb_4O_2$ -type

A quaternary oxyantimonide, $Ba_5Cd_2Sb_4O_2$, was also synthesized as a side product in the reaction targeted in the ternary pnictide phase [107]. It crystallizes in the monoclinic crystal system with the space group $C2/m$, Pearson symbol $mS26$. The anionic substructure consists of polyanionic ${}^2_\infty[Cd_2Sb_4]^{6-}$ layers made of edge-shared $[CdSb_4]$ tetrahedra and joined through Sb–Sb dumbbell. O^{2-} anions and Ba^{2+} cations between the layers form a $[BaO]$ slab with distorted tetrahedral coordination of O atoms (Figure 13). Thus, $Ba_5Cd_2Sb_4O_2$ is considered a double-salt made of $Ba_3Cd_2Sb_4$ structure [169] with two intercalated $[BaO]$ moieties. This electron-precise phase can be rationalized as $(Ba^{2+})_5(Cd^{2+})_2(Sb^{2-})_2(Sb^{3-})_2(O^{2-})$, which is supported by the electronic structure calculations reporting a bandgap of ca. 0.3 eV, indicative of a narrow-band semiconductor.

3.3.3.6 $Nd_{10}Au_3As_8O_{10}$ -type

Four transition metal pnictide oxides $RE_{10}M_3As_8O_{10}$ ($RE = Nd, Sm$; $M = Au, Pd$) were synthesized from the mixture of rare earth elements, appropriate rare-earth sesquioxides, arsenic, arsenic oxides, and gold/palladium [108, 109]. They crystallize with the space group $I4/m$ with $Nd_{10}Au_3As_8O_{10}$ structure type, Pearson symbol $tI62$. Two different layers can be distinguished for this layered crystal structure (Figure 14). Oxide anions are tetrahedrally coordinated by rare-earth metals, thus forming positively charged $[Nd_{10}O_{10}]^{10+}$ layers made of edge-sharing tetrahedra. The second planar layer is formed by arsenic and

Figure 12: Crystal structures of monoclinic $Ba_2Mn_2As_2O$ (a) and hexagonal $Ba_2Mn_2Sb_2O$ (b). Unit cells are outlined. Ba atoms are dark-gray, Mn atoms are blue, Pn atoms are orange, and O atoms are red.

Figure 13: Crystal structure of monoclinic $\text{Ba}_5\text{Cd}_2\text{Sb}_4\text{O}_2$ phase. Unit cell is outlined. Ba atoms are dark-gray, Cd atoms are blue, Sb atoms are orange, and O atoms are red.

Figure 14: Crystal structure of $\text{Nd}_{10}\text{Au}_3\text{As}_8\text{O}_{10}$ phase. Unit cell is outlined. Nd atoms are dark-gray, Au atoms are blue, As atoms are orange, and O atoms are red.

gold atoms, where the latter are bonded to four arsenic dumbbells in square-planar coordination or distorted rectangular coordination (Figure 1e). Such layers have been already observed in pnictide compounds with the formula $\text{Ca}_{10}(\text{MAs})_{10}(\text{Pt}_3\text{As}_8)$ (M = transition metal) [170]. While this type of coordination is common for Pd^{2+} atoms, such an environment is rare for Au. $\text{Nd}_{10}\text{Pd}_3\text{As}_8\text{O}$ exhibits a structural phase transition near 160 K according to the

resistivity data. Low-temperature modification crystallizes in monoclinic crystal system with the space group $C2/c$ (Table 2), which results from periodic displacements of the palladium atoms out of the mirror plane.

Pd-bearing compounds are charge-balanced according to the notation $(\text{Nd}^{3+})_{10}(\text{Pd}^{2+})_3(\text{As}^{2-})_8(\text{O}^{2-})_{10}$ and exhibit experimentally confirmed semiconducting behavior [109]. The electron-precise description is somewhat schematic due to the comparable electronegativity values of Pd and As, yet calculations confirm a covalent character of the layer. At the same time, resistivity measurements for isotopic gold compounds display a metallic character of studied compounds [108].

3.3.4 Non-layered multinary pnictide oxides

3.3.4.1 $\text{AE}_5\text{M}_2\text{Pn}_5\text{O}$ -type

Several quaternary phases with the formula $\text{AE}_5\text{M}_2\text{Pn}_5\text{O}_x$ ($\text{AE} = \text{Ba}, \text{Eu}$; $M = \text{Zn}, \text{Cd}$; $\text{Pn} = \text{As}, \text{Sb}$; $x = 0.5-1$) crystallize with the centrosymmetric space group $Cmcm$, Pearson symbol $oS52$, with $\text{Eu}_5\text{Cd}_2\text{Sb}_5\text{F}$ structure [110–112]. An anionic substructure can be described as one-dimensional double-stands of corner-shared MPn_4 tetrahedra with Pn-Pn bonds that connect the tetrahedra $[\text{M}_2\text{Pn}_5]^{9-}$ to form pentagonal quasi-channels with one out of five AE atoms is contained within the channels. An isolated O^{2-} anion is tetrahedrally coordinated by four AE^{2+} cations (Figure 15a). Although the initial discovery of this structural family was serendipitous, it was possible to achieve quantitative yields from reactions between elements and barium peroxide in the case of $\text{Ba}_5\text{Cd}_2\text{Sb}_5\text{O}_{0.5}$. An approximate 50%-occupancy of oxygen satisfies charge-balance conditions according to the notation $(\text{Ba}^{2+})_5(\text{Cd}^{2+})_2(\text{Sb}^{2-})_2(\text{Sb}^{3-})_3(\text{O}^{2-})_{0.5}$ and confirmed by electronic band structure calculations [111]. At the same time, Eu-bearing phases are $\text{Eu}_5\text{M}_2\text{Pn}_5\text{O}$ ($M = \text{Zn}, \text{Cd}$; $\text{Pn} = \text{As}, \text{Sb}$) are one-electron-short narrow bandgap semiconductors according to the notation $(\text{Eu}^{2+})_5(\text{M}^{2+})_2(\text{As}^{2-})_2(\text{As}^{3-})_3(\text{O}^{2-})(h^+)$, which hints at the possibility of mixed-valent $\text{Eu}^{2+}/\text{Eu}^{3+}$ state [110, 112].

3.3.4.2 $\text{La}_2\text{AuP}_2\text{O}$ -type

$\text{RE}_2\text{AuP}_2\text{O}$ ($\text{RE} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$) phosphide oxides were obtained from mixtures of the rare-earth elements, binary rare-earth oxides, gold powder, and red phosphorus in sealed silica tubes [113, 114]. Compounds crystallize in a monoclinic crystal system with the space group $C2/m$, Pearson symbol $mS24$ with $\text{La}_2\text{AuP}_2\text{O}$ structure type. The anionic substructure consists of $[\text{AuP}_2]^{4-}$ polyanions in a hexagonal rod packing motif. Such substructure is characterized by reduced dimensionality, where gold atoms

Figure 15: Crystal structures $AE_5M_2Pn_5O$ (a), RE_2AuP_2O (b), and $RE_9Au_{5-x}Pn_8O_6$ (c). Unit cells are outlined. AE and RE atoms are dark-gray, M and Au atoms are blue, Pn atoms are orange, and O atoms are red.

exhibit distorted trigonal-planar phosphorus coordination of P^{3-} anions and $[P_2]^{4-}$ dumbbells (Figure 15b). Cationic layers can be described as *cis*-edge-sharing $[ORE_{2/2}RE_{3/3}]$ tetrahedra located between polyanionic ribbons. RE_2AuP_2O phases are charge-balanced according to the notation presented to the doubled composition $(RE^{3+})_4(Au^+)_2[P_2]^{4-}(P^{3-})_2(O^{2-})_2$.

3.3.4.3 $Ce_9Au_5As_8O_6$ -type

Several RE–Au–As–O ternary system members can be described with the formula $RE_9Au_{5-x}As_8O_6$ ($RE = Ce, Pr$; $x \approx 0.09–0.25$) [115]. They have been synthesized similarly to the previously described $RE_{10}M_3As_8O_{10}$ phases with the incorporation of the rare-earth oxides into the reaction mixture. These compounds represent a new structure type and crystallize with space group $Pnnm$, Pearson symbol $oP116$. An anionic substructure consists of a complex 3D network made by $[Au_{5-x}As_8]^{(15+x)-}$ ions linked by homoa-tomic As–As dumbbells as illustrated in Figure 15c. Two gold sites exhibit positional disorder and are partially occupied, which results in departing from the charge balance. Six crystallographically independent oxygen atoms with distorted tetrahedral RE coordination are condensed in the edge-sharing linkage, which resembles a stripe oriented along the *c*-axis. Thus, $[ORE_{4/4}]$ and $[ORE_{4/3}]$ tetrahedra form $[RE_4O_3]_2^{12+}$ cationic unit, which along with RE^{3+} cations maintain charge balance described by an electron precise formula $(Pr^{3+})_9(Au^+)_5(As^{3-})_4([As_2]^{4-})(O^{2-})_6$ [115].

4 Summary and outlook

Pnictide oxides belong to the unique class of heteroanionic compounds composed of oxide (O^{2-}) and pnictide (Pn^{3-}) anions. Several hundreds of compounds formed by more than 40 elements were gathered within nine ternaries and at least 28 multinary structure types. Layered *d*-metal oxypnictides dominate compositional and structural abundancy with more than 200 compositions of 20 different structures. However, the field of pnictide oxides with 4*d*-, 5*d*-elements, or group 13 metals, is still relatively unexplored. A newfangled report on gallate pnictides $Ba_9[GaO_4]_3Pn$ ($Pn = Sb, Bi$) and Zintl phase $Ba_2[GaO_2As]$ indicates the conceptual existence of such class of materials [171].

Further developments of novel inorganic pnictide oxides are eagerly anticipated as research on such materials is aligned with the current trends in materials chemistry and physics. Exploration and study of compounds with multiple anions has attracted and will continue to attract much attention [3]. Due to the difference of radii, charge, and electronegativity for pnictide and oxide anions, dimensionality, crystal and electronic structures, and physical properties can be controlled. The presence of two different anions increases the tunability of the bandgap, thus can be beneficial for the band engineering and further tuning structure-properties relationships. The applicability of pnictide oxide systems is underestimated, focusing primarily on the superconducting properties of layered

d-metal pnictide oxides. However, the enormous structural diversity of semiconducting oxypnictides may promote different applications, such as thermoelectric, non-linear optical, or luminescent.

While explorational synthesis remain a primary approach for the discovering of novel oxypnictides, a high-throughput computational methods already show a promise in predicting hitherto unknown pnictide oxides [172]. We also point out the necessity of revising the properties of known structures, which will enhance the progress on the rapidly developing field of heteroanionic materials.

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