Renaissance of Topotactic Ion-Exchange for Functional Solids with Close Packed Structures

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Abstract: Recently, many new, complex, functional oxides have been discovered with the surprising use of topotactic ion-exchange reactions on close-packed structures, such as found for wurtzite, rutile, perovskite, and other structure types. Despite a lack of apparent cation-diffusion pathways in these structure types, synthetic low-temperature transformations are possible with the interdiffusion and exchange of functional cations possessing ns² stereoactive lone pairs (e.g., Sn(III)) or unpaired nd electrons (e.g., Co(III)), targeting new and favorable modulations of their electronic, magnetic, or catalytic properties. This enables a synergistic blending of new functionality to an underlying three-dimensional connectivity, i.e., [-M–O–M–O–],ν, that is maintained during the transformation. In many cases, this tactic represents the only known pathway to prepare thermodynamically unstable solids that otherwise would commonly decompose by phase segregation, such as that recently applied to the discovery of many new small bandgap semiconductors.

Introduction

Historically, topotactic ion-exchange reactions have been a foundational component in the development of functional solids for many key technologies, including for the preparation of functional batteries, supercapacitors, fuel cells or zeolites to name a few.²⁻⁴ Facile ion exchange in these types of materials is well established as arising within crystalline structures exhibiting the capacity for high ion-mobility. For example, this typically occurs between the layers or through the pore openings that are found in layered or porous crystalline structures.²⁻⁴ Additionally, thermodynamically unstable compounds, i.e., metastable compounds, can frequently be synthesized via maintenance of the underlying crystalline structure during the ion-exchange reaction.²⁻⁴ Thus, low-temperature ion-exchange reactions provide a valuable kinetic handle for the formation of new, and frequently metastable, crystalline solids.

Until recently, however, the advantages of ion-exchange reactions have remained significantly less explored for close-packed structures, such as for those in the highly common wurtzite, rutile, or spinel structure types shown in Figure 1. Their three-dimensional connectivity, [-M–O–M–O–],ν, is advantageous for achieving a high carrier mobility, long-range magnetic ordering and many other properties. The tantalizing possibility of literally thousands of undiscovered solids having these structure types, synthetic low-temperature transformations are possible with the interdiffusion and exchange of functional cations possessing ns² stereoactive lone pairs (e.g., Sn(III)) or unpaired nd electrons (e.g., Co(III)), targeting new and favorable modulations of their electronic, magnetic, or catalytic properties. This enables a synergistic blending of new functionality to an underlying three-dimensional connectivity, i.e., [-M–O–M–O–],ν, that is maintained during the transformation. In many cases, this tactic represents the only known pathway to prepare thermodynamically unstable solids that otherwise would commonly decompose by phase segregation, such as that recently applied to the discovery of many new small bandgap semiconductors.

Cation Exchange in Close-Packed Structures

An initial question to pose is under what conditions would close-packed solids be capable of exhibiting ion exchange? Assuming an excess of exchangeable cations and concentration gradient (ΔC/Δx), according to kinetic exchange theory the rate determining step is chemical diffusion within the solid, with the fraction (f) of cation exchange at equilibrium being a function of particle radius (r), chemical diffusion coefficient (Dc), and time (t) as derived:[1,12,13] f = 1 - (6/π²) ∑[exp(-Bt/Dc)] / n² (1), and B = π²Dc/r² and n = 1 to ∞. This percentage represents the extent of reaching the maximum attainable cation exchange as deter-

![Figure 1](https://doi.org/10.1002/chem.202200479)
minded by thermodynamics, which may be some fraction of full exchange. Illustrated in Figure 2, for even small chemical diffusion constants \((D_e)\) of \(\sim 10^{-10} \text{ cm}^2 \text{ s}^{-1}\), nearly complete cation exchange (95%) is attainable on the order of about 4 weeks for even surprisingly large 100 µm particles. For crystal-like sizes in the nanoscale range of \(\sim 20\) to \(40\) nm in diameter, equilibrium can be reached within a few days for a \(D_e\) even as small as \(10^{-19} \text{ cm}^2 \text{ s}^{-1}\). Whether a solid exhibits a sufficient \(D_e\) at the low reaction temperatures of 500–800 K depends on its composition and structure.

Many binary metal chalcogenides easily satisfy these conditions, with a relatively large \(D_e\) in the low temperature range of \(\sim 400\)-700 K of \(\sim 10^{-10}\) to \(10^{-7} \text{ cm}^2 \text{ s}^{-1}\) (FeS, MnS, NiS) and up to as large as \(10^{-5}\) to \(10^{-3}\) (\(\alpha\)-AgS and Cu$_2$S).

Hence, metal chalcogenides have been intensely investigated in low-temperature, solution-based exchange reactions in a growing number of recent studies, such as starting from Cu$_2$S with a distorted antifluorite structure. This has yielded unique synthetic access to metastable polymorphs of binary chalcogenides, yielding the metastable CoS and MnS in either the wurtzite type or zinc-blende type structures \([16,17]\).

Starting from the metal-oleylamine complexes, these exchange reactions occur rapidly and topotactically in trioctylphosphine at only 373 K with the maintenance of the underlying close-packed structure, for example, Cu$_2$S (hcp)—CoS (hcf) for the wurtzite structure, and kinetically stabilizing new metastable polymorphs. By comparison, metal oxides exhibit \(D_e\) values up to an order of magnitude smaller (or less) than metal sulfides \([14,15]\).

Nonetheless, the solution-based exchange of Fe(II) for Co(II) cations at the particles’ surfaces at only \(\sim 500\) K has recently been used to prepare core-shell FeO/CoFe$_2$O$_4$ particles with the inverse spinel structure type \([20]\). Of note, these particles were found to show enhanced magnetic remanence, coercivity, as well as superparamagnetic blocking temperature as compared to homogeneous magnetite.

Recent research has made clear the successful synthetic approaches possible via the low-temperature cation exchange of close-packed structures, despite having very small chemical diffusion coefficients. The maintenance of their underlying anion sublattice, whether it be hexagonal or cubic close-packed, has enabled the study of a growing number of new binary compounds and a renaissance of research activity that had previously been considered as unpractical using this synthetic approach.

### Cation Exchange in the Preparation of Functional Multinary Oxides

Topotactic cation exchange of close-packed structures has also recently proven productive in the synthesis of many new, complex, multinary oxides, i.e., M‘MO$_x$. The basic strategy has involved the maintenance of not only the anion sublattice, but the preservation of the underlying \([\text{-M–O–M–O–}]_n\) connectivity during the exchange of a secondary metal cation (M'). This enables the addition of new functionality to an existing \([\text{-M–O–M–O–}]_n\) framework, such as for the visible-light sensitization of existing structures by the incorporation of Cu(I), Ag(I), Fe(II) or Sn(II) cations. Described below, many small bandgap semiconductors have been discovered by this approach starting from close-packed structures having the wurtzite, rutile, pyrochlore and perovskite type structures.

Replacement of a single type of metal cation (M') in a M’MO$_x$ solid relies upon its selective diffusion through the \(\text{‘MO}_{x}\)-based network, as found for many types of transition-metal oxides containing alkali and alkaline earth cations. For example, new visible-light photocatalysts have been synthesized with wurtzite-type structures \([21,22]\), as given in the reactions below:

\[
\beta\text{-NaGaO}_2 + \text{CuCl} \rightarrow \beta\text{-CuGaO}_2 + \text{NaCl}
\]

\text{(wurtzite type)}

\[
\text{Na}_2\text{ZnGeO}_4 + 2\text{CuCl} \rightarrow \text{Cu}_2\text{ZnGeO}_4 + 2\text{NaCl}
\]

\text{(double wurtzite type)}

Thermodynamically, these reactions are driven by the co-formation of the highly stable NaCl salt. Kinetically, the sodium cations diffuse through the close-packed structure, Figure 1, within micrometer-sized particles to exchange at the surfaces with the Cu(I) cations of the molten CuCl at only 425 to 525 K. This approach maintains the underlying ‘GaO$_2$’ or ‘ZnGeO$_2$’ lattices while the cation substitution occurs within the tetrahedral cavities containing the Na cation, Figure 1a. Both \(\beta\text{-CuGaO}_2\) and Cu$_2$ZnGeO$_4$ exhibit highly dispersed conduction bands and have favorably low electron effective masses of \(\sim 0.2\) \(m_e^*/m_0\). After a topotactic exchange of Cu(I) cations that provides a higher energy valence band, each exhibits a small, direct
bandgap (~1.4 – 1.5 eV). This added feature addresses the need for incorporating the strong, broad-wavelength absorption of sunlight together with a low effective electron mass. Similar examples of Ag(I) cation exchange have been reported for related structure types as well.\textsuperscript{[23,24]}

The topotactic exchange of Fe(II) cations has also been demonstrated in the triple-rutile structure for LiMWO\textsubscript{6} (M = Nb or Sb), a reported Li-ionic conductor.\textsuperscript{[25]} The exchangeable Li cations are coordinated within its octahedral sites. For large, micrometer-sized particles, a nearly complete cation exchange with Fe(II) cations in a 0.2 M aqueous solution occurs at only 333 K of up to ~90–92\%, or Li\textsubscript{1-x}Fe\textsubscript{x}/2MWO\textsubscript{6} (x = 0.9 to 0.92; 2 : 1 ratio of Li:Fe).\textsuperscript{[26,27]} The 'MWO\textsubscript{6}' networks, having buckled close-packed layers, are preserved with the incorporation of Fe(II) cations over 25\% of the octahedral sites. The thermodynamic driving force of the reaction has yet to be explored, as both solids are metastable. There is a significant redshift of the band gap from ~3.0 eV down to ~1.71 eV or ~2.06 eV, for M = Nb and Sb respectively. The Fe(II) cations occur in a high spin, 3d\textsuperscript{6}, configuration with an antiferromagnetic transition occurring at ~20 K. In photocatalytic tests, the latter shows visible-light activity for the degradation of rhodamine blue.

The most intensely investigated topotactic exchange reactions within close-packed structures have perhaps involved the Sn(II) cation using an aqueous solution or one of its halide-salt fluxes. A common motivation is to prepare visible-light, semiconductor photocatalysts with a higher energy valence band formed by the Sn(II) cation. These have involved metal oxides in the pyrochlore\textsuperscript{[28–30]} and other structure types.\textsuperscript{[31–34]} The Maggard and Jones groups have pioneered recent studies of Sn(II) exchange into the perovskite structure type, BaMWO\textsubscript{3} (M = Ti, Zr, or Hf) with close-packed 'BaO\textsubscript{3}' layers, as illustrated in Figure 3 and in the reactions below:

\begin{align*}
\text{BaHfO}_3 + x \text{SnClF} & \rightarrow (\text{Ba}_{1-x}\text{Sn}_x)\text{HfO}_3 + x \text{BaClF} \\
\text{BaZr}_{1/2}\text{Ti}_{1/2}\text{O}_3 + x \text{SnClF} & \rightarrow (\text{Ba}_{1-x}\text{Sn}_x)\text{Zr}_{1/2}\text{Ti}_{1/2}\text{O}_3 + x \text{BaClF}
\end{align*}

In a novel twist, the exchangeable Ba cations occupy sites within the close-packed layers (rather than within the tetrahedral or octahedral cavities), while the 'MO\textsubscript{3}' sublattice remains preserved. The formation of the stable BaClF salt drives the overall reaction to form the highly metastable Sn(II) perovskites, containing from ~50\% to 100\% Sn(II) cations on the A-sites.

Figure 3. Topotactic exchange of Sn(II) cations into BaMWO\textsubscript{3} perovskites, yielding (a) shell-core SnZr\textsubscript{1/2}Ti\textsubscript{1/2}O\textsubscript{3}–BaZr\textsubscript{1/2}Ti\textsubscript{1/2}O\textsubscript{3}, (b) large particles of Sn(II)-mixed Ba\textsubscript{1-x}Sn\textsubscript{x}HfO\textsubscript{3} and (c) nano-eggshells of pure SnHfO\textsubscript{3}, with insets of TEM/EDS images.
This leads to both a smaller bandgap of down to ~1.95 eV and visible-light photocatalytic activity for the production of molecular oxygen.\[31\]

Prior studies have shown chemical diffusion constants of Ba cations in the perovskite structure on the order of 10\(^{-18}\) to 10\(^{-20}\) cm\(^2\) s\(^{-1}\) at 1200 K,\[32\] i.e., falling at the outer edges of the practical synthesis limits in Figure 2. In general, reaction diffusion coefficients for solids are usually higher by up to 3 or 6 orders of magnitude compared to self-diffusion coefficients.\[33\]

As expected, the homogeneity and extent of Sn(II)-diffusion show a sensitive dependence on the particle sizes/morphology and chemical composition. Topotactic Sn(II)-exchange on highly-faceted and smooth particles typically results in thin ~30 to 80 nm shells, as shown for the SnZr\(_{1/2}\)Ti\(_{1/2}\)O\(_3\)-BaZr\(_{1/2}\)Ti\(_{1/2}\)O\(_3\) shell-core particles in Figure 3a. More homogeneous distributions of the Sn(II) cation can be achieved by reactions with particles having rough edges, Figure 3b, likely owing to presence of grain boundaries and cracks that facilitate greater cation interdiffusion and exchange. Alternatively, a reduction of the particle sizes down to ~50 to 100 nm can also be effective, as shown for the nano-eggshell morphologies in Figure 3c. These hollow particles consist of thin shells that have been used to shorten the diffusion lengths necessary to attain high purity SnHFO\(_2\). The latter is currently under investigation. In prior related research, the topotactic exchange of Ni(II) cations into the perovskite-type NaTaO\(_3\) has also been reported using flux reaction conditions, yielding the new Nb\(_{6}\)TaO\(_3\).\[34\]

Experimental evidence is clear that future research into topotactic synthetic investigations currently surging in new investigations and being developed for a wide range of potential applications.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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1. W. A. England, J. B. Goodenough, P. J. Wiseman, *J. Solid State Chem.* 1983, 49, 289–299.
2. J. Gopalakrishnan, *Chem. Mater.* 1995, 7, 1265–1275.
3. R. Uppuluri, A. S. Gupta, A. S. Rosas, T. E. Mallouk, *Chem. Soc. Rev.* 2018, 47, 2401–2430.
4. D. L. M. Cordova, D. C. Johnson, *ChemPhysChem* 2020, 21, 1345–1368.
5. M. A. Hayward, *Semicond. Sci. Technol.* 2014, 29, 064010(1-8).
6. A. Parija, G. R. Waetzig, J. L. Andrews, S. Banerjee, *J. Phys. Chem. C* 2018, 122, 25709–25728.
7. J. R. Chamorro, T. M. McQueen, *Acc. Chem. Res.* 2018, 51, 2918–2925.
8. P. A. Maggard, *Acc. Chem. Res.* 2021, 54, 3160–3171.
9. C. J. Bartel, C. Sutton, B. R. Goldsmith, R. Ouyang, C. B. Musgrave, L. M. Ghiringhelli, M. Scheffler, *Sci. Adv.* 2019, 5, eaao0693(1-9).
10. M. K. Filip, F. Giustino, *Proc. Nat. Acad. Sci.* 2018, 115, 5397–5402.
11. J. Koeptgens, C. J. Bartel, G. Ceder, *Chem. Commun.* 2020, 56, 1952–1955.
12. W. C. Bauman, J. Eichhorn, *J. Am. Chem. Soc.* 1947, 69, 2890–2836.
13. D. Reichenberg, *J. Am. Chem. Soc.* 1953, 75, 589–597.
14. S. Mrowec, K. Przybylski, *High Temp. Mater. Processes* 1964, 6, 1–79.
15. J. A. Van-Orman, K. L. Crispin, *Rev. Mineral. Geochem.* 2010, 72, 757–825.
16. A. E. Powell, J. M. Hodges, R. E. Schaal, *J. Am. Chem. Soc.* 2016, 138, 471–474.
17. J. L. Fenton, R. E. Schaal, *Angew. Chem. Int. Ed.* 2017, 56, 6464–6467; *Angew. Chem.* 2017, 129, 6564–6567.
18. G. Gariano, V. Lesnyak, R. Brescia, G. Bertoni, Z. Dang, R. Gaspari, L. De Trizio, L. Manna, *J. Am. Chem. Soc.* 2017, 139, 9583–9590.
19. M. Sarayuma, R. Sato, T. Teranishi, *Acc. Chem. Res.* 2021, 54, 765–775.
20. M. Sytnyk, R. Kirchschlager, M. I. Bodnarchuk, D. Primetzhofer, D. Ludwig, A. Meingast, G. Kothleitner, M. V. Kovalenko, W. Heiss, *Nanoscale* 2013, 13, 586–593.
21. T. Omata, H. Nagatani, I. Suzuki, M. Kita, H. Yanagi, N. Ohashi, *J. Am. Chem. Soc.* 2014, 136, 3378–3381.
22. M. Kita, I. Suzuki, N. Ohashi, T. Omata, *Inorg. Chem.* 2017, 56, 14277–14283.
23. D. Arney, P. A. Maggard, *ACS Catal.* 2012, 2, 1711–1717.
24. J. Boltersdorf, T. Wong, P. A. Maggard, *ACS Catal.* 2013, 3, 2943–2953.
25. H. Ohtsuka, A. Yamaji, T. Okada, *Sol. St. Ion.* 1984, 14, 283–288.
[26] V. Meena, J. Malik, T. K. Mandal, ACS Appl. Electron. Mater. 2021, 3, 2504–2511.
[27] V. Meena, T. K. Mandal, Inorg. Chem. 2019, 58, 2921–2924.
[28] S. Uma, J. Singh, V. Thakral, Inorg. Chem. 2009, 48, 11624–11630.
[29] M. Weiss, T. Bredow, R. Marschall, Chem. Eur. J. 2016, 24, 18535–18543.
[30] M. Weiss, R. Marschall, Nanoscale 2018, 10, 9691–9697.
[31] J. Boltersdorf, B. Zoellner, C. Fancher, J. L. Jones, P. A. Maggard, J. Phys. Chem. C 2016, 120, 19175–19188.
[32] Y. Zhou, J. Le, Y. Cao, N. An, Y. Zhou, J. Li, D. Liu, Y. Kuang, J. Mater. Chem. A 2021, 9, 21085–21093.
[33] S. C. O’Donnell, C.-C. Chung, A. Carbone, R. Broughton, J. L. Jones, P. A. Maggard, Chem. Mater. 2020, 32, 3054–3064.
[34] E. A. Gabilondo, S. C. O’Donnell, R. Broughton, J. L. Jones, P. A. Maggard, J. Solid State Chem. 2021, 302, 122419(1-10).
[35] M. F. Kessel, Anion and Cation Diffusion in Barium and Strontium Titanate, Ph.D. Thesis (Aachen, 2012).
[36] V. I. Dybkov, Reaction Diffusion and Solid State Chemical Kinetics, Trans Tech Publications: Zurich, Switzerland (2010).
[37] M. A. Patino, T. Smith, W. Zhang, P. S. Halasyamani, M. A. Hayward, Inorg. Chem. 2014, 53, 8020–8024.