Expanding frontiers in materials chemistry and physics with multiple anions

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During the last century, inorganic oxide compounds laid foundations for materials synthesis, characterization, and technology translation by adding new functions into devices previously dominated by main-group element semiconductor compounds. Today, compounds with multiple anions beyond the single-oxide ion, such as oxyhalides and oxyhydrides, offer a new materials platform from which superior functionality may arise. Here we review the recent progress, status, and future prospects and challenges facing the development and deployment of mixed-anion compounds, focusing mainly on oxide-derived materials. We devote attention to the crucial roles that multiple anions play during synthesis, characterization, and in the physical properties of these materials. We discuss the opportunities enabled by recent advances in synthetic approaches for design of both local and overall structure, state-of-the-art characterization techniques to distinguish unique structural and chemical states, and chemical/physical properties emerging from the synergy of multiple anions for catalysis, energy conversion, and electronic materials.

The continuing growth of many modern technologies is driven by the development of functional solid-state materials, such as metal oxides, fluorides, and nitrides that adopt a range of structural types and compositions. The accumulation of knowledge based on experimental data (or at times "chemical intuition") and computational modeling and validations has led to extensive knowledge of these "single-anion" materials and affords further prediction of properties. Most of these results derive from variations in metal cation chemistry, as opposed to the anion, when examining structure-property relationships.

A multiple or mixed-anion compound is a solid-state material containing more than one anionic species in a single phase, such as oxyfluorides (oxide-fluoride) and oxynitrides (oxide-nitride). Unlike oxides, which exhibit diverse chemistries and structures often known from mineralogy, the structures of most mixed-anion compounds, among other aspects, are less explored with much to learn. This is readily seen when looking at the local structure of these compounds where the metal cation is bonded to more than one anionic ligand to form a heteroleptic polyhedron (Box 1). The different anionic characteristics, such as charge, ionic radii, electronegativity, and polarizability (Table 1) add new dimensions to control and tune the
Applications of oxides date back to prehistoric times, when our ancestors found useful properties from natural stones including, e.g., arrowheads, magnets, pigments, gems, and even medicines. Subsequent efforts have been devoted to improvements and hunting for new functions. The 20th century was a prosperous era, with discoveries of synthetic oxides that sustain modern technology, as exemplified by the ferroelectric BaTiO$_3$, yttria-stabilized zirconia (YSZ) for solid oxide fuel cells, and Li$_x$MnO$_2$, a cathode material for lithium batteries. The successful story of oxides (and other single-anion compounds, such as fluorides, nitrides, and chlorides) is largely due to their stability and ease of synthesis, along with development of structural characterization techniques, such as X-ray diffraction. Numerous inorganic compounds (51,856 oxides, 1581 nitrides, 2978 fluorides in the Inorganic Crystal Structure Database (ICSD, https://icsd.fiz-karlsruhe.de), as of 5 October 2017) have been reported, most of which can be prepared by high-temperature solid-state reactions over 1000 °C. A result of extensive research over the last century is that new materials accessible by ‘heat and beat’ exploration of new cation combinations may be exhausted soon.

Focusing on the anions within a compound offers a solution to this problem. This can enhance the possible combinations of elements, but also offers more diversity. Cation-based compounds are based on common coordination polyhedra as building units (e.g., CuO$_4$ square planes). However, if several oxide anions are replaced with other anions, new and unusual coordination geometries may result. When these polyhedra, as new building blocks, are arranged to form an extended array, one can expect enhanced properties or fundamentally new phenomena. Since anions exhibit different characteristics (e.g., ionic radii, valence, polarizability, and electronegativity), selecting different anions can introduce a new dimension of flexibility for materials design and function. Despite such possibilities, the number of mixed-anion compounds available are limited: the number of recorded materials in ICSD are 1266 for oxyfluorides, 612 for oxynitrides, 47 for oxyhydrides, 655 oxychalcogenides, and 312 oxypnictides. Note that mixed-anion compounds do not necessarily possess a heteroleptic coordination geometry around a transition metal. For example, a number of structures are comprised of alternating layers, each with a homoleptic coordination by a different anion, as found in Sr$_2$MnO$_2$Cu$_{1.5}$S$_2$ with alternating Sr$_2$MnO$_2$ and Cu$_{1.5}$S$_2$ layers.$^{102}$

Although some excellent overviews of mixed anion compounds have been provided,$^{2,5,12,16,81,82,102}$ each covers relatively narrow range of materials and disciplines. This review article is attempting to capture the broader fundamentals of these materials and draw new insights among materials classes.
electronic and atomic structure of materials, which may support phenomena inaccessible to a single-anion analog. Such anion-centered chemistry and physics is still in its infancy; there is much unexplored space, making it perhaps the most untapped field of materials sciences and giving new challenges and opportunities. In this review, we aim to describe the current status and scope, as well as outline future prospects and challenges surrounding mixed-anion (mostly oxide based) compounds, in particular, focusing on crucial roles of multiple anions in synthesis, characterization, and chemical and physical properties. Note that we had to be selective in materials and references because of the limited space. We provided mainly reviews or selected references, which could be an entry point to the literature search for readers who need additional information.

### Mixed-anion directed strategies
Understanding of mixed-anion compounds is still growing, but recent studies have unveiled several key features that are otherwise inaccessible in traditional single-anion compounds, as summarized in Fig. 1. Replacing oxide ligands in coordination octahedra or tetrahedra with other anions can differentiate the binding energy (Fig. 1e), which may benefit chemical reaction and anionic diffusion (Fig. 1f). It might also cause a (local) symmetry breaking (Fig. 1d) or create a cis/trans degree of freedom (Fig. 1c). The latter is a familiar ingredient in coordination chemistry, but less so in solid-state chemistry. Additionally, the crystal field splitting (CFS) can be tuned to the extent that is only allowed in coordination complexes, while retaining the original polyhedral shape and connectivity (Fig. 1a). An extensive modification of

### Table 1 Basic parameters of anions-forming elements and their ions

| Atomic properties | Anionic properties |
|-------------------|-------------------|
| Isotope with non-zero nuclear spin, I | Formal valence/electronic configuration |
| Natural abundance (%) | Coordination number/ionic radius (pm) |
| Neutron coherent scattering length (fm) | Polarizability (Å³) |
| Ionization energy (kJ/mol) | \(|\text{He}\) |
| Electron affinity (kJ/mol) | \(|\text{Ne}\) |
| Pauling’s electronegativity | \(|\text{MgO}\) |

| H | 1/2 | 99.985 | 0.15 | -3.7390 | -3.7406 | 6.671 | 1312.0 | 72 | 2.20 | -1 | 127-152 |
| N | 1 | 99.63 | 0.04 | 5.803 | 5.803 | 9.36 | 1402.3 | 141 | 3.04 | -3 | IV 146 |
| O | 1/2 | 99.762 | 0.2 | 5.84 | 5.84 | 9.37 | 1313.9 | (-780) | 3.44 | -2 | II 135 |
| F | 1/2 | 100 | 5.654 | 1681.0 | 328 | 3.98 | 3.98 | -1 | [Ne] |
| P | 1/2 | 100 | 5.13 | 1011.8 | 72 | 2.19 | 2.19 | -3 | [Ar] |
| S | 3/2 | 95.02 | 0.76 | 5.874 | 5.874 | 2.847 | 2.847 | 2.58 | -2 | II 135 |
| Cl | 3/2 | 75.77 | 11.65 | 24.23 | 3.08 | 9.5770 | 1251.2 | 349 | 3.16 | -1 | II 128.5 |
| As | 3/2 | 75.77 | 11.65 | 24.23 | 3.08 | 9.5770 | 1251.2 | 349 | 3.16 | -1 | II 128.5 |
| Se | 1/2 | 7.6 | 8.25 | 6.795 | 6.795 | 7.970 | 8.25 | 195 | 2.55 | -2 | II 135 |
| Br | 3/2 | 50.69 | 49.31 | 6.79 | 6.79 | 6.79 | 6.79 | 190 | 2.55 | -3 | [Ar] |
| Sb | 5/2 | 100 | 5.28 | 1008.4 | 295 | 2.66 | 2.66 | -3 | [Ar] |
| Te | 5/2 | 100 | 5.28 | 1008.4 | 295 | 2.66 | 2.66 | -3 | [Ar] |
| I | 5/2 | 100 | 5.28 | 1008.4 | 295 | 2.66 | 2.66 | -3 | [Ar] |
| Bi | 5/2 | 100 | 5.28 | 1008.4 | 295 | 2.66 | 2.66 | -3 | [Ar] |

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Note: a Ref. 105; isotopes with zero nuclear spin are indicated in parentheses
b Ref. 105
c NIST center for neutron research, neutron scattering lengths and cross sections, https://www.ncnr.nist.gov/resources/n-lengths/
d Ref. 106
e Ref. 106; second electron affinity is indicated in parentheses
f Ref. 106
g Ionic radii with\(^{107}\) and without\(^{106}\) specifying the coordination number. Ionic radii for H are derived from those discussed in ref. 108
h Values with chemical formula in parentheses are those experimentally estimated in compounds with rock salt structure. The equations as a function of the anion molar volume, \(V\), evaluated in ref. 110.
band (electronic) structures is also noteworthy, leading to a reduced dimensionality (Fig. 1g) and an upward shift of valence band maximum (VBM) (Fig. 1b).

Oxyhydrides (oxide hydrides), containing oxide and negatively charged hydride (H\(^+\)) anions, are rare but can be remarkable materials. Several features specific to hydride are given in Fig. 2. Hydrogen is the simplest (and lightest) element with one electron and one proton, giving the hydride anion distinct characteristics that differentiate it from other anions. For example, its bipolar nature and moderate electronegativity allow covalent, metallic, and ionic bonding, depending on the electronegativity of the element with which hydrogen bonds. This is schematically represented by the unconventional periodic table of elements (Fig. 2b)\(^1\), where values of electronegativity, ionization potential, and electron affinity are shown in the upper left, lower left, and lower right corner of each box. Related to this, the extraordinary flexibility in size of hydride (Fig. 2a) and possible reactions involving the zwitterionic nature (Fig. 2d) may bring about unprecedented functions. The flexible nature of hydride is also evident in its polarizability, as the refractive index of LiH (1.985) is significantly larger than that of LiF (1.392) despite the fewer number of electrons. Finally, H\(^+\) is the only anion which does not possess \(p\) orbitals in the valence shell. The lack of \(p\) orbitals in the outermost shell (Fig. 2c) significantly distinguishes its chemical bonding nature and its magnetic interaction with other anions.

**Synthesis beyond heat and beat**

Conventional inorganic materials are mostly oxides, due to the fact that the Earth’s atmosphere contains mainly reactive oxygen (and inert nitrogen). Thus, metal oxides are conventionally synthesized by high-temperature solid-state reactions, sometime called ‘heat and beat’ (or ‘shake and bake’) processing. A major difficulty in preparing mixed-anion compounds in the same way lies in the differing volatilities of precursors (oxides, chlorides, hydrides, and so on), so simple heating of mixed starting reagents often ends up with single-anion compounds, though some can be prepared in air (e.g., \(\text{LaCl}_3 + 0.5\text{O}_2 \rightarrow \text{LaOCl} + \text{Cl}_2\)). For this reason, the preparation of mixed anion compounds often requires controlled atmospheres, such as in vacuum or under various flowing gases (\(\text{Cl}_2, \text{F}_2, \text{NH}_3, \text{CS}_2, \text{and so on}\) (Fig. 3a) or exploits alternative synthesis methods, including soft-chemistry (Fig. 3b), solvothermal synthesis, or thin-film growth techniques (Fig. 3c) and high-pressure synthesis (Fig. 3d).
For example, a high-temperature ammonolysis reaction (under NH3 flow) is employed9, instead of inert N2, to obtain many oxynitride semiconductors, including AMO2N (A = Ba, Sr, Ca; M = Ta, Nb) with a high dielectric constant due to the larger polarizability of nitrogen (Fig. 1e)10. However, the ammonolysis reaction involves the dissociation of NH3·N2 and H2 (Fig. 3a) and thus provides a highly reducing atmosphere, which gives a certain constraint on available metals. To increase the reactivity of ammonia, a microwave oven is used to generate an ammonia plasma9.

The high reactivity of the anionic species, often gaseous in elemental form, can conversely be an advantage in tailoring anions in extended solids at low temperature. Topochemical insertion and exchange reactions (Fig. 3b), which provide metastable mixed-anion phases from precursors (typically oxides) in a rational, chemically designed manner, have been developed over the last two decades11. A proper choice of reagents and host structures is essential in directing reactions in a desired way. Consider for example oxyfluorides: a F2 treatment can give an oxidative fluorination involving F-intercalation (e.g., LaSrMn3+O4 – LaSrMn5+O2F2), while poly(tetrafluoroethylene), known as Teflon, acts as a reductant and may lead to reducible fluorination involving O/F-exchange (e.g., RbLaNb5+O2 – RbLaNb4.5+O2F)5,6.

The hydride anion is strongly reductive in nature, with a large standard redox potential of ~2.2 V (H+/H2 vs. SHE), so a transition metal oxyhydride appears impossible to stabilize. However, topochemical reaction using metal hydrides, such as CaH2, has opened a new avenue, yielding as the first example LaSrCo1.7H0.7 (Co1.7+, d7.3) in 20027. Density functional theory (DFT) calculations revealed the presence of fairly strong σ bonding between Co eg and H 1s orbitals8. On the other hand, the formation of BaTiO2.4H0.6 (Ti3+; d6), SrVO2H (V3+; d2), and SrCr2O4H (Cr3+; d3) is not readily rationalized since Ti/V/Cr d orbitals and H 1s orbitals are orthogonal (Fig. 2c)9-11. Since all the known transition-metal oxyhydrides exist with alkali and alkaline earth elements12, inclusion of any highly electropositive cation appears to be needed to make hydrogen with its moderate electronegativity (Fig. 2b) become negatively charged. This may explain why TiO2 does not incorporate hydride.

The observation of H/D exchange in BaTiO2.4H0.6 when heated in deuterium gas at ~400 °C indicates the labile nature of H in the reaction (Fig. 1f)10. The lability of hydride in BaTiO2.4H0.6 when heated to activate the nitrogen molecule. This hydride exchange chemistry is general, yielding other mixed-anion compounds, such as oxide-hydride-hydroxide BaTiO2.4H0.6(1/2O)12.14.

Solvolothermal synthesis is a synthetic method in which reactions occur in solution (i.e., water in the case of hydrothermal synthesis) inside a sealed vessel at temperatures near the boiling point of the solvent and pressures greater than atmospheric pressure15. Liquid-phase transport of the reactants allows for rapid nucleation and subsequent growth of a crystalline product with controlled morphology. This method produces crystals at lower temperatures and on shorter timescales than typical solids-state reactions. It also increases the likelihood of formation of
mixed-anion compounds (e.g., halide hydroxides, oxyhalides), which are often unfavored at higher temperatures. Solvothermal syntheses have been very successful in producing materials with acentric coordination environments that lead to noncentrosymmetric (NCS) structures having desirable properties, such as piezoelectricity, pyroelectricity, and nonlinear optical activity.16
Direct fluorination of oxides with \( F_2(g) \) or \( HF(g) \) is quite effective with minimal risk of side products. The handling of caustic, reactive gases, however, requires particularly specialized gas-phase reactors. In contrast, hydrothermal synthesis in hydrofluoric acid, or solutions of alkali fluorides, may be the easiest and safest route. The Tellon pouch approach is an efficient process to allow for fast development of discovery-based syntheses of new materials because various reactions can be performed in separate, small Tellon reaction pouches under identical, autogeneous conditions in an autoclave (Fig. 3c). Up to six reactions can be run in a 125 mL vessel.

Crystallographic long range ordering of oxide and fluoride anions has historically been a challenge, but materials based on anionic coordination polyhedra \([\text{MO}_n\text{O}_m]^{2-}\) (where \( m, n \approx (1, 2) \) for \( \text{M} = \text{V}^{3+}, \text{Nb}^{5+}, \text{Ta}^{5+}, (2, 2) \) for \( \text{M} = \text{Mo}^{6+}, \text{W}^{6+}, \) and \( 3, 3 \) for \( \text{M} = \text{Mo}^{4+} \)) have been solvothermally prepared without apparent anion-site disorder (Fig. 3c)\(^{16}\). In the ordered perovskite KNaNbOF\(_5\) and CsNaNbOF\(_5\) (with the general formula \( \text{AMaNO}_2\text{N}_2 \)) the interactions of the \([\text{NbOF}_5]^{2-}\) anion with the combination of Na/K or Na/Cs differ significantly. The NCS structure (KNaNbOF\(_5\)) maintains a larger primary electronic distortion of the \([\text{NbOF}_5]^{2-}\) anion along with a low coordination number of the K\(^+\) ion, consistent with the largest bond strain index. In contrast, the Cs\(^+\) ions of the centrosymmetric structure (CsNaNbOF\(_5\)) can exhibit higher coordination numbers and the \([\text{NbOF}_5]^{2-}\) anion exhibits a greatly reduced primary distortion. Theoretically, the group-theoretical method was applied to investigate anion ordering in the cubic perovskite, establishing 261 ordered low-symmetry structures, each with a unique space-group symmetry\(^{17}\). These idealized structures are considered as aristotypes with different derivatives formed by tilting of MO\(_6\) octahedra, providing a guide for designing NCS properties.

Thin film growth of oxides using pulsed laser deposition (PLD) or molecular beam epitaxy (MBE) is another useful bottom-up approach to construct desired artificial lattices, which has significantly contributed to the progress of condensed matter physics in the last two decades\(^{18}\). More rarely, thin film growth has been shown to be a promising method to prepare mixed-anion compounds, avoiding potential problems in anion diffusion. Oxynitrides films are fabricated by nitrogen plasma-assisted PLD, while polyvinylidene fluoride (PVDF) is used to topochromically convert oxide films to oxyfluoride ones. TaON films grown on a (LaAlO\(_3\))\(_{0.5}\)(SrAl\(_{0.5}\)Ta\(_{0.5}\)O\(_3\))\(_{0.7}\) substrate adopt a metastable backbone structure with anion vacancies, leading to high-mobility electron transfer\(^{19}\). Tensile and compressive stresses from the substrate enable tailoring of the anion arrangement of a given structure. Compressively strained SrTaO\(_2\text{N}\) films show a partial cis-to-trans conversion of TaO\(_2\text{N}_2\) octahedra (Fig. 3c)\(^{20}\). An anion order/disorder transition can also be induced by strain engineering\(^{21}\). However, we note that there are still very few reports on mixed-anion films and most are thin film studies targeting optical (or surface) coating applications.

High-pressure- and high-temperature conditions are typically used to stabilize dense materials through solid-state reactions or structural transformations. High-pressure reactions in sealed vessels prevent loss-of-volatile elements and so are particularly useful for anions, such as nitride to prevent loss-of-gaseous nitrogen (Fig. 3d). Autoclaves can be used for reactions under nitrogen up to kbar pressures, but many syntheses of oxynitrides have used direct reactions between solid oxides and nitrides (or oxynitrides) in multi-anvil presses where pressures can be extended to 10’s of kbar (GPa) values. The spinel Ga\(_2\)O\(_3\)N\(_2\) and AZrO\(_2\text{N}_2\) perovskites (A = Pr, Nd, and Sm)\(^{22}\) were synthesized by direct solid-state reaction between oxides and nitrides or oxynitrides under GPa pressures. The use of solid reagents (instead of NH\(_3\)) offers access to oxynitrides with middle-to-late transitions metals. A polar LiNbO\(_3\)-type structure MnTaO\(_2\text{N}_2\) with a helical spin order was recently synthesized at 6 GPa and 1400 °C\(^{24}\). A non-polar analog ZnTaO\(_2\text{N}_2\) was also prepared\(^{25}\). New light atom materials have also been reported, such as the sphalerite-related boron oxynitride B\(_2\)N\(_2\)O\(_3\) synthesized from direct reaction between B\(_2\)O\(_3\) and hexagonal-BN at 15 GPa and temperatures above 1900 °C\(^{26}\). Pressurization of baddeleyite-structured TaON drives a transition to a cotunnite-type structure with a very high bulk modulus of 370 GPa (Fig. 3d)\(^{27,28}\).

Chemical and structural analyses

Single crystal or powder diffraction methods are used to characterize many crystalline substances. A particular challenge for mixed-anion materials is to determine the distribution and degree of order-disorder of two or more anions. This complexity presents a challenge for both experiment and materials simulation (Fig. 3e), where equilibrium structures consisting of ordered or disordered anion configurations may be used for electronic structure calculations, e.g., those based on DFT or many-body methods. Ultimately to assess the properties of a mixed-anion material, the structure must be known. To that end, a number of structure-search algorithms, including cluster expansions\(^{28}\), special quasi-random structures\(^{29}\), and genetic algorithms\(^{30}\), frequently applied to multicomponent alloys and single-anion compounds, could be used to assess phase stability and solve structures in multi-anion compounds. In combination with experimental methods (below), a more complete description of the local and crystal structure can be obtained. These methods are also important for obtaining interaction energies for effective model Hamiltonians to describe ordering and ferroic transitions\(^{31}\).

Experimentally, the anion distribution may be studied directly using the scattering contrast between the anionic elements or indirectly through the different sizes or coordination environments of the anions in the structure. Direct X-ray scattering contrast is poor between elements from the same row of the periodic table, such as N/O/F or As/Se/Br, and neutron scattering may be useful in some cases, for example, to differentiate N and O which have respective neutron scattering lengths of 9.36 and 5.83 fm (Table 1) in oxynitrides. Neutron scattering also enables the positions of these light atoms to be determined more precisely in the presence of heavy metal atoms than is usually possible from X-ray refinements.

Anions that have very similar X-ray and neutron scattering factors, such as oxide and fluoride may be distinguished by their structural environments if well-ordered within a crystal structure. Differences in formal charge and size are captured by the popular bond valence sum (BVS) method\(^{32}\), but even a simple approach based on apportioning ideal bond valences from Pauling’s second crystal rule was found to account for anion orders in many oxylalides and oxynitrides (Fig. 4a)\(^{33}\). Increasing the formal anion charge tends to promote more covalent bonding to the metal cations and this can also enable anions to be distinguished; for example, vanadium forms very short ‘vanadyl’ bonds to oxide but not fluoride in V\(_{4+}\) and V\(_{5+}\) oxyfluorides.

Between the limits of fully ordered and randomly disordered anions, there are many cases of intermediate anion orders with local clustering or extended correlations that may give rise to non-random site occupations in the averaged crystal structure. A particularly widespread example of such correlated disorder is found in AMO\(_2\text{N}_2\) and AMON\(_2\) perovskite oxynitrides where layers of zig-zag MN chains (Fig. 4c) result from strong-covalent interactions between high-valence transition metals M and nitride anions that promote local cis-MN\(_2\) (or MO\(_3\)N\(_2\)) configurations.
Fig. 4 Chemical and structural characterizations for mixed-anion compounds. Hierarchical representations from long-range ordered structures to correlated disordered states, and to local structures. 

a Prediction of anion distributions in mixed-anion (O, N, F, Cl, and Br) crystals based on the Pauling’s second rule: a correlation between the charge of an anion site with the calculated bond strength sums for the relevant site from X-ray diffraction (XRD) and neutron diffraction (ND) refinements33. For example, the apical site of the Nb(O,F)6 octahedron in K2NbO3F is favorably occupied by F–, while the equatorial site by N3– in Sr2TaO3N. 

b Identification of H+ using the correlation between the chemical shift (δ) of 1H-NMR and the M–H distance (dM–H), where M is the neighboring cation (Fig. 2a)44. An opposite dependence is seen for OH–. 

c Characterization of cis- and trans-coordination in AMO2N perovskites (Fig. 1c). (Right) A tetragonal SrTaO2N structure (P4/mmm) with the equatorial site occupied equally by O/N and the apical site occupied completely by O, giving disordered cis-chains, where thick/thin lines correspond to M–N/M–O–M connections34. This model was deduced from the average site occupancies in b. The correlated anion disorder in AMON2 perovskites is chemically symmetric through reversal of O and N. PDF analysis of neutron total scattering data for BaTaO2N reveals local O/N ordering originated from favorable cis-configuration of TaO4N2 octahedra39. (Left) The trans-coordination in SrTaO2N film under lateral compressive strain is probed by polarized XANES and STEM-EELS40. Some data are reproduced with permission from each journal.
This order has been deduced from powder neutron refinements of O/N site occupancies in materials, such as SrMoO₅N (M = Nb, Ta)⁴, LiTaON₂⁵, and AVO₂N (A = Pr, Nd)³⁶,³⁷ perovskites. Local O/N correlations are also present in silicon oxynitrides where covalency tends to equalize the SiO₄–N₄ compositions of all nitridosilicate tetrahedra, for example, in melilite-type Y₂Si₃O₇N₄³⁸. Analysis of total X-ray or neutron scattering data, including diffuse features from short-range correlations, as well as the Bragg scattering, has been used to construct the pair distribution function (PDF) of interatomic distances in many materials. Fitting of the PDF can be a powerful tool for revealing short range structural correlations in crystalline materials, as well as in amorphous substances³⁹. Scattering or size contrast between anions can be used to determine their local order, for example, neutron PDF analysis revealed the prevalence of local cis-TaN₂ configurations in the perovskite BaTa₂O₇N (Fig. 4c)⁴₀.

Complementary information for analyzing the neutron- or X-ray-PDFs can be acquired by other techniques, such as electron energy loss spectroscopy (EELS) combined with scanning transmission electron microscopy (STEM), X-ray absorption near edge structure (XANES) of X-ray absorption spectroscopy (Fig. 4c), and magic angle-spinning (MAS) nuclear magnetic resonance (NMR) (Fig. 4b), which provide not only anion composition but also the local structures. As opposed to the above diffraction methods that may have difficulty in distinguishing among O, F, and N, state-of-the-art STEM-EELS can determine atomic occupancy with a resolution of each atomic column in a crystal lattice. This is particularly advantageous for thin film samples, in which crystal orientation is well controlled but precise structural analysis by diffraction methods is not as applicable. XANES is also effective for identifying the above elements and determining their chemical states. Perovskite (Ca₁₋ₓSrₓ)TaO₃N epitaxial films with controlled strains were analyzed using XANES with a polarized light source⁴¹. From the intensity of the Ta-5d peak, it was concluded that N prefers the Ta-5d orbital, while F prefers the Ta-5d orbital. Additionally, Ta-5d orbitals were found to be covalently bonded with Ta-5d orbitals, while F prefers the Ta-5d orbital. This was confirmed by XANES of X-ray absorption spectroscopy (Fig. 4c), and magic angle-spinning (MAS) nuclear magnetic resonance (NMR) (Fig. 4b), which provide not only anion composition but also the local structures. As opposed to the above diffraction methods that may have difficulty in distinguishing among O, F, and N, state-of-the-art STEM-EELS can determine atomic occupancy with a resolution of each atomic column in a crystal lattice. This is particularly advantageous for thin film samples, in which crystal orientation is well controlled but precise structural analysis by diffraction methods is not as applicable. XANES is also effective for identifying the above elements and determining their chemical states. Perovskite (Ca₁₋ₓSrₓ)TaO₃N epitaxial films with controlled strains were analyzed using XANES with a polarized light source⁴¹. From the intensity of the Ta-5d peak, it was concluded that N prefers the Ta-5d orbital, while F prefers the Ta-5d orbital. Additionally, Ta-5d orbitals were found to be covalently bonded with Ta-5d orbitals, while F prefers the Ta-5d orbital.
solid solutions between Si$_3$N$_4$ and Al$_2$O$_3$, by X-ray diffractometry is insufficient because X-ray scattering factors within the Si–Al and O–N pairs are similar; however, the high-resolution MAS-NMR method overcomes this challenge. Local coordination around the $^{29}$Si and $^{27}$Al nuclei was determined by MAS-NMR and their integration gives a full structural model for such oxy-nitride materials and, coupled with ab initio calculations, preferential Al–O clustering.

High sensitivity is a hallmark of $^1$H-NMR, enabling detection of H$^-$ with a concentration as low as 0.1% of the total anions. Coexistence of H$^+$ (or OH$^-$) and H$^-$ ions in a single material is not trivial because their thermodynamic stability is different and depends on oxygen partial pressure, $p$(O$_2$). However, these two species sometimes coexist due to non-equilibrium or high-temperature equilibrium. Recent $^1$H-NMR has identified a ‘hidden’ hydride anion and its local environment in hydroxyl-oxides like apatite Ca$_{10}$(PO$_4$)$_6$(OH)$_$_2$.

Here, the size minimum (CBM, or VBM) timescale of 10,000 years at room temperature. Formation of conductivity as the reverse of the above reaction proceeds with a hidden $^1$H-NMR (Fig. 2a) substantially changes the electron density (and relevant magnetic field shielding) at $^1$H nuclei and hence the isotropic chemical shift of $^1$H-NMR (Fig. 4b).

Cage structures can incorporate various anionic species. Mayenite 12CaO·7Al$_2$O$_3$, with a positively charged cage structure is shown to host many mono- or divalent guest anions ($^8$F, $^8$Cl, $^5$S, $^6$O, $^{15}$N, $^{12}$C, $^{13}$C, $^{18}$F, $^{19}$F, $^7$N, $^2$O, $^2$H$^-$, H$^-$) (Fig. 1b). Raman and electron paramagnetic spin resonance (EPR) measurements show that active oxygen species of O$_2^-$, O$_2^-$, and O$^{2-}$, less stable than O$^{2-}$ in oxide crystals and usually formed on surfaces transiently, can stably exist in the cage. In a slightly hydride-doped mayenite, an irradiation of UV light induces a chemical reaction in the cage: H$^+$ + O$^{2-}$ $\rightarrow$ 2e$^-$ + OH$^-$ (Fig. 2d). Here, the c$^\circ$ conformation is within the cage, like $F^-$ centers in alkali halides, and is responsible for a ‘permanent’ electrical conductivity as the reverse of the above reaction proceeds with a timescale of 10,000 years at room temperature. Formation of transient atomic hydrogen during the photo-dissociation of H$^-$ is monitored by EPR, revealing that its lifetime of the atomic hydrogen is a few minutes at 40 K.

### Chemical properties

#### Optical applications

Many oxides have a wide band gap and so are transparent. Valence band engineering according to Fig. 1b is useful to make them responsive to visible light, the main component of solar spectrum. When the oxide anion is substituted by other anions with less electronegativity like nitride, the oxide lattice. A layered lanthanum oxychloride LaOCl is a Cl-ion conductor.

Another interesting feature from the mixed-anion system is photochromism, recently found in Ca$_4$ReO$_4$Cl$_2$ with the Re$^{6+}$ ion in a 5$d^2$ configuration (Fig. 5b). The heavily distorted octahedral coordination of Re$^{6+}$ by one a$^\circ$F$^-$ and five O$^{2-}$ anions along with the spatially extended 5$d$ orbitals gives rise to unique CFS energy levels (Fig. 1a), much greater than for 3$d$ orbitals owing to stronger electrostatic interactions exerted from the ligands. The uni-directional alignment of these octahedra along the c-axis makes the d–d transitions highly anisotropic. As a result, this compound exhibits very different colors depending on the viewing direction, i.e., distinct photochromism.

#### Anion conductors

Certain anions are mobile in solids. The merit of a mixed-anion system is that it allows for anion diffusion by one (more ionic, less highly charged) anion and structural stability by the other (more covalent, more highly charged) anion (Fig. 1e, f). This concept can be directly assessed using electronic structure methods, where calculations of intrinsic defect levels and diffusion barriers can be correlated with changes in the anion lattice. A layered lanthanum oxychloride LaOCl is a Cl-ion conductor.

While La$_2$O$_3$ and LaCl$_3$ are both sensitive to the oxide lattice, a layered lanthanum oxychloride LaOCl is a Cl-ion conductor. While La$_2$O$_3$ and LaCl$_3$ are both sensitive to the oxide lattice, a layered lanthanum oxychloride LaOCl is a Cl-ion conductor.
**Fig. 6** Mixed-anion driven physical functions. **a** Superconducting transition temperatures as a function of the year of discovery, where symbols of mixed-anion compounds are highlighted in color. Layered structures of parent high-Tc superconductors HINCl [53], LaOFeAs [54], and Sr2CuO2Cl2 [80] are shown (Fig. 1g). **b** Top) Geometrical frustration in ZnCu3(OH)6Cl2, Cu3V2O7(OH)2·2H2O and BaCu3V2O9(OH)2 with the S = 1/2 kagome lattice [85, 87]. A Cu-triangle unit is formed by the chlorine anion of three trans-Cu(OH)2Cl2 octahedra in the former, while sharing the OH anion of three trans-CuO2(OH)2 octahedra in the latter two compounds. Different orbital-ordering patterns appear in these compounds, leading to various exotic quantum states. (Bottom) A spin liquid ground state and inelastic neutron scattering on ZnCu3(OH)6Cl2 showing fractionalized excitations [96]. **c** (Upper) Crystal and electronic structures of SrVIII2O8H with trans-VO4H2 octahedra [95]. H-1s orbitals, orthogonal with V t2g orbitals act as orbital scissors (or π-blockers), resulting in 2D electronic structures (Fig. 2c). (Lower) 2D-to-1D crossover in serial n-legged spin ladders, SrnxV2O2n+1Hn (Fig. 1g) [90]. **d** (Upper left) Band dispersions of the cation/anion co-substituted (Bi,Sb)x(Te,Se)y with a tunable Dirac cone [91]. (Upper right) Topological surface state quantum Hall effect in the intrinsic topological insulator (Bi,Sb)x(Te,Se)y [92]. (Lower left) Giant bulk Rashba effect in BiTeI with polar facial-BiTeI3 octahedral layers (Fig. 1d) [93]. (Lower right) Spectroscopic imaging scanning tunneling microscopy of BiTeI evidencing the ambipolar 2D carriers at the surface, indicating the formation of lateral p-n junctions [94]. Some data shown here are reproduced with permission from each journal.

H+ anion conductors are expected to provide high-energy storage and conversion devices because H+ has an appropriate ionic size for fast diffusion (Fig. 2a), a low electronegativity (Fig. 2b) and a high-standard redox potential of H+/H2 (−2.3 V), close to that of Mg/Mg2+ (−2.4 V). A pure H+ conduction in K2NiF4-type La2LiH2O3 has recently been demonstrated, using an all-solid-state TiH2/La2LiH2O3/Ti cell (Fig. 5c) [71]. The two-dimensional (2D) H+ diffusion is further facilitated by introducing H− vacancies, leading to the activation energy of 68.4 kJ mol−1 for La0.6Sr0.4LiH1.6O2.

**Battery electrodes.** Mixed-anion chemistry of oxyfluorides offers a new handle to tune the redox potential of battery electrodes. Here, instead of ‘direct’ valence (anion) band control described in Fig. 1b, anion substitution enables an ‘indirect’ manipulation of the conduction band. The redox potential of the LiFSeOF phase (tavorite) is higher than the LiFePO4 phase (olivine) by 750 mV [72]. This primarily results from the weaker (more ionic) Fe−F bond as compared with the Fe−O bond (Fig. 1e), which stabilizes the antibonding band of Fe eg orbitals (Fig. 5c). Furthermore, Ag2V2O5F2 (SVO) is a battery material potentially used in cardiac defibrillators owing to a fast discharge rate and high-current density [73]. The silver density in SVOF is greater than that of the currently used industry standard cathode material Ag2V2O5 (SVO) [74] and thus the current density above 3 V for SVOF (148 mA h/g) is greater than that for SVO (100 mA h/g). The current
density above 3 V is sufficient and the potential at which it is delivered (3.52 V) is 300 mV greater than SVO owing to the fluoride incorporation (Fig. 1b).

Multivalent batteries exhibit a number of potentially valuable advantages compared to current lithium technology. The first functional multivalent battery was constructed in 2000; this prototype used a magnesium metal anode against a low-voltage functional multivalent battery. By tuning the anionic composition in Pb(Te1−xSx), the p-type semiconductor LaCuSO4, the semiconducting LaAgSO4, layered order of nitride and halide anions in BiCuSeO with (Cu2Se2)2Vd blocks the π–π* interactions (Fig. 6c). The application of pressure to the Mott insulator drives a transition to a metal at ~50 GPa. Interestingly, despite the enormous compressibility of hydride (Fig. 2a), which is twice as compressible as oxide (Fig. 2a), the electronic structure of the metallic phase is quasi-2D, meaning that the hydride ligand acts as a ‘π-blocker’. The dimensional control from 2D to 1D is possible in the n-legged spin ladder oxyhydrides Sr6+1V4+2nO2n+2Hn (n = 1, 2, ..., ∞) (Fig. 1g).

During the last decade, there has been remarkable progress in physics involving topological phases of matter, for which mixed-anion compounds play crucial roles in advancing this field. Binary chalcogenides Bi2Se3 and Bi2Te3 were thought to be potential three-dimensional topological insulators, but both suffered from native point defects and unintentional carrier doping. Alloying with these two compounds along with Sb-for-Bi substitution has established a highly insulating bulk and accessible Dirac carriers, accompanied by the observation of a sign change of the Dirac carriers (holes vs electrons) with chemical potential (Fig. 6d). The precise carrier control has been also utilized to achieve a topological surface state quantum Hall effect (Fig. 6d).

The layered polar semiconductor Bi2Te3 shows a huge bulk Rashba-type spin splitting (Fig. 6d) that arises from the strong inversion asymmetry along the trigonal c-axis induced by distinct covalent Bi-Te and ionic Bi-I bonds in the facial-BiTeI3 coordination (Fig. 1d). This built-in bulk polarity induces 2D quantum magnetic and superconducting properties, especially in low-dimensional structures that are often found in mixed-anion materials. In the early copper oxide superconductor studies, two copper oxyhalides, Sr2CuO2F2,84 and (Ca0.4Na0.6Cu2O2Cl3,85 played a role in understanding the superconducting mechanism (Fig. 6a). Although, these compounds possess F− and Cl− ions instead of O2− ions at the apical site above and below the Cu2+ ions, they are superconducting with Tc = 46 and 26 K, respectively. This fact challenged the theoretical models proposing a vital role of the apical oxygen in the superconducting mechanism.

Now it is well established that the high-Tc superconductivity occurs within the CuO2 sheet having a strong covalency between the Cu dxy−p and O 2p states, while the apical-site anions (oxide ions) are more ionic (Fig. 1e), resulting in the 2D electronic state. In V4+ oxyfluorides, the V = O vanadyl oxide anions do not link to other cations whereas fluorides readily form V=–F–V bridges, enabling many structural topologies to be achieved. DQVOF (Diammonium Quinuclidinium Vanadium OxyFluoride; [NH4]2[2CuH12N][V4O12F13]) is notable as a geometrically frustrated kagome bilayer material with a gapless spin liquid ground state, instead of the conventional Néel order (Fig. 6b). Various synthetic copper minerals with Cu2+ (S = 1/2 ion) and mixed anions have been studied as geometrically frustrated quantum magnets that can also show exotic ground states. A good example is herbertsmithite, ZnCu3(OH)6Cl2 (Fig. 6b), in which the Cu2+ ion is coordinated by two axial Cl− ions and four equatorial OH− ions with their spin residing on the dxy−p orbital. The Cu2+ spins form a 2D kagome lattice and are coupled to each other by strong superexchange interactions only via the OH− ions. The compound exhibits no long-range order down to 50 mK with fractionalized excitations (Fig. 6b), owing to the strong frustration on the kagome lattice. Volborthite Cu3V2O7(OH)2H2O and vesignelite BaCu3V2O7(OH)2 with trans-CuO2(OH)1 octahedra having different orbital arrangements composed of dxy−p/dx−dy and dxy−p orbitals, respectively, enrich the phase diagram of the kagome antiferromagnet.

The lack of p orbitals in the valence shell of H+ (1s) effectively blocks the π-symmetry exchange pathways (Fig. 2c), a situation occurring in SrVIIIO2H with (t2g)7, where the in-plane exchange Vdxy−p−Vdx−dy is much greater than the out-of-plane one via Vdx−p−Vdx−dy interactions (Fig. 6c). The application of pressure to the Mott insulator drives a transition to a metal at ~50 GPa. Interestingly, despite the enormous compressibility of hydride (Fig. 2a), which is twice as compressible as oxide (Fig. 2a), the electronic structure of the metallic phase is quasi-2D, meaning that the hydride ligand acts as a ‘π-blocker’. The dimensional control from 2D to 1D is possible in the n-legged spin ladder oxyhydrides Sr6+1V4+2nO2n+2Hn (n = 1, 2, ..., ∞) (Fig. 1g).
electronic surface structures with heavy depleted (1-termination) and accumulated (Te-termination) electrons forming π–π junctions (Fig. 6d). Although BiTeI is a nontopological insulator at ambient pressure, it is proposed that the strong spin-orbit interaction allows a pressure-induced transition to a strong topological insulator, where, due to the broken inversion symmetry, a Weyl semimetal emerges between the two insulating phases.

**Outlook**

Increasing interest in solids based on mixed anions is expected to lead to new materials, some of which will make significant contributions to catalysis, energy conversion, and electronic devices, and will ultimately benefit industry in the coming decades. Functionality based on the earth-abundant, light elements usually present as anionic species (O, N, H, S, Cl, and so on) also offers the advantage of avoiding the inherent scarcity problems of metals, such as lanthanides. The metastability of mixed-anion compounds increases the complexity of synthesis and can limit the ways in which these materials can be used in devices. Therefore, chemically stabilizing these phases has to be considered when they are adapted for applications.

Synthetically, there will still be much room to develop methodologies. For example, multiple synthetic tools are used together (e.g., topochemical reaction under high pressure) or in a multistep process (e.g., solvothermal reaction followed by electrochemical reaction), both providing further platforms to manipulate multiple anions in extended solids. One of the important challenges is how to control anion order/disorder— one idea may be to utilize the size flexibility of hydride (Fig. 2a) to induce an order-disorder transition by (chemical) pressure. Furthermore, exploratory synthesis can be joined with computational tools ranging from DFT calculations to machine learning to expedite the screening process.

Regarding catalysis, this review has focused on visible-light-driven water splitting, but we believe that mixed-anion compounds can offer a variety of new possibilities, which would provide a large impact on chemical industry. In fact, an oxyhydride BaTiO2.5H0.5 has been very recently found to be an active catalyst for ammonia synthesis, which is remarkable given that Ti and oxygen-based materials (Fig. 1h) may be used to synthesize a labile ligand in solid state chemistry. J. Am. Chem. Soc. 137, 5315–5321 (2015).

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