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Russian Science  
Foundation

Crystallography and Crystal Chemistry  
VIII International School-Conference of  
Young Scientists 2023

# Minerals as prototypes for developing novel materials for battery applications



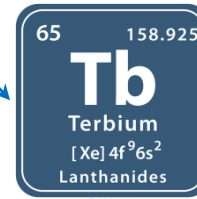
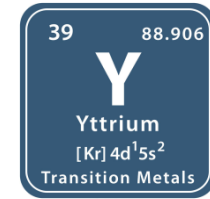
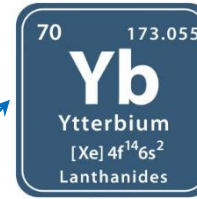
**Dr. Anatoliy S. Volkov**

PhD in Chemistry, Research Scientist  
Center for Energy Science and Technology  
Skoltech, Moscow, Russian Federation

November 9<sup>th</sup>, 2023

# 01

# Relation between Chemistry and Geology



Ore deposit  
processing technologies

Mining  
resources




## Approved structural data

**IMA status:** Approved

**Approval year:** 2003

**First published:** 2004

**Type description reference:** Pautov, L. A., Agakhanov, A. A., Sokolova, E., Hawthorne, F. C. (2004) Maleevite, BaB<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> and pekovite, SrB<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>, new mineral species from the Dara-i-Pioz alkaline massif, Northern Tajikistan: description and crystal structure. *The Canadian Mineralogist*, 42 (1) 107-119  
doi:10.2113/gscanmin.42.1.107 

**J | A | C | S**  
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

pubs.acs.org/JACS



Communication

### Kanatzidisite: A Natural Compound with Distinctive van der Waals Heterolayered Architecture

Luca Bindi,\* Xiuquan Zhou, Tianqi Deng, Zhi Li, and Christopher Wolverton\*



Cite This: *J. Am. Chem. Soc.* 2023, 145, 18227–18232



Read Online

Nabokoit



Atlasovite



Elasmochloite



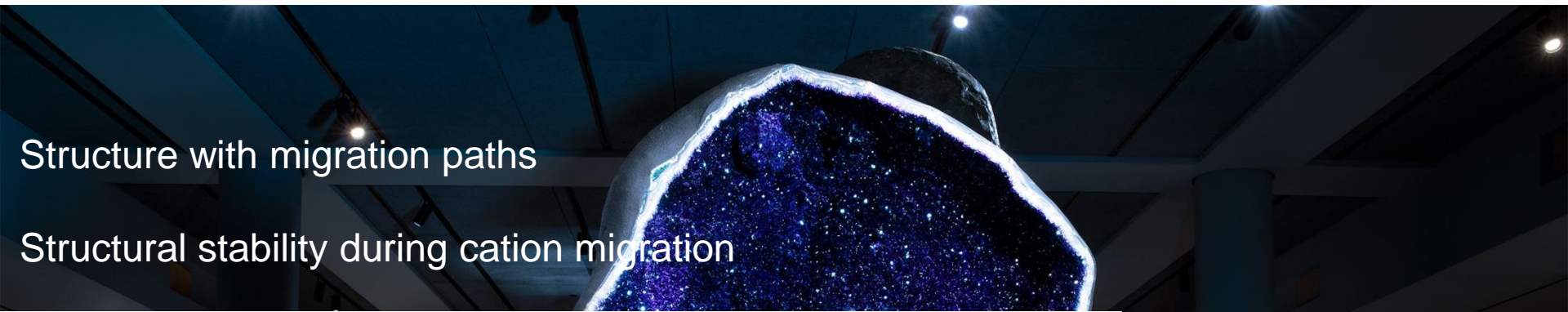
Favreauite



### Hydrothermal Synthesis and a Composite Crystal Structure of Na<sub>6</sub>Cu<sub>7</sub>BiO<sub>4</sub>(PO<sub>4</sub>)<sub>4</sub>[Cl,(OH)]<sub>3</sub> as a Candidate for Quantum Spin Liquid

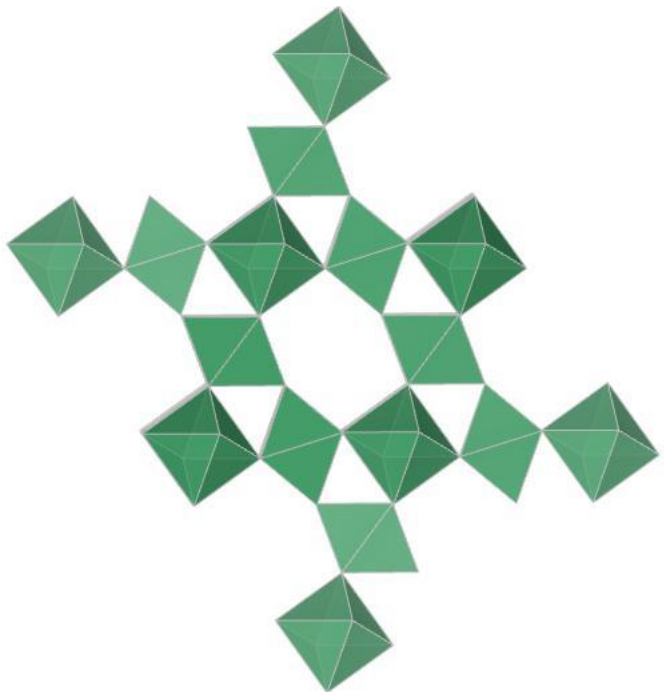
Olga V. Yakubovich,\* Larisa V. Shvanskaya, Galina V. Kiriukhina, Anatoly S. Volkov, Olga V. Dimitrova, and Alexander N. Vasiliev





Structure with migration paths

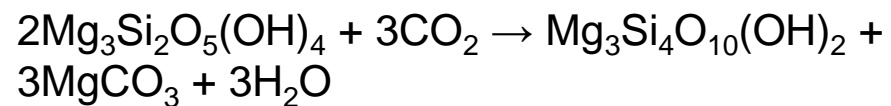
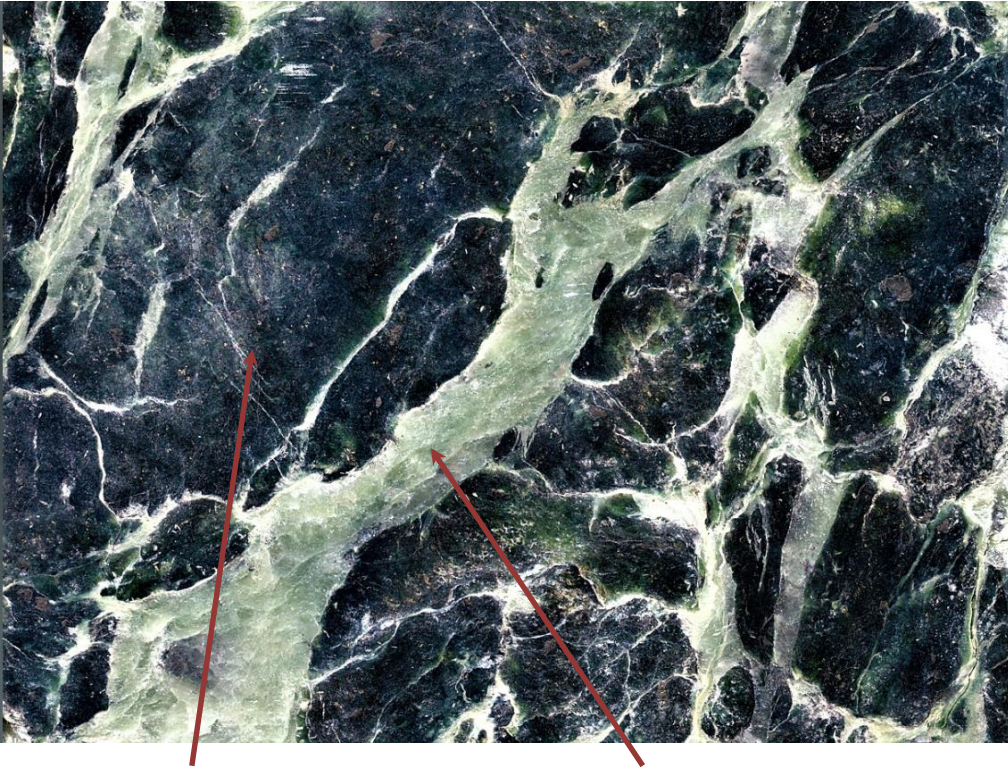
Structural stability during cation migration



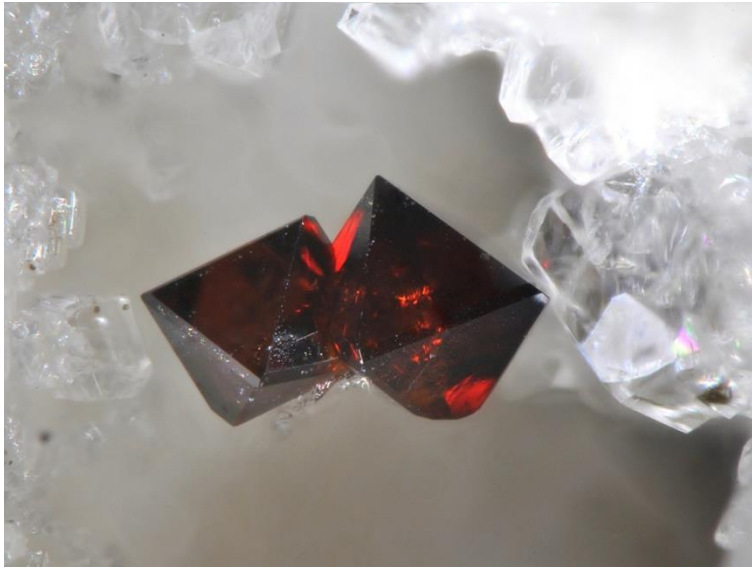
# 04

# Metasomatism

is the chemical alteration of a rock by hydrothermal and other fluids. It is the replacement of one rock by another of different mineralogical and chemical composition.

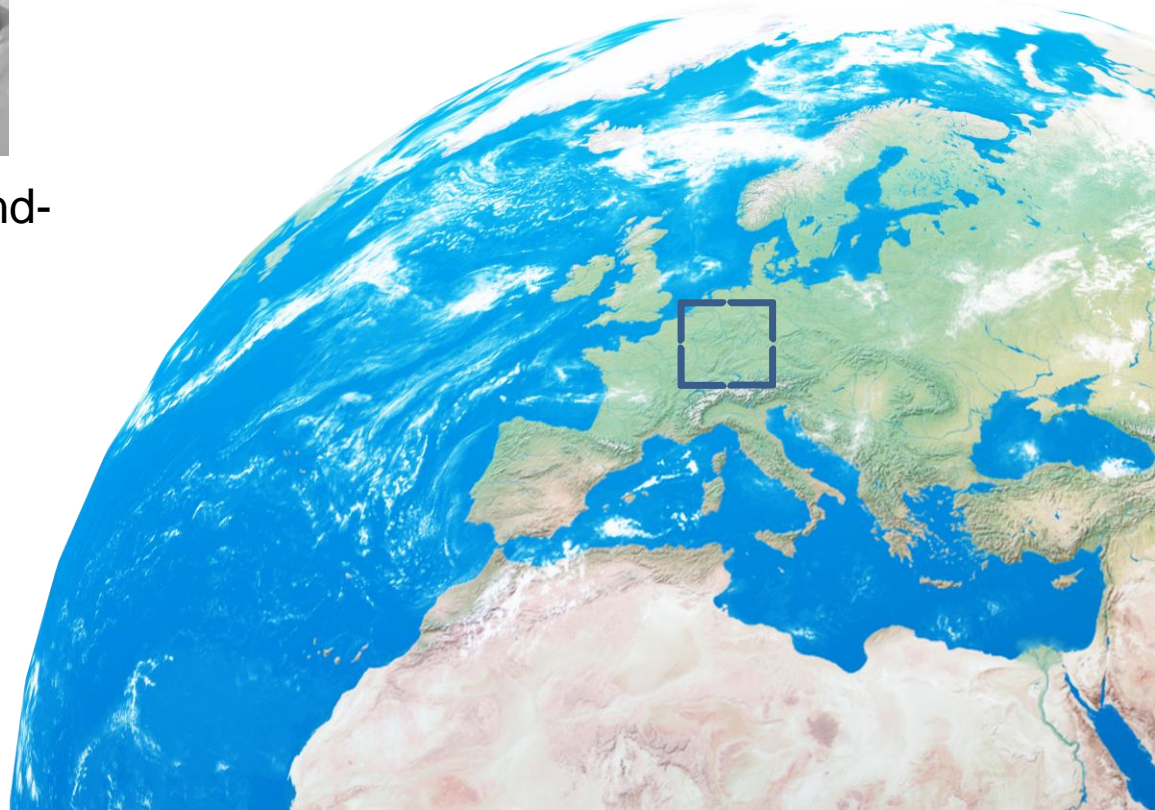






Mendig, Mayen-Koblenz, Rhineland-Palatinate, Germany

Name	Pyrochlore
Formula	$\text{NaCaNb}_2\text{O}_6\text{F}$
Crystal system	Cubic
Space group	$\text{Fd}\bar{3}\text{m}$
Cell Parameters	$a = 10.590(5) \text{ \AA}$



# Pyrochlore

Name	Fluornatropyrochlore
Formula	$(\text{Na,Pb,Ca,REE,U})_2\text{Nb}_2\text{O}_6\text{F}$
Crystal system	Cubic
Space group	$\text{Fd}\bar{3}\text{m}$
Cell Parameters	$a = 10.505(5) \text{ \AA}$



Lovozero complex





# Pyrochlore

Name	Hydroxykenopyrochlore
Formula	$(\square, \text{Ce}, \text{Ba})_2(\text{Nb}, \text{Ti})_2\text{O}_6(\text{OH}, \text{F})$
Crystal system	Cubic
Space group	$\text{Fd}\bar{3}\text{m}$
Cell Parameters	$a = 10.590(5) \text{ \AA}$



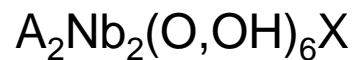
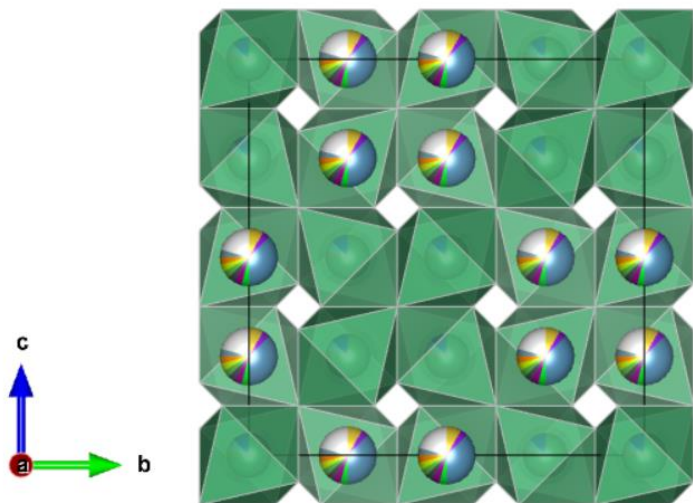
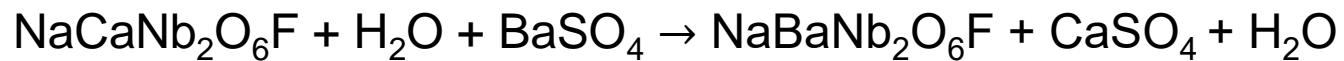
<https://www.mindat.org/photo-284496.html>





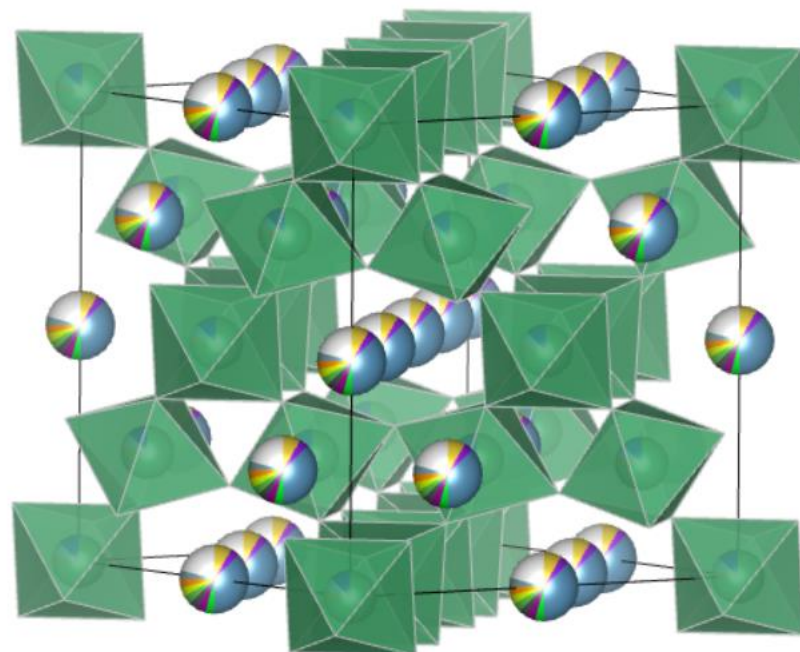
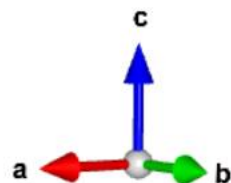
## 08

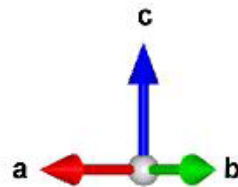
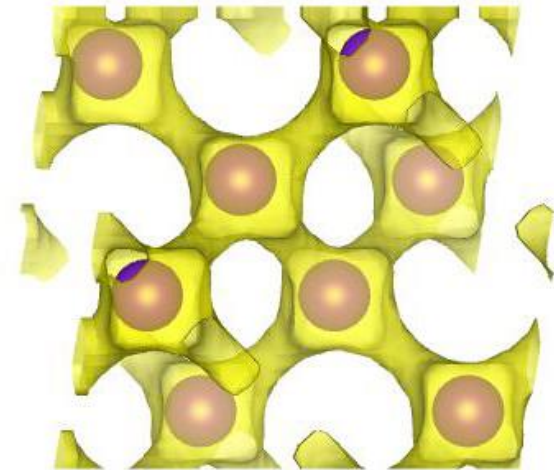
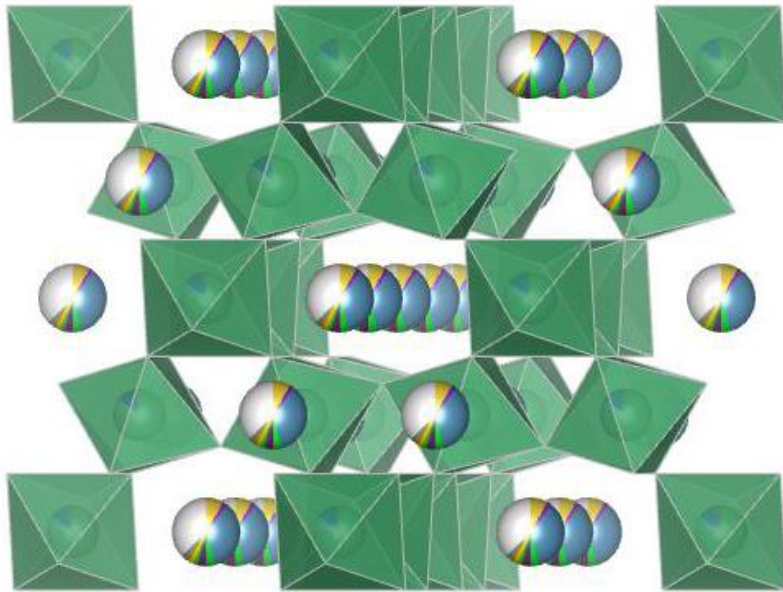
## Pyrochlore



A is Na, Ca,  $\text{Sn}^{2+}$ , Sr,  $\text{Pb}^{2+}$ ,  $\text{Sb}^{3+}$ , Y,  $\text{U}^{4+}$ ,  $\text{H}_2\text{O}$  or  $\square$ .

X is OH, F, O,  $\text{H}_2\text{O}$  or  $\square$



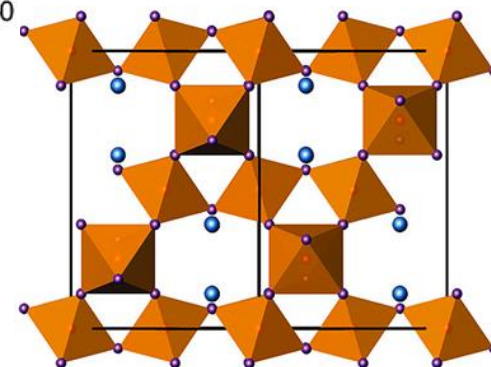
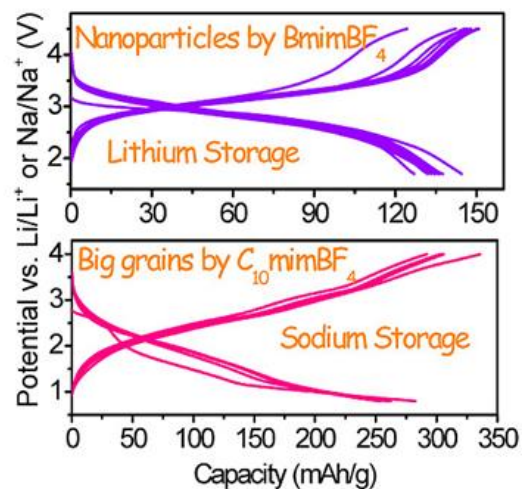
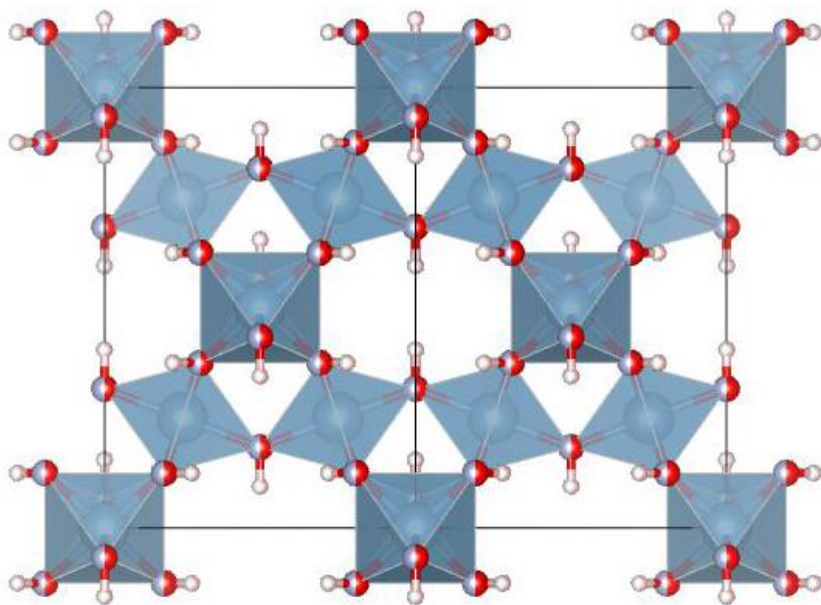
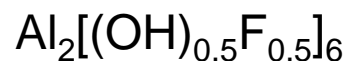


0.5 eV



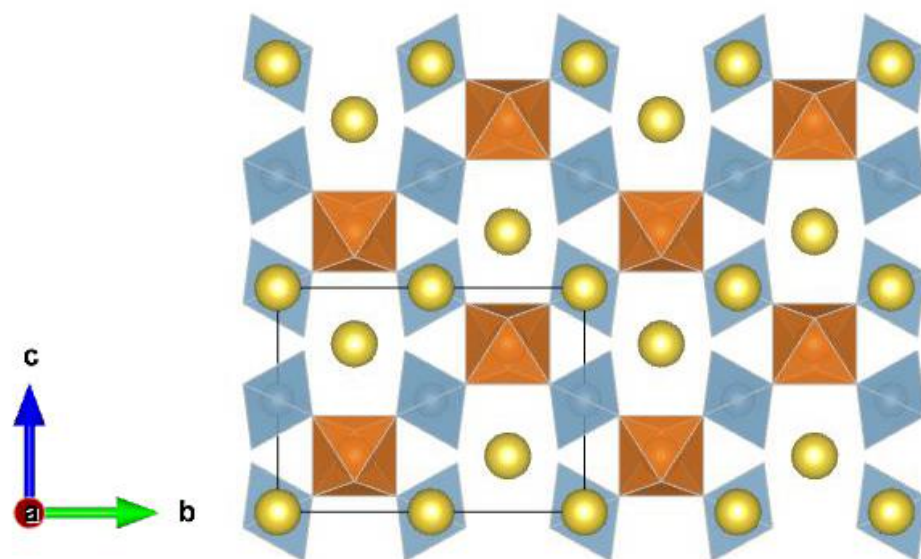
## An $\text{FeF}_3 \cdot 0.5\text{H}_2\text{O}$ Polytype: A Microporous Framework Compound with Intersecting Tunnels for Li and Na Batteries

Chilin Li,<sup>\*,†,‡</sup> Congling Yin,<sup>‡</sup> Lin Gu,<sup>§</sup> Robert E. Dinnebier,<sup>‡</sup> Xiaoke Mu,<sup>||</sup> Peter A. van Aken,<sup>||</sup> and Joachim Maier<sup>‡</sup>





Name	Weberite
Formula	$\text{Na}_2\text{MgAlF}_7$
Crystal system	Orthorhombic
Space group	Immm
Cell Parameters	$a = 7.31 \text{ \AA}$ , $b = 7.06 \text{ \AA}$ , $c = 9.99 \text{ \AA}$





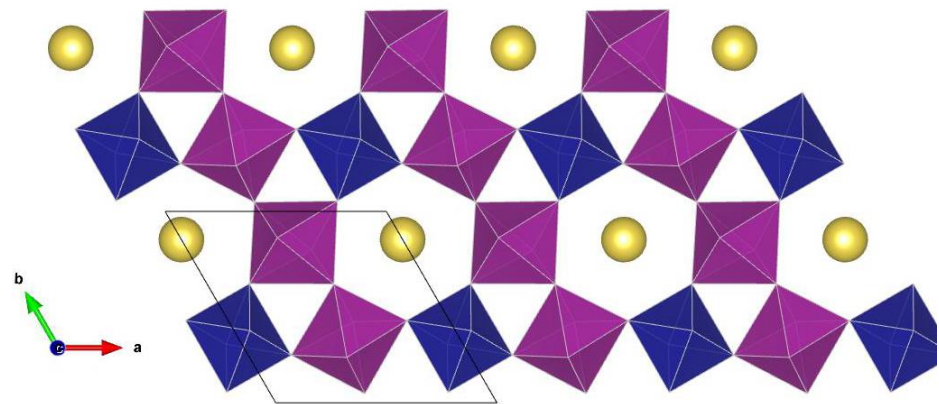
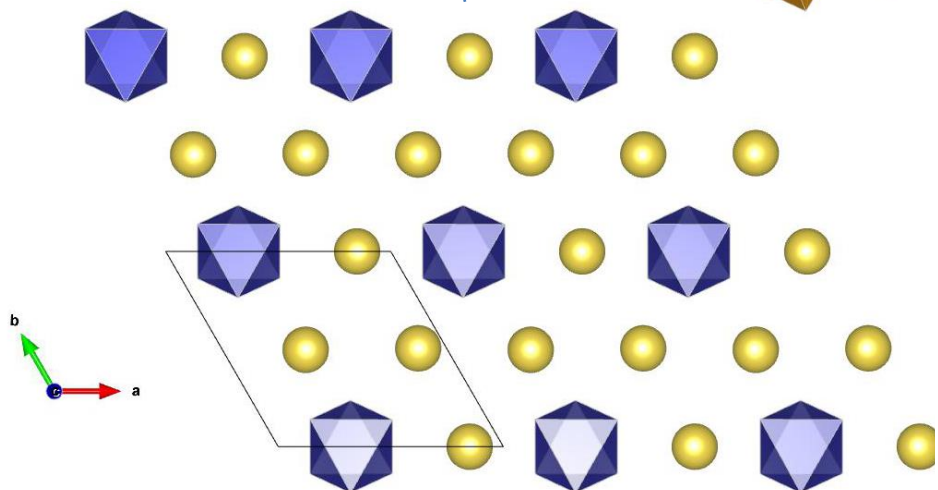
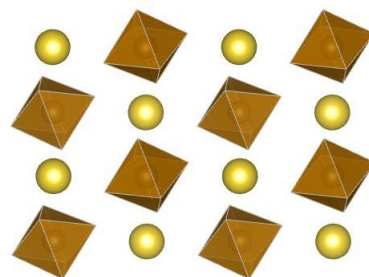
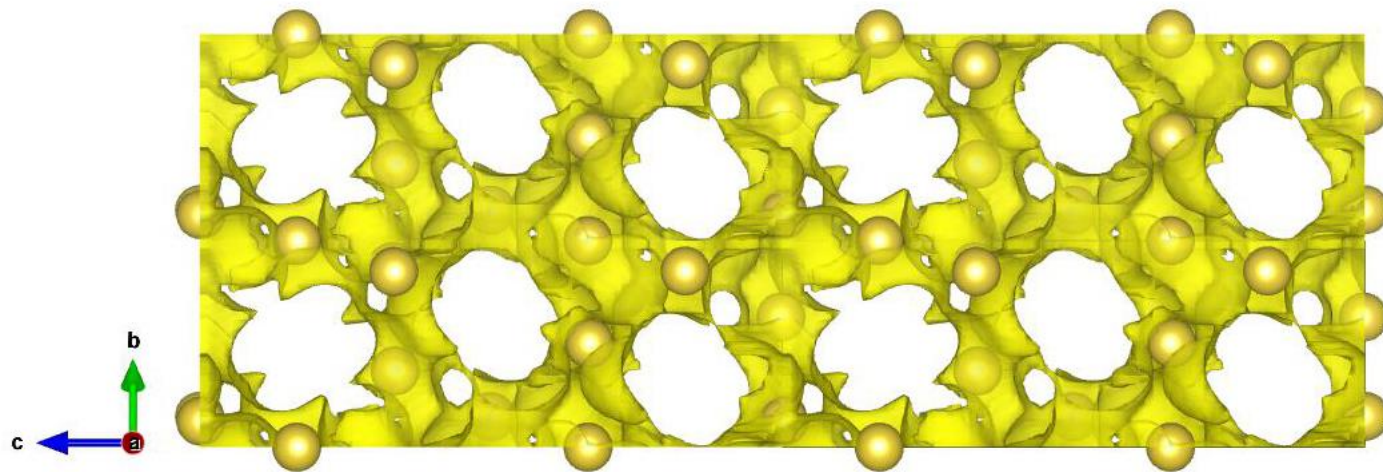
# 12

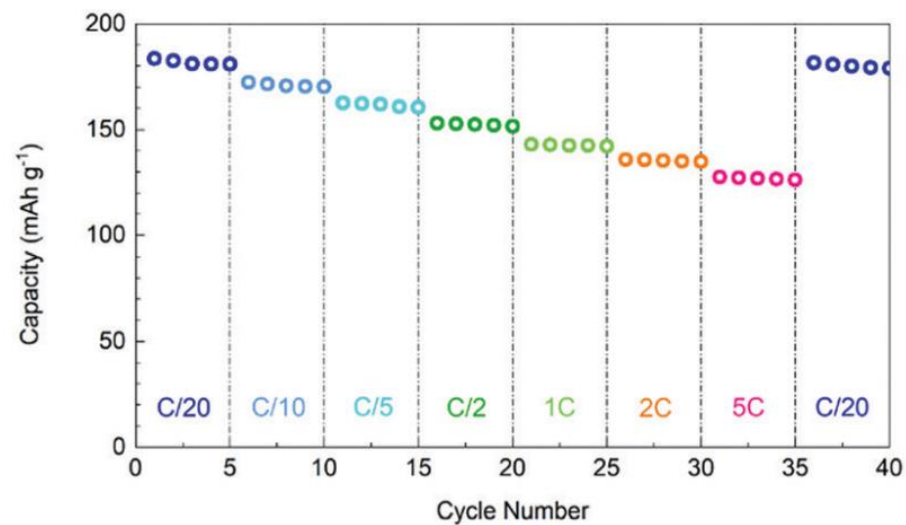
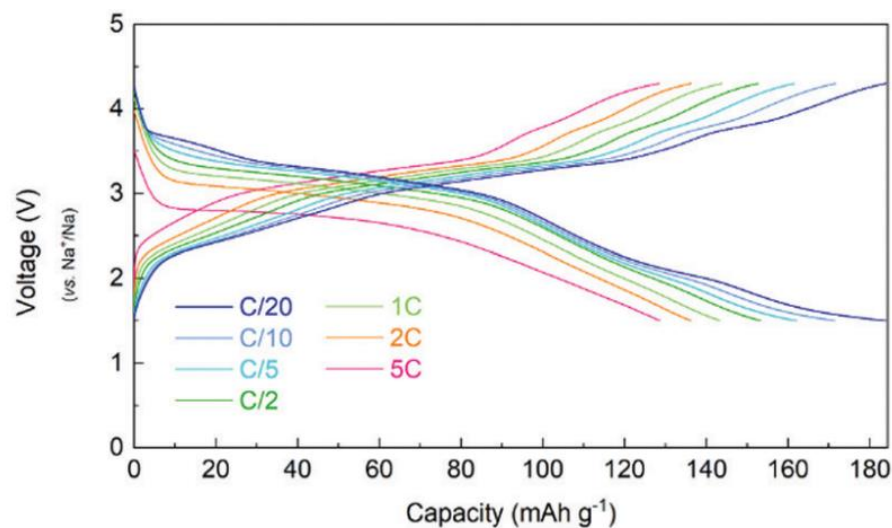
# Weberite

$P3_121$

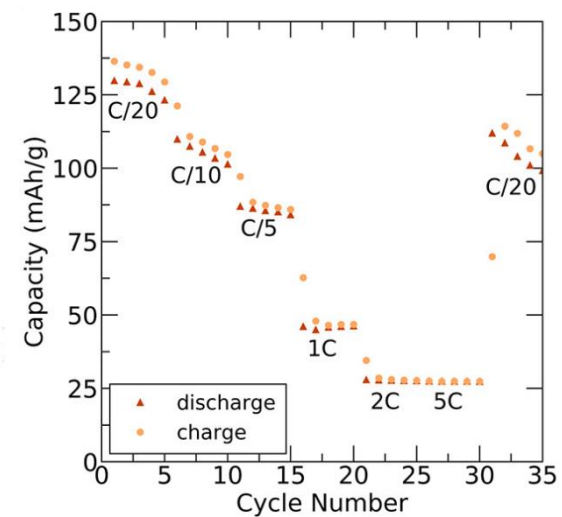
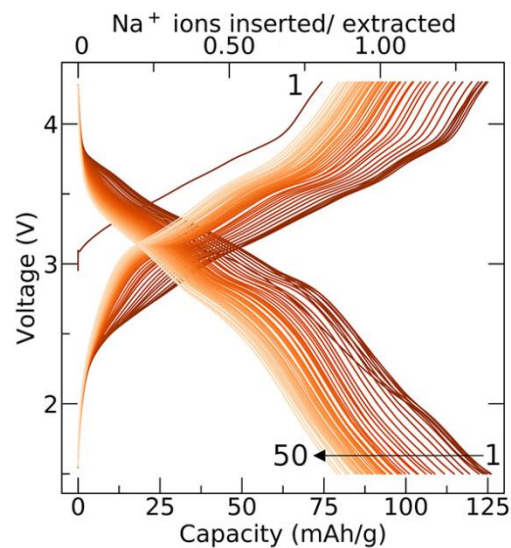
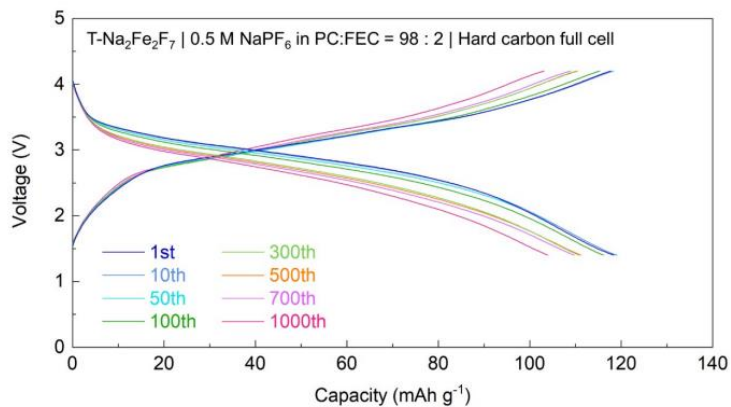
$a$	$b$	$c$
7.421	7.421	18.166

1 eV



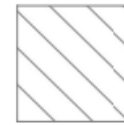
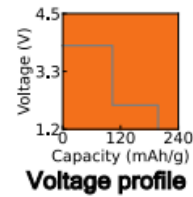
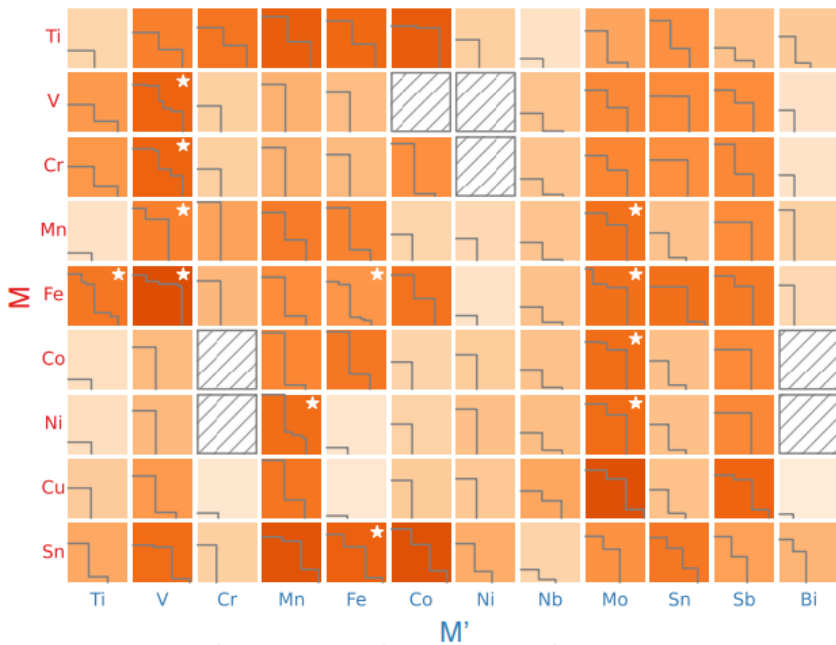


Hyunyoung Park, et al. *Energy & Environmental Science* vol. 14(3) pp. 1469-1479 (2021)



Foley, Emily E., et al. *Chemistry of Materials* 35.9, 3614-3627, (2023)

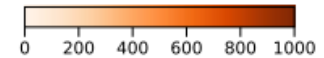




N / A

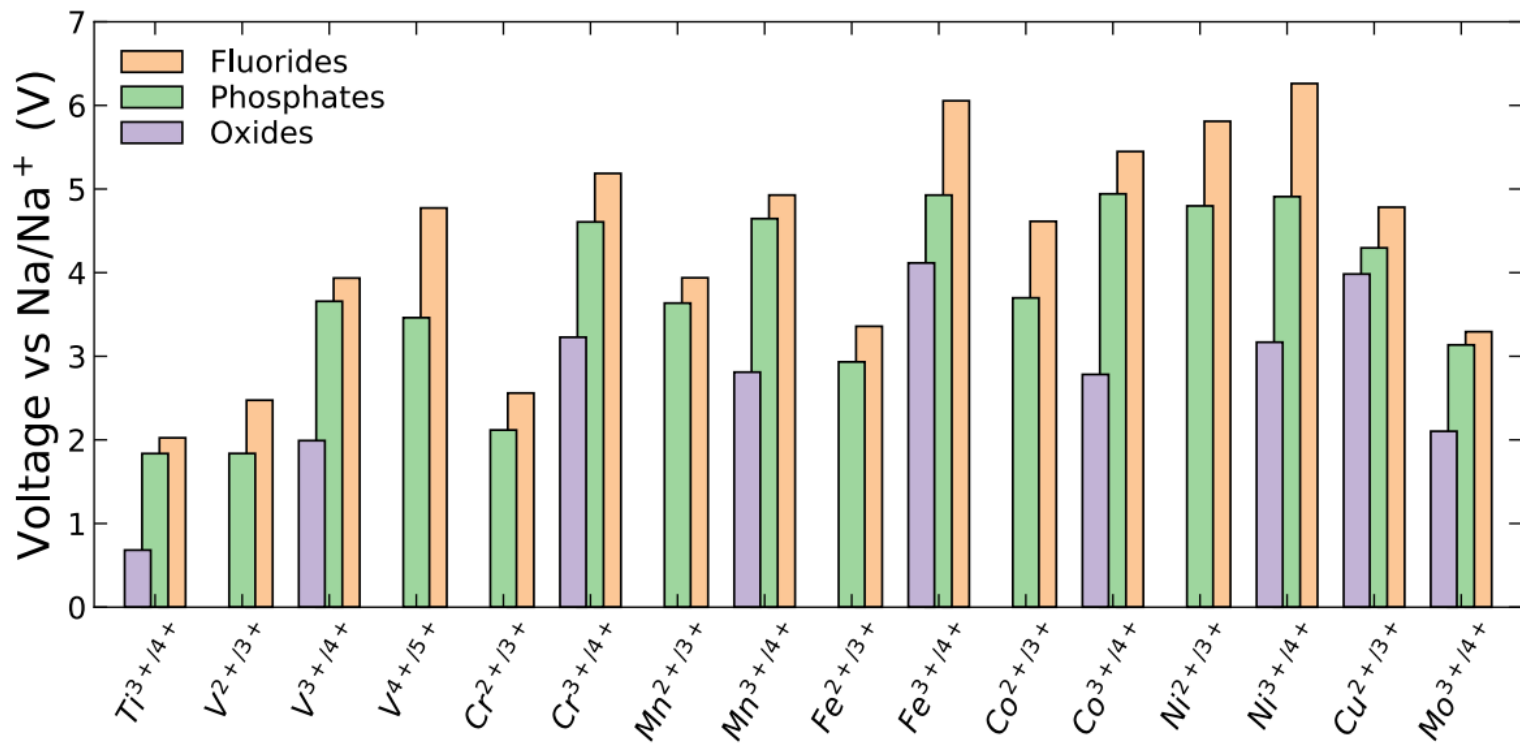


Promising compound



Specific energy (Wh/kg)

Lu, Tenglong, et al. arXiv preprint arXiv:2310.04222 (2023)





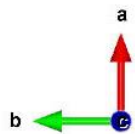
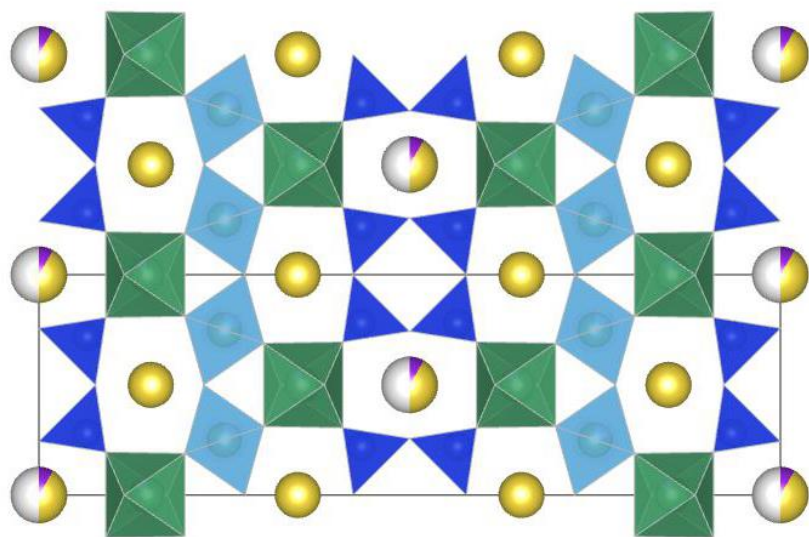
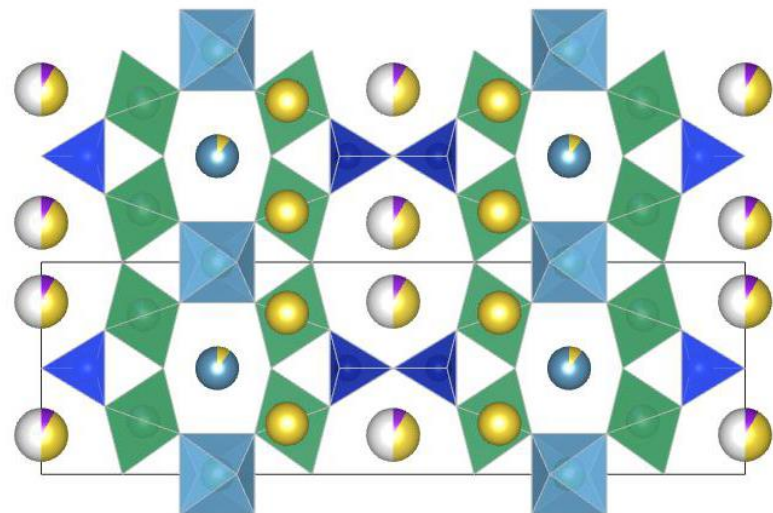
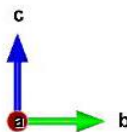
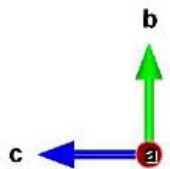
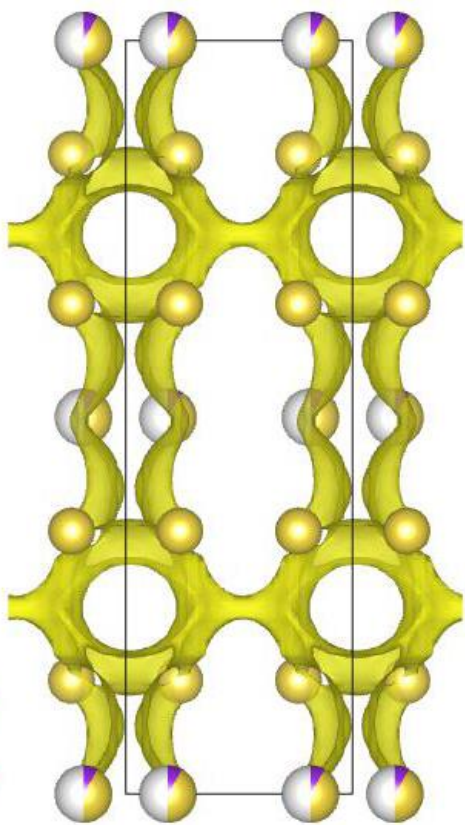
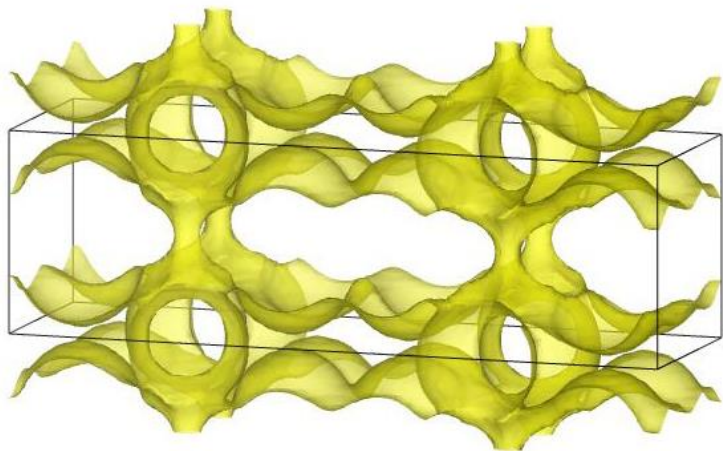
Name	Komarovite
Formula	$(\text{Ca}, \text{Mn})(\text{Nb}, \text{Ti})_2[\text{Si}_2\text{O}_7](\text{O}, \text{F})_3 \cdot 3.5\text{H}_2\text{O}$
Crystal system	Orthorhombic
Space group	Cmmm
Cell Parameters	$a = 21.30 \text{ \AA}$ , $b = 14.00 \text{ \AA}$ , $c = 17.19 \text{ \AA}$

Name	Fersmanite
Formula	$\text{Ca}_4(\text{Na}, \text{Ca})_4(\text{Ti}, \text{Nb})_4(\text{Si}_2\text{O}_7)_2\text{O}_8\text{F}_3$
Crystal system	Triclinic
Space group	$P\bar{1}$
Cell Parameters	$a = 7.21 \text{ \AA}$ , $b = 7.21 \text{ \AA}$ , $c = 20.45 \text{ \AA}$ $\alpha = 95.15^\circ$ , $\beta = 95.6^\circ$ , $\gamma = 89.04^\circ$



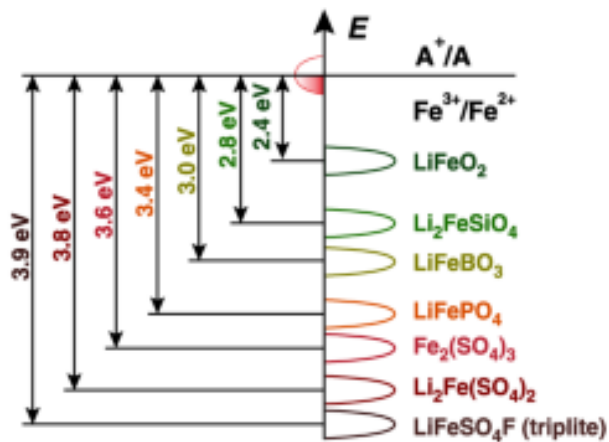
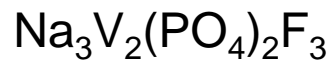
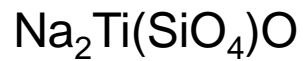
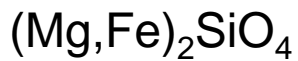
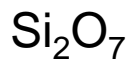
*AS fersman*

# Komarovite

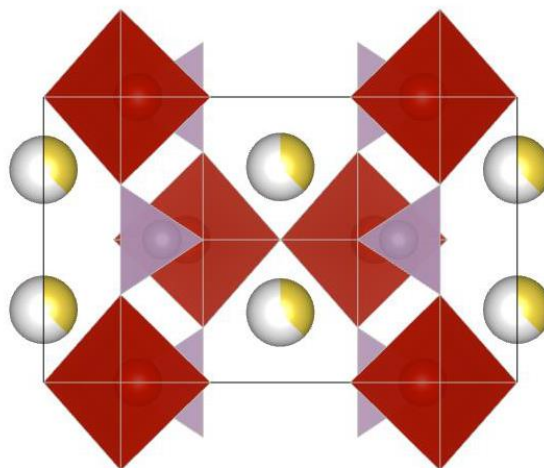
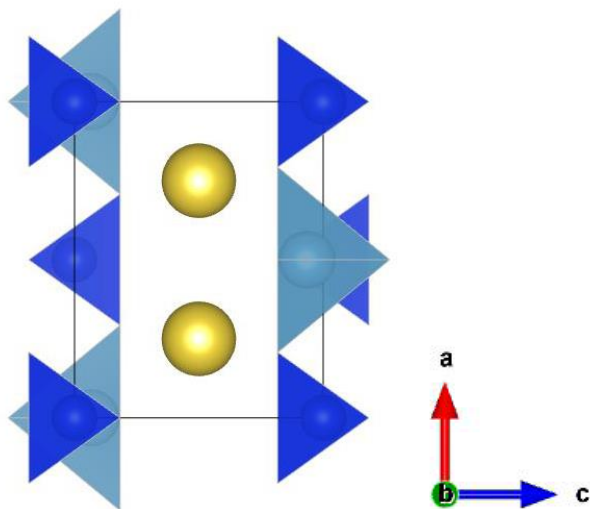
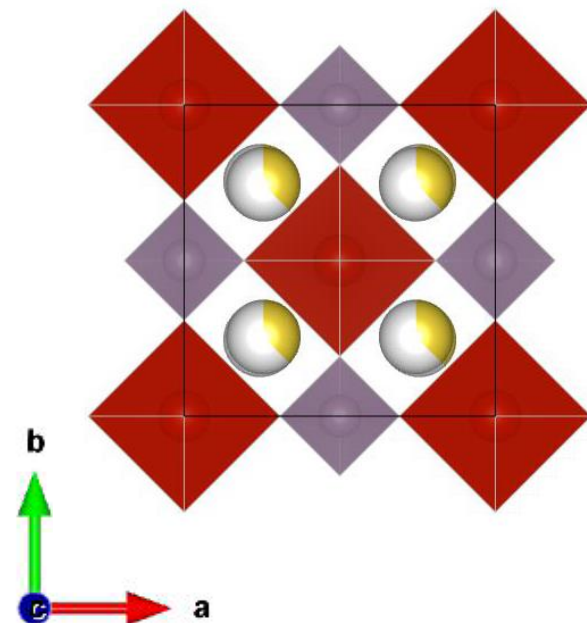
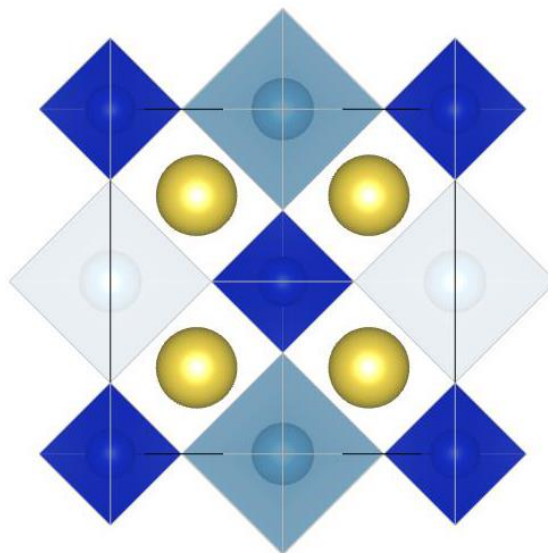




# Silicate

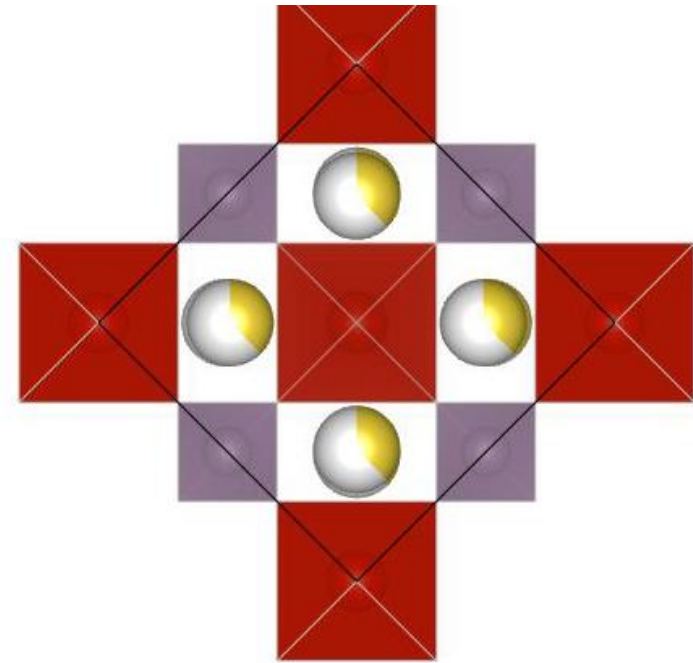
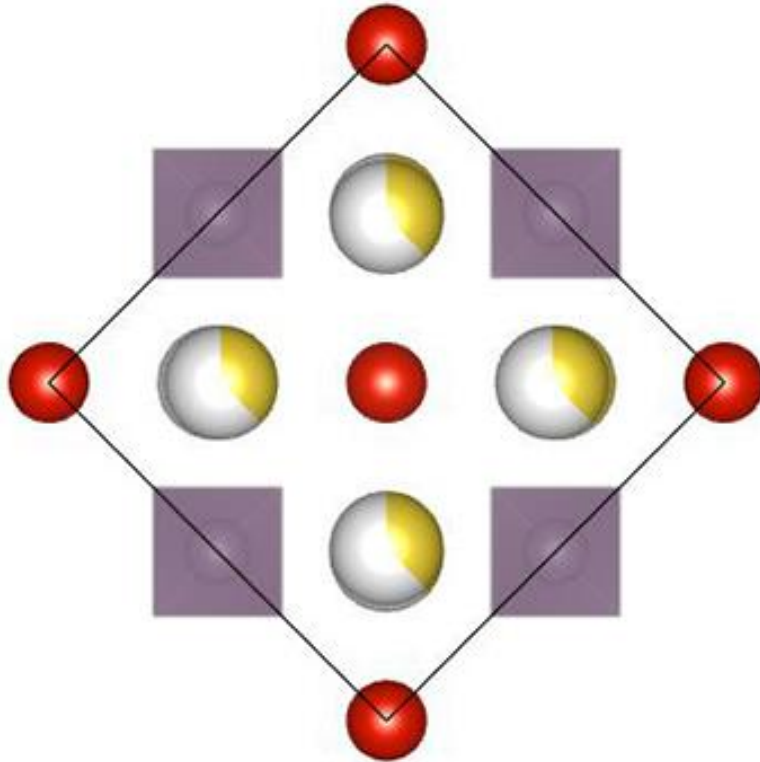


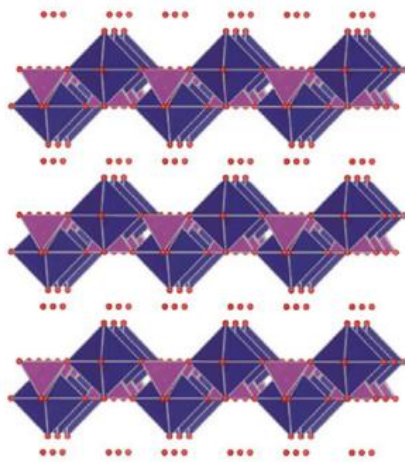
Abakumov, Artem M., et al. *Nature Communications* 11.1 : 4976 (2020)




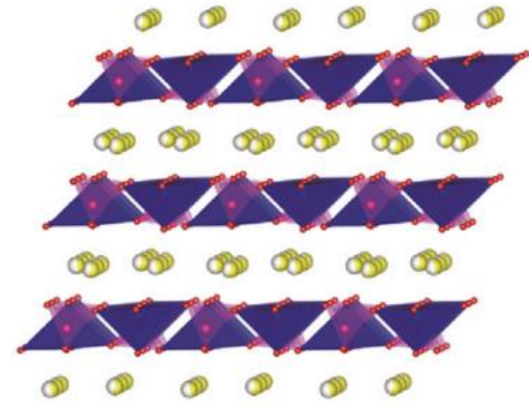
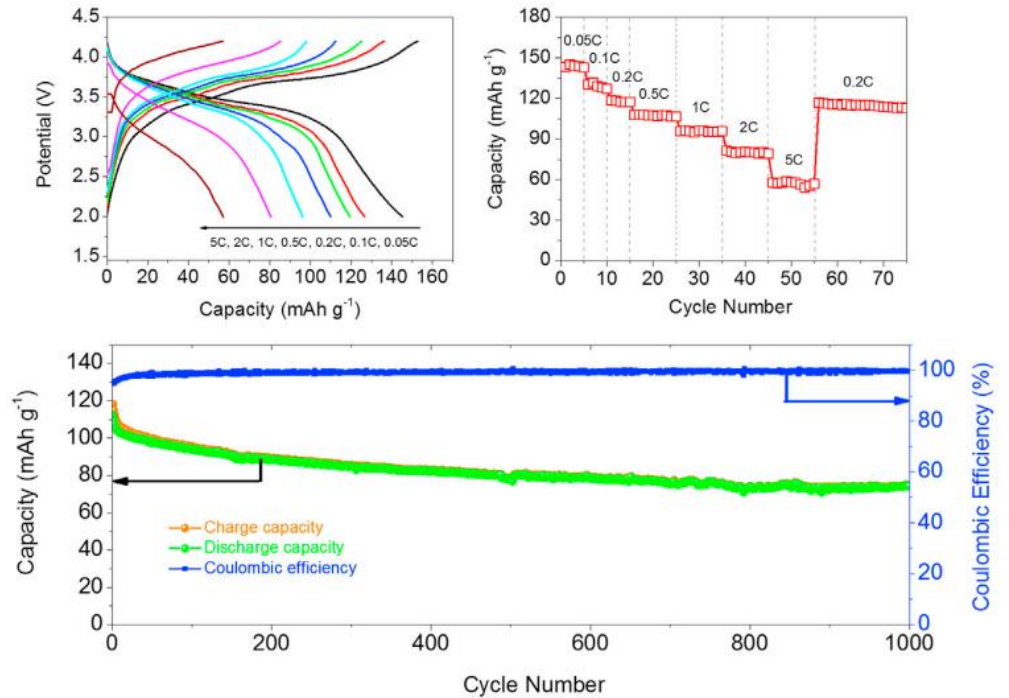
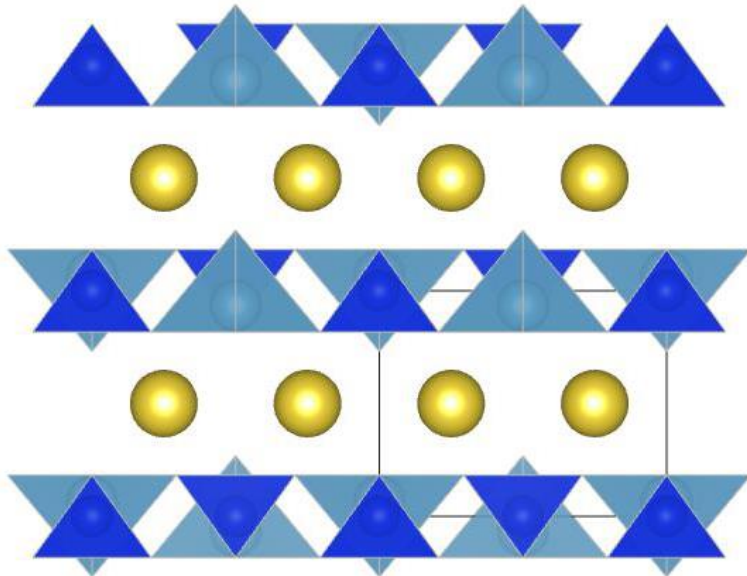
Name	Sulphohalite
Formula	$\text{Na}_6(\text{SO}_4)_2\text{FCl}$
Crystal system	Cubic
Space group	$\text{Fm}\bar{3}\text{m}$
Cell Parameters	$a = 10.068 \text{ \AA}$

$$\begin{array}{c}
 O^5_h = \text{Fm}\bar{3}\text{m} \\
 \downarrow \\
 D^{17}_{4h} = \text{I}4/\text{mmm} \\
 \downarrow \qquad \qquad \downarrow \\
 D^{11}_{2d} = \text{I}\bar{4}2\text{m} \quad D^{14}_{4h} = \text{P}4_2/\text{mnm}
 \end{array}$$



VOPO<sub>4</sub>·2H<sub>2</sub>O

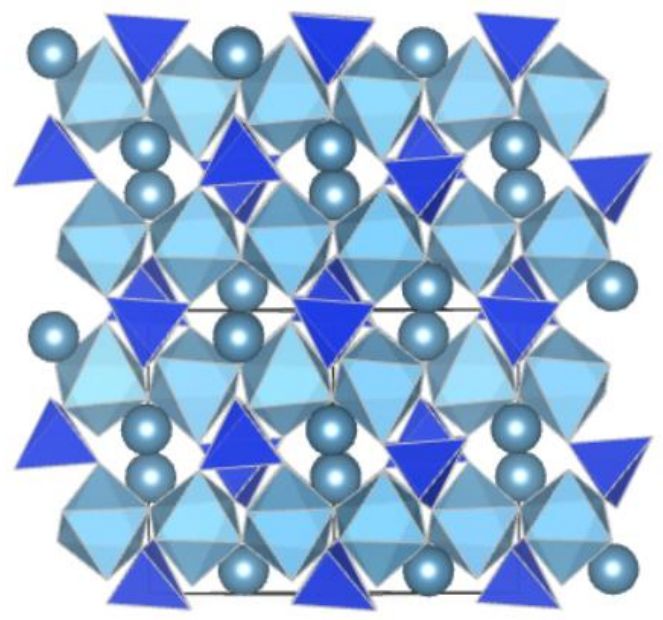
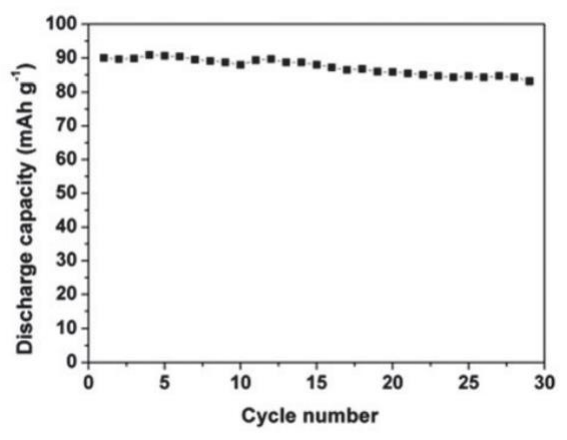
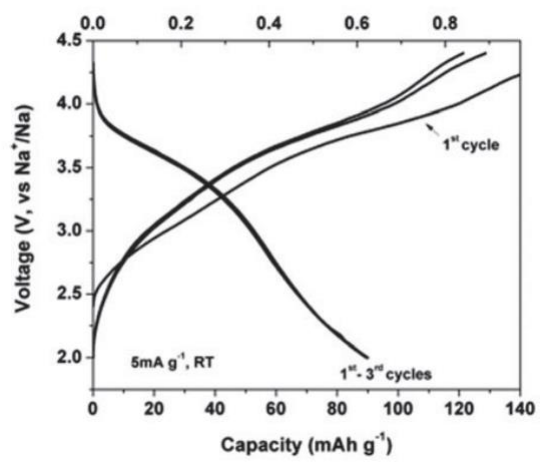
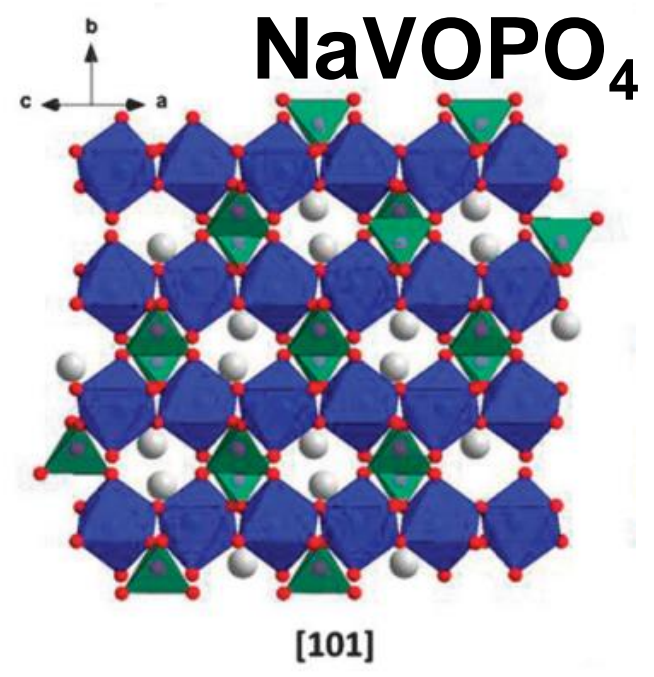
Solvothermal  
  
 NaI/C<sub>4</sub>H<sub>10</sub>O<sub>2</sub>

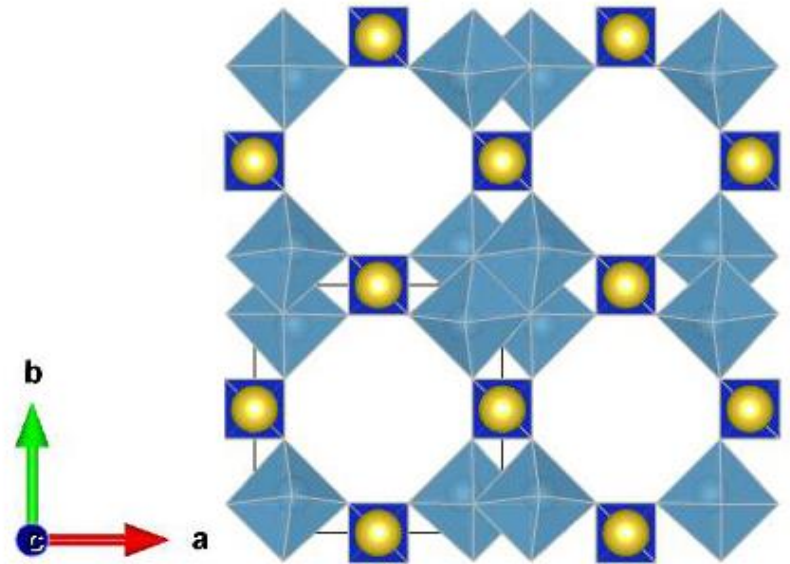
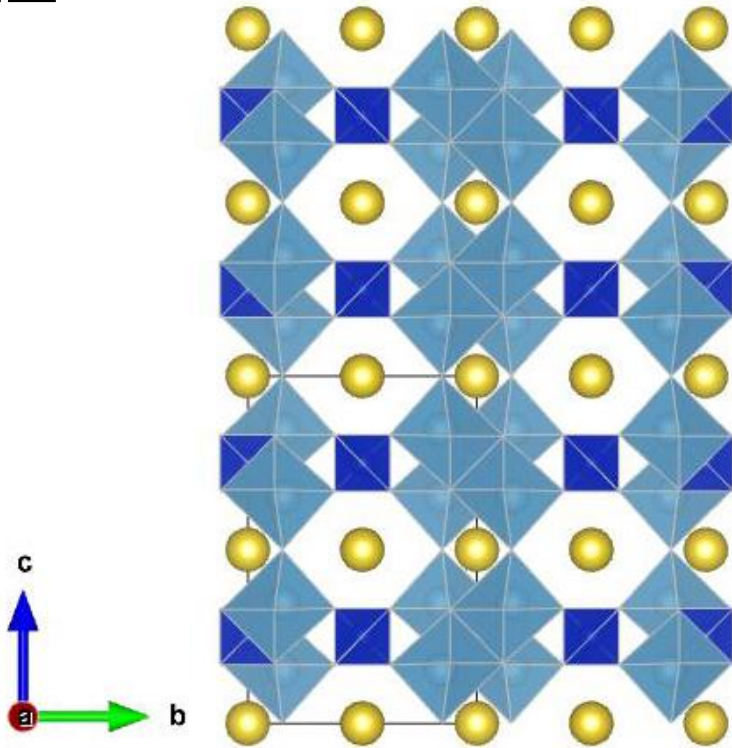
NaVOPO<sub>4</sub>



Name	Titanite
Formula	CaTi(SiO <sub>4</sub> )O
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /c
Cell Parameters	a = 7.06 Å, b = 8.71 Å, c = 6.55 Å β = 113.79°

Symmetry: Monoclinic  
Space group: P2<sub>1</sub>/c  
Lattice parameters: a = 6.518(5) Å, b = 8.446(4) Å, c = 7.115(1) Å, β = 115.25(0)°, V = 354.3(1) Å<sup>3</sup>



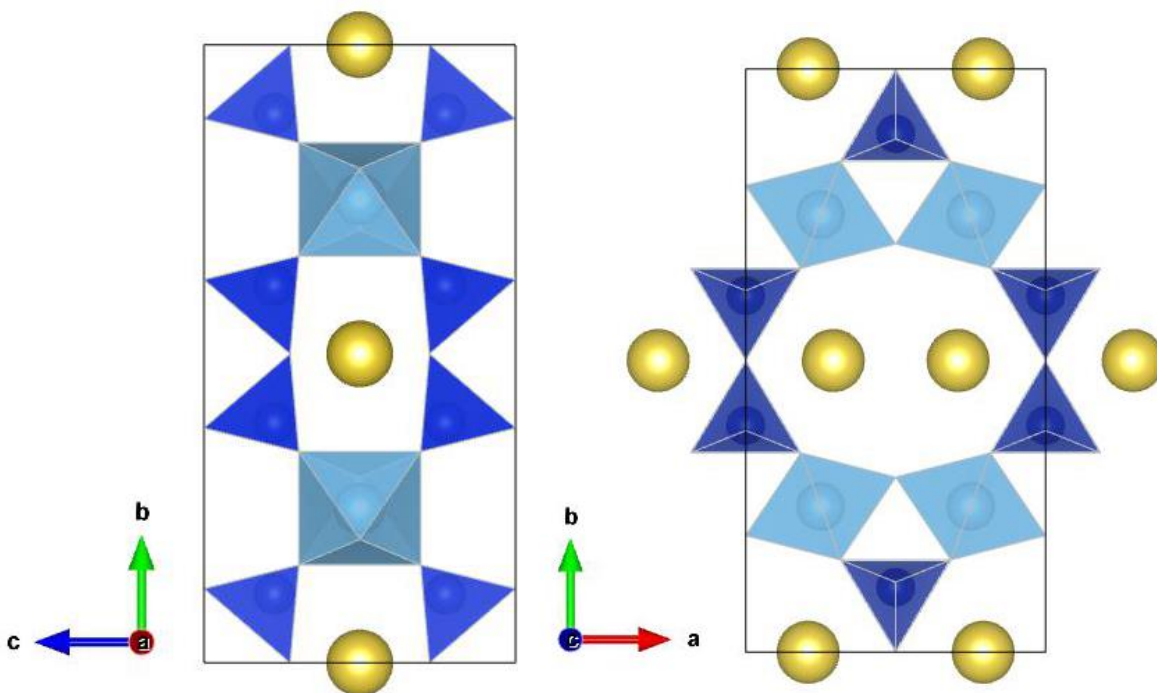


Name	Sitinakite
Formula	$\text{KNa}_2\text{Ti}_4(\text{SiO}_4)_2\text{O}_5(\text{OH}) \cdot 4\text{H}_2\text{O}$
Crystal system	Tetragonal
Space group	$P4_2/mcm$
Cell Parameters	$a = 7.819(2) \text{ \AA}$ $c = 12.099(4) \text{ \AA}$



# Silicate

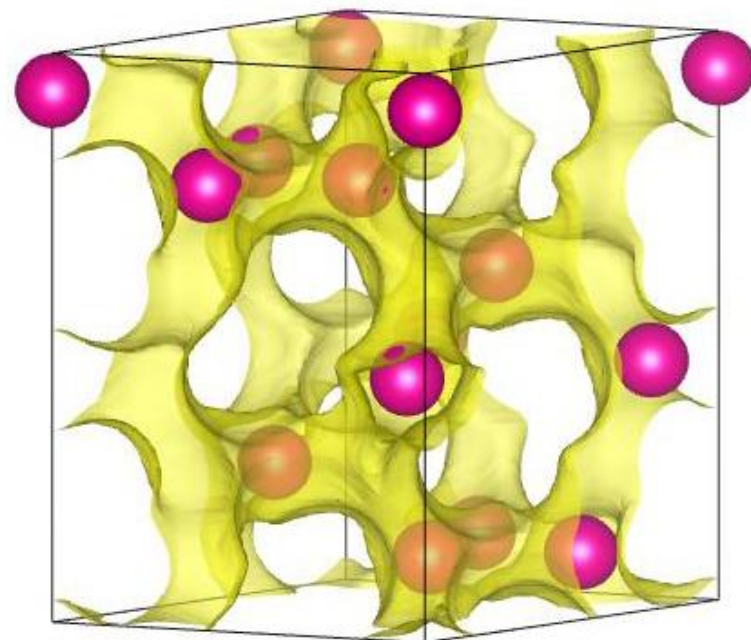
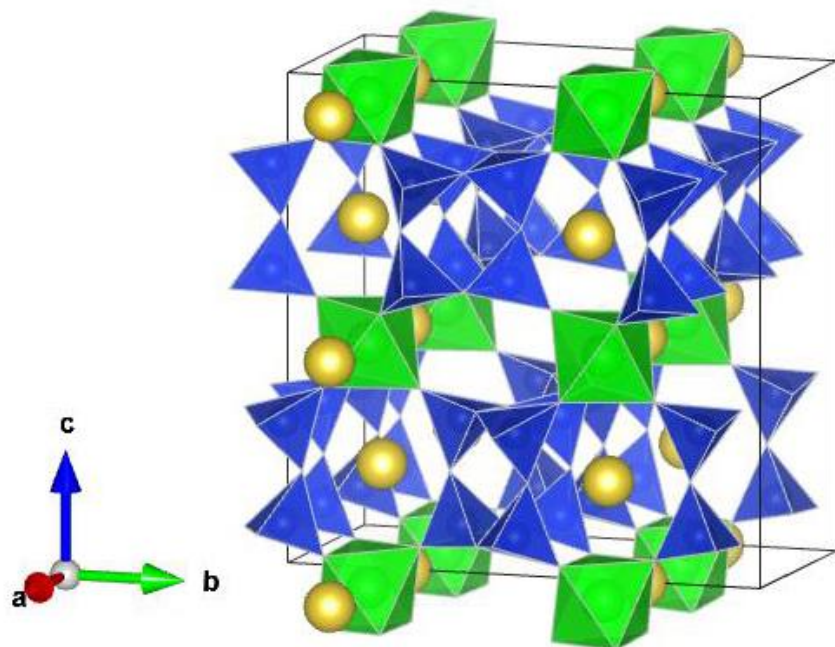
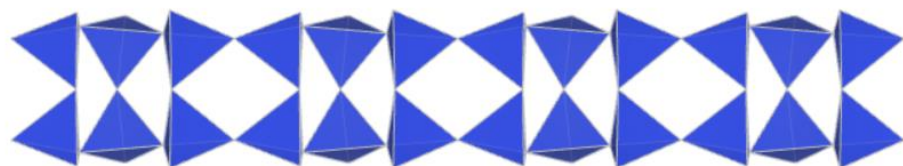
Name	Labuntsovite
Formula	$\text{Na}_{1.33}\text{TiSi}_2\text{O}_6 (\text{O}_{0.34}\text{OH}_{0.66}) \cdot 2.58\text{H}_2\text{O}$
Crystal system	Orthorhombic
Space group	Cmmm
Cell Parameters	$a = 7.278 \text{ \AA}$ , $b = 14.134 \text{ \AA}$ , $c = 7.118 \text{ \AA}$





Name	Elpidite
Formula	$\text{Na}_2\text{ZrSi}_6\text{O}_{15} \cdot 3\text{H}_2\text{O}$
Crystal system	Orthorhombic
Space group	Pbcm
Cell Parameters	$a = 7.14 \text{ \AA}$ , $b = 14.68 \text{ \AA}$ , $c = 14.65 \text{ \AA}$

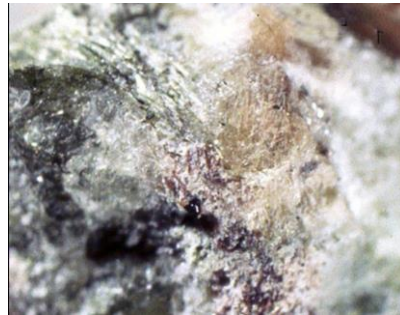
Name	Hilairite
Formula	$\text{Na}_2\text{Zr}[\text{SiO}_3]_3 \cdot 3\text{H}_2\text{O}$
Crystal system	Trigonal
Space group	R3
Cell Parameters	$a = 10.477 \text{ \AA}$ , $c = 15.377 \text{ \AA}$



Name	Sidorenkite
Formula	$\text{Na}_3\text{Mn}^{2+}(\text{CO}_3)(\text{PO}_4)$
Crystal system	Monoclinic
Space group	$P2_1/m$
Cell Parameters	$a = 8.997\text{\AA}$ , $b = 6.741\text{\AA}$ , $c = 5.163\text{\AA}$ $\beta = 90.16(4)^\circ$



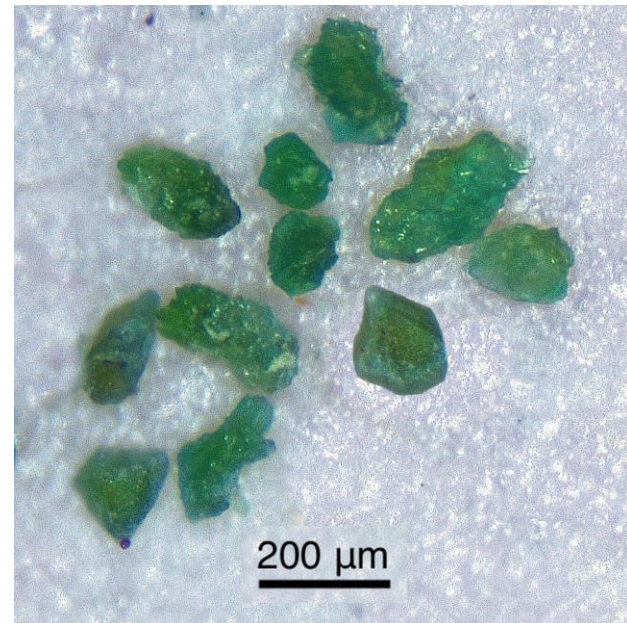
Бонштедтит  
 $\text{Na}_3\text{Fe}^{2+}(\text{CO}_3)(\text{PO}_4)$



Крофордит  
 $\text{Na}_3\text{Sr}(\text{CO}_3)(\text{PO}_4)$



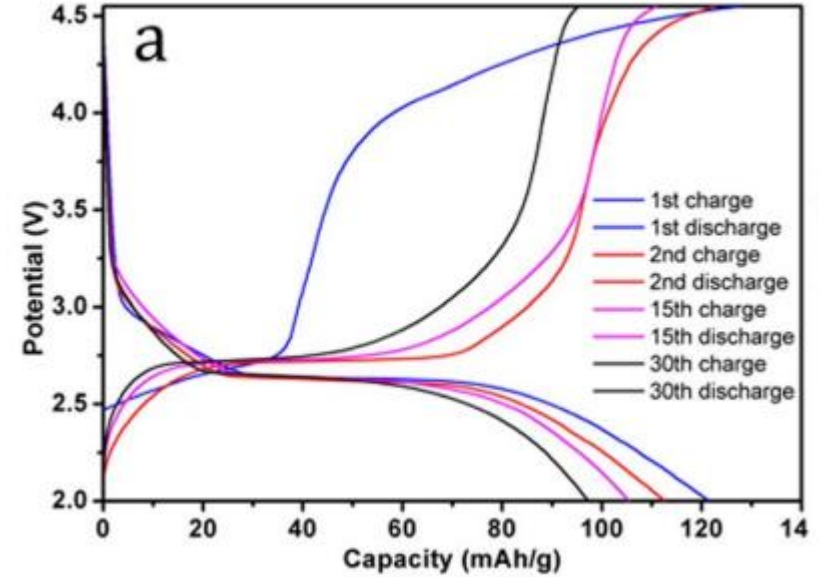
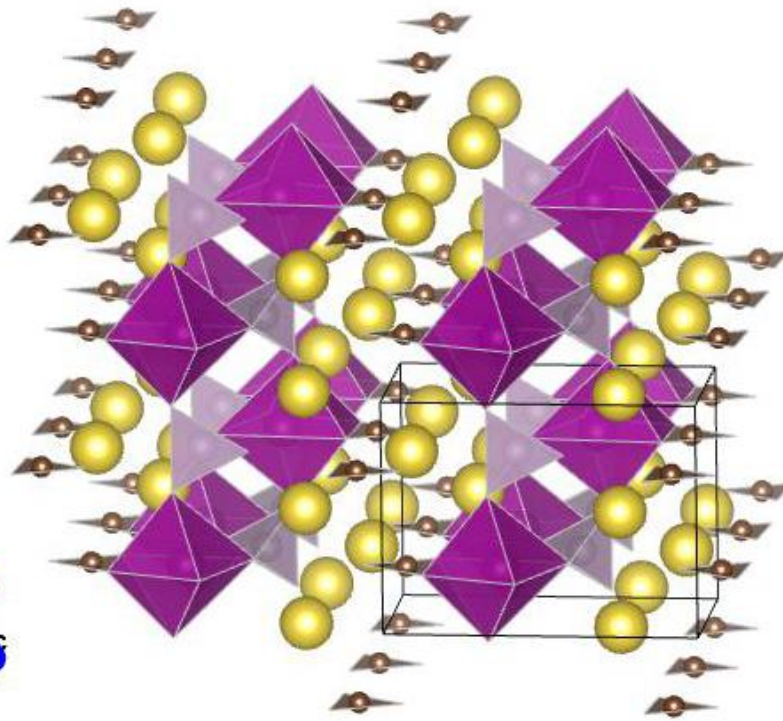
Бредлиит  
 $\text{Na}_3\text{Mg}(\text{CO}_3)(\text{PO}_4)$



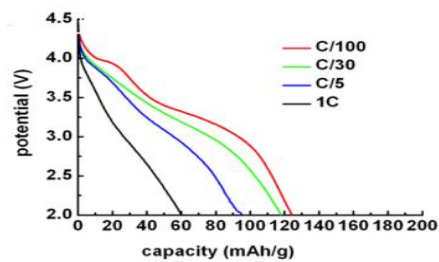
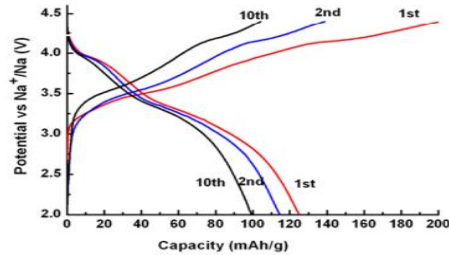
$\text{Na}_3(\text{VO})^{2+}(\text{PO}_4)(\text{CO}_3)$



# Na<sub>3</sub>MnPO<sub>4</sub>CO<sub>3</sub>



Huang, Weifeng, et al. *Scientific reports* 4.1, 4188 (2014)

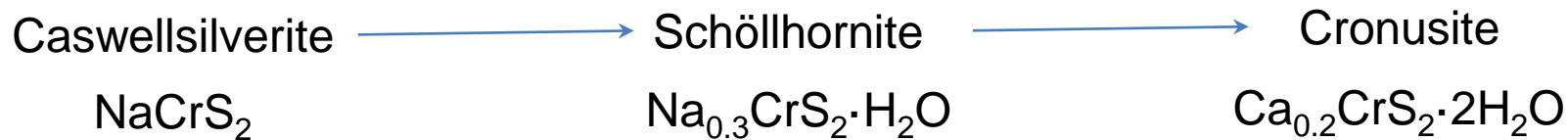
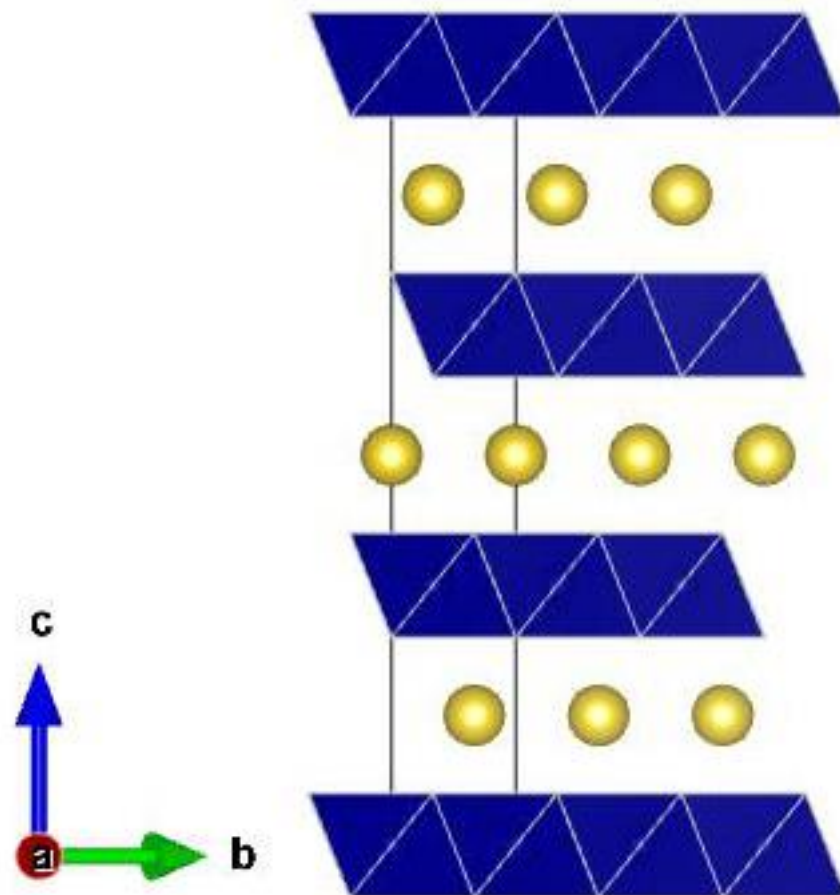


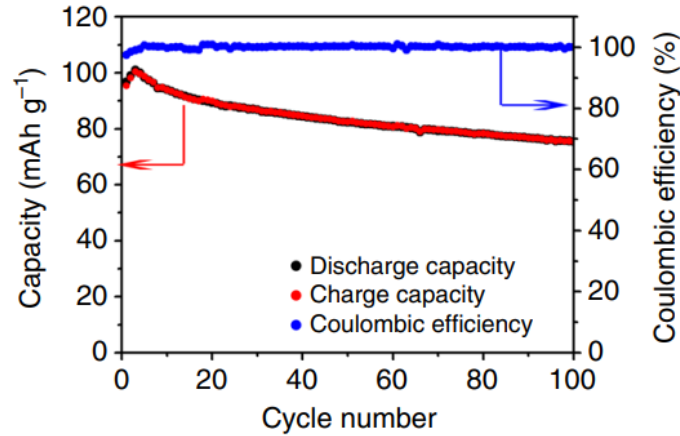
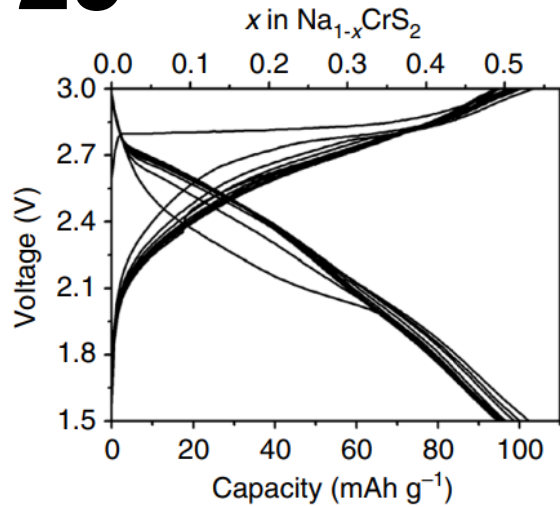
	Synthesis method	Average size (nm)	Carbon source	Content s of carbon	Discharge capacity at 1 <sup>st</sup> cycle	Cyclability
Na <sub>3</sub> MnPO <sub>4</sub> CO <sub>3</sub>	Hydrothermal method	~20	Carbon black	34 wt. %	107 mAh/g (1/30C)	No reports
Na <sub>3</sub> MnPO <sub>4</sub> CO <sub>3</sub>	Ball milling method	~400	Carbon black	20 wt. %	103mAh/g (1/30C)	73 mAh/g after 15 cycles
Na <sub>3</sub> MnPO <sub>4</sub> CO <sub>3</sub>	Hydrothermal method	~400	Carbon black	20 wt. %	67 mAh/g (1/30C)	15 mAh/g after 10 cycles
Na <sub>3</sub> MnPO <sub>4</sub> CO <sub>3</sub>	Hydrothermal method	~100	Carbon black	30 wt. %	125 mAh/g (1/100C)	90 mAh/g after 15 cycles
Na <sub>3</sub> MnPO <sub>4</sub> CO <sub>3</sub>	Mechanical milling method	~100	Acetylene black	20 wt. %	134 mAh/g (1/30C)	97 mAh/g after 30 cycles
Na <sub>3</sub> MnPO <sub>4</sub> CO <sub>3</sub>	Mechanical milling method	~100	Acetylene black	20 wt. %	116 mAh/g (1/10C)	78 mAh/g after 30 cycles

Chen, H., et al. *Chemistry of Materials*, 25(14), 2777–2786 (2013)

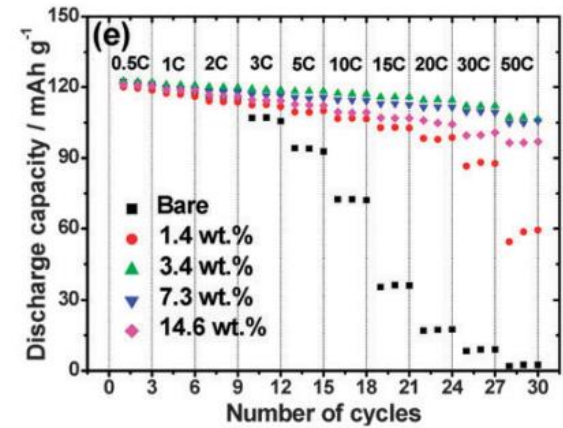
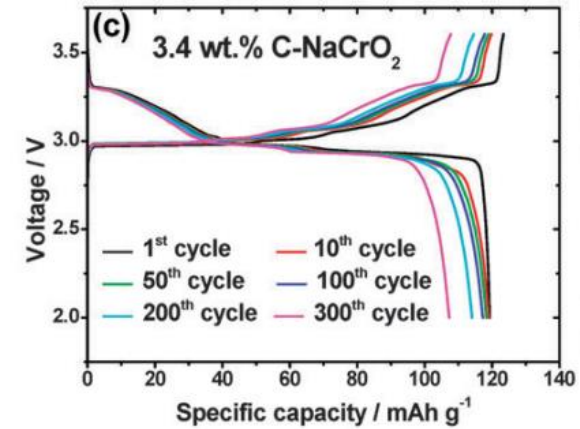


Name	Caswellsilverite
Formula	$\text{NaCrS}_2$
Crystal system	Trigonal
$Fd\bar{3}m$	$R\bar{3}m$
Cell Parameters	$a = 3.54 \text{ \AA}$ , $c = 19.35 \text{ \AA}$

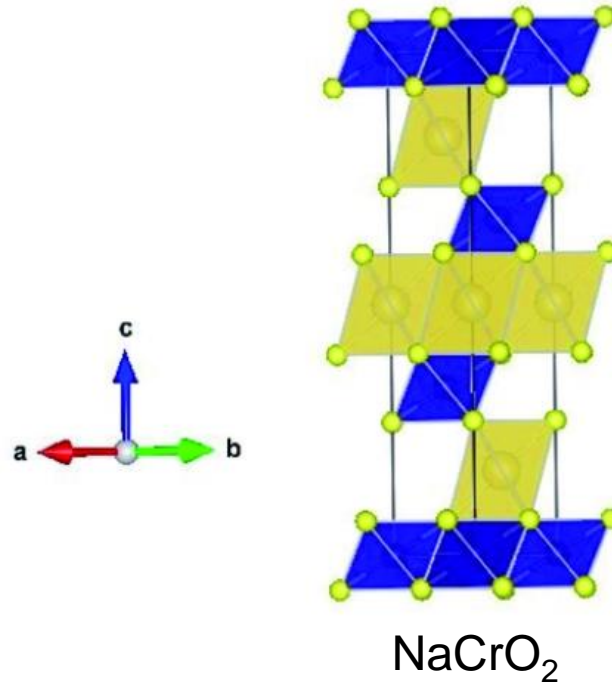
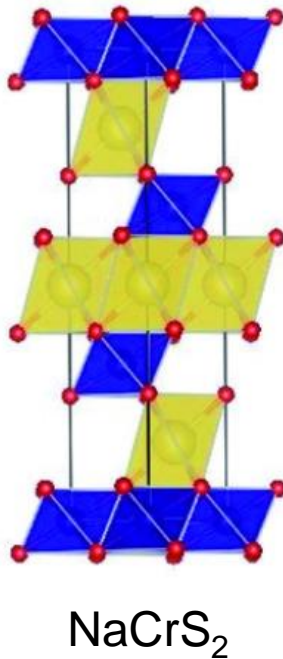




Shadike, Z., et al. *Nature Communications*, 8(1), (2017)



Yu, C.-Y., et al. *Energy & Environmental Science*, 8(7), 2019–2026, (2015)



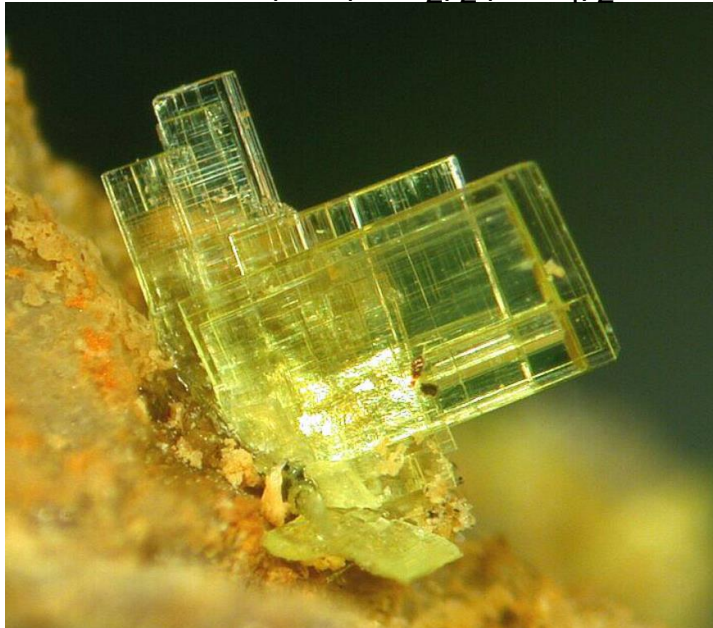




Uranocircite ( $\text{Ba}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$ )



Torbernite ( $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O}$ )



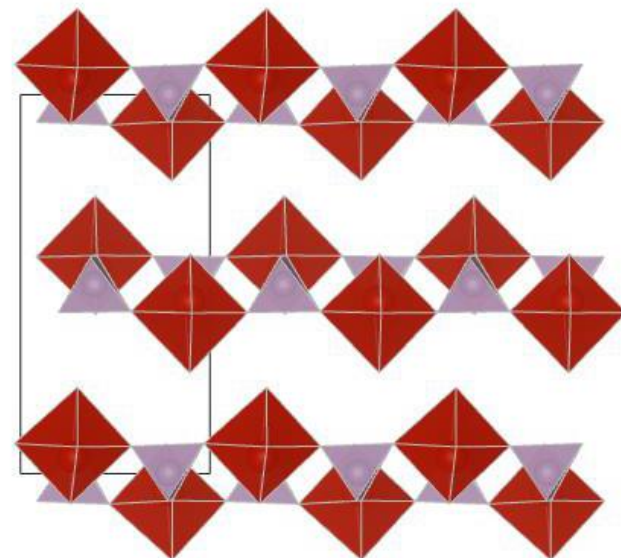
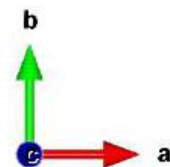
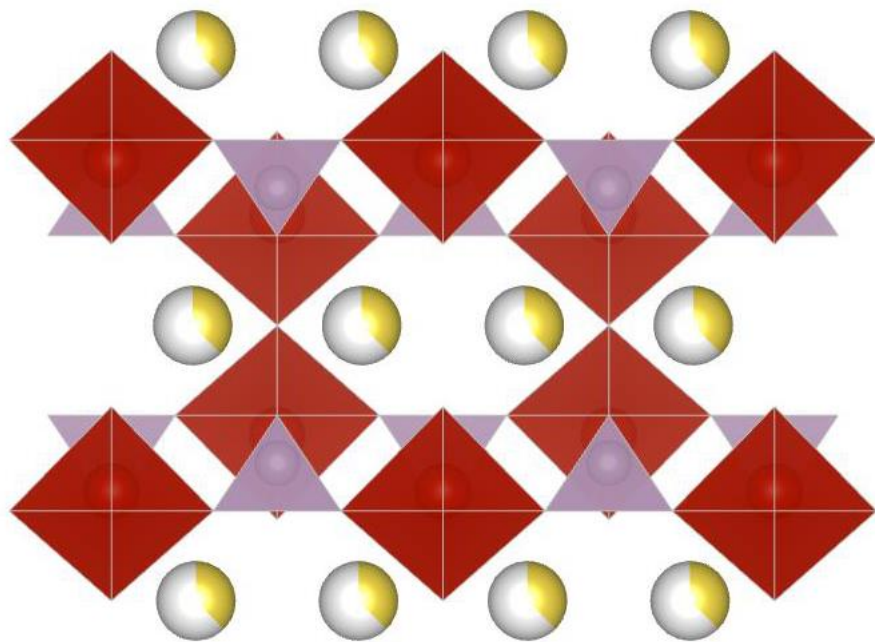
Autunite ( $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$ )



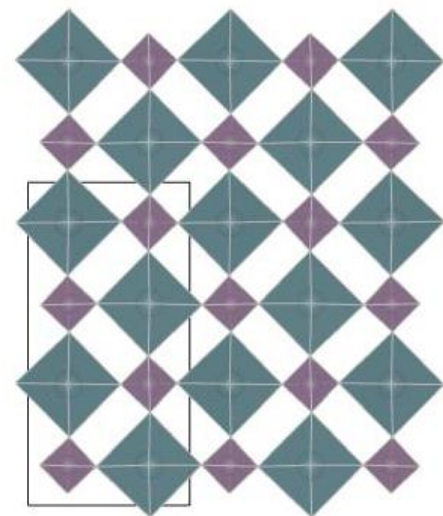
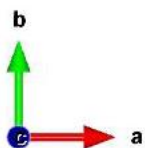
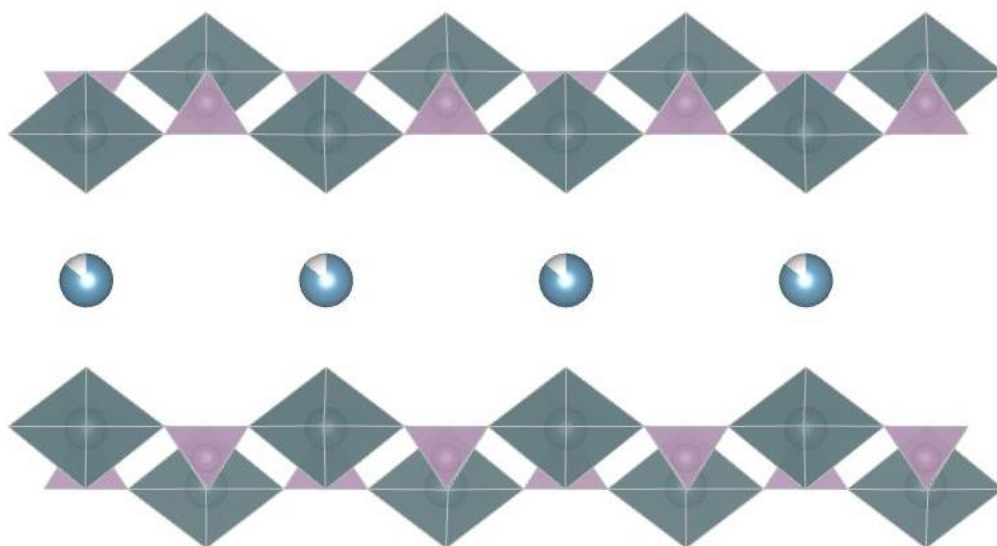
Saléeite ( $\text{Mg}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$ )

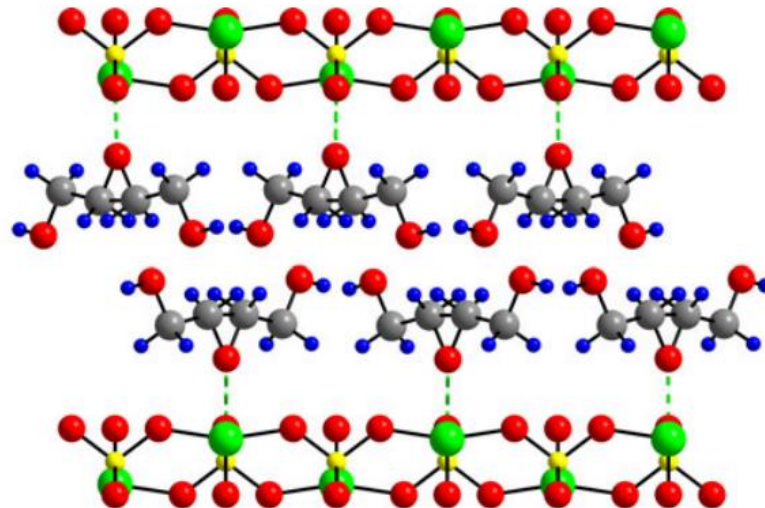
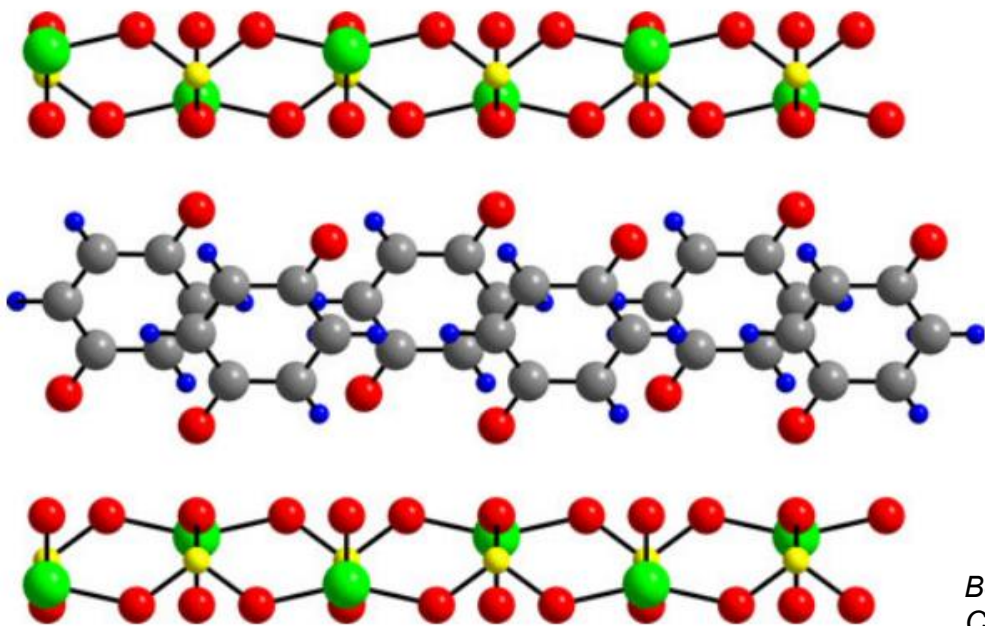
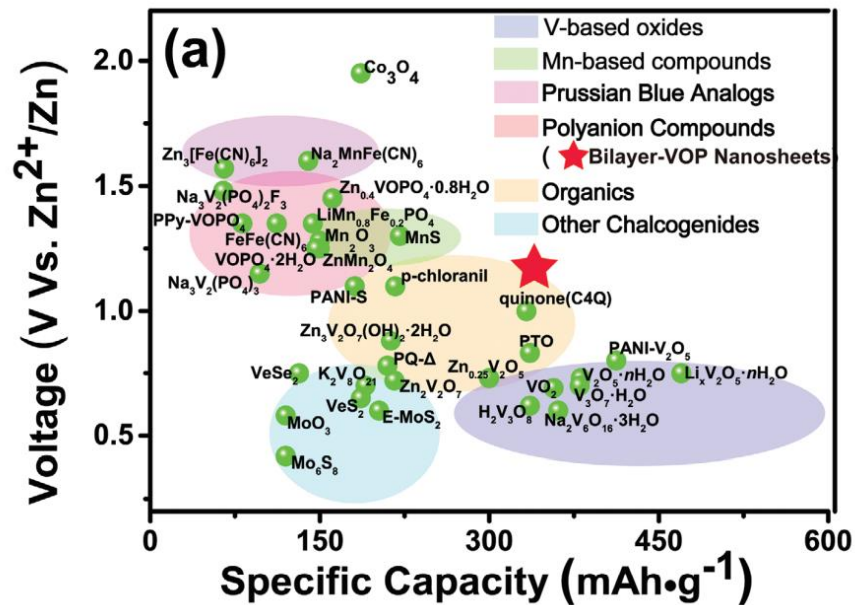
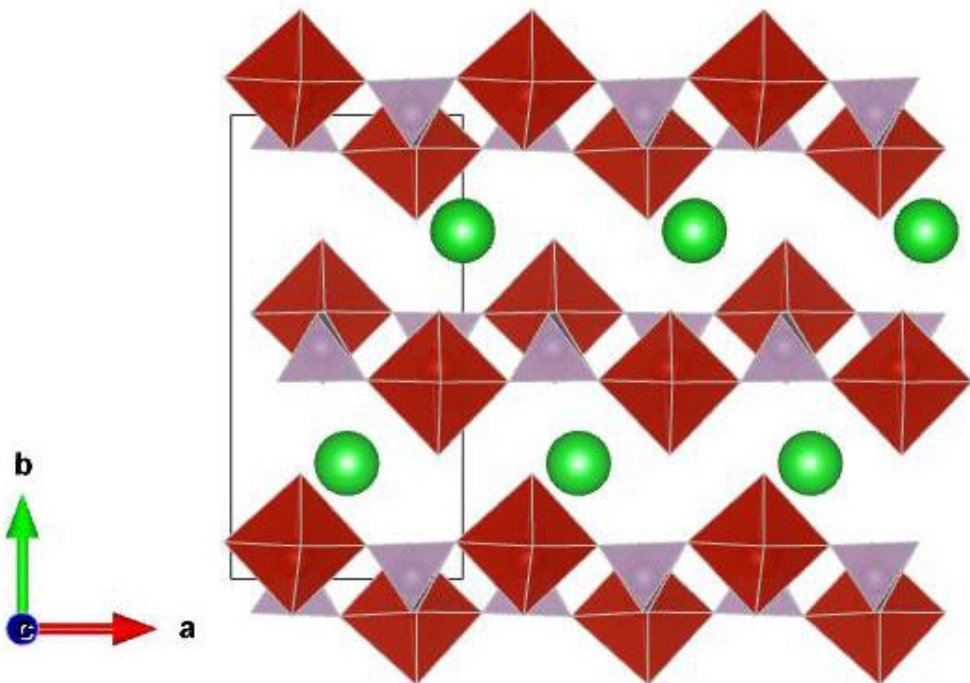


# NaVOPO<sub>4</sub>



# VOPO<sub>4</sub>·2H<sub>2</sub>O








*Review*

# Mineral-Inspired Materials: Synthetic Phosphate Analogues for Battery Applications

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**Thx**

