

From a Layer to a Ring: A Kinetic Study for the Ion-Exchange Reactions of a New Tellurite, $\text{Li}_2\text{Mo}_3\text{TeO}_{12}$ Using the Powder X-Ray Diffraction

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Abstract

A new alkali metal molybdenum tellurite, $\text{Li}_2\text{Mo}_3\text{TeO}_{12}$ (LMT), has been synthesized through a hydrothermal reaction. The title compound crystallizes in the monoclinic space group, $P2/c$, and reveals a sinuous layered structure that is composed of highly distorted MoO_6 and TeO_4 polyhedra. The distortion of the constituent polyhedra is originating from the cationic size effect of Li^+ cations located between the anionic layers. Since the unusually strong distortions of TeO_4 polyhedra destabilize the overall structures, the decomposition and recombination reactions in ion-exchange experiments from LMT to $\text{A}_4\text{Mo}_6\text{Te}_2\text{O}_{24}\cdot x\text{H}_2\text{O}$ ($\text{A} = \text{K, Rb, and Cs}$; $x = 4$ or 6) were observed. A kinetic study of the ion-exchange reaction has been investigated using the powder X-ray diffraction at different temperatures. Our experiments indicate that the reactions are predominantly controlled by an intercalation of alkali metal cations, which was followed by a nucleation. As the size of cations increases, the decomposition rate of the title compounds was slowed down attributed to the difficulty of the intercalation of incoming alkali metals. After the decomposition, the separated anionic groups were combined to an aggregated form, $[\text{Mo}_6\text{Te}_2\text{O}_{24}]^{4-}$, which was subsequently surrounded by alkali metal cations. The anionic aggregate composed of six MoO_6 octahedra and two TeO_3 polyhedra reveal a hexagonal ring structure, which is capped by two TeO_3 polyhedra from the above and below. The activation energies for each reaction are also calculated by the Arrhenius equation.

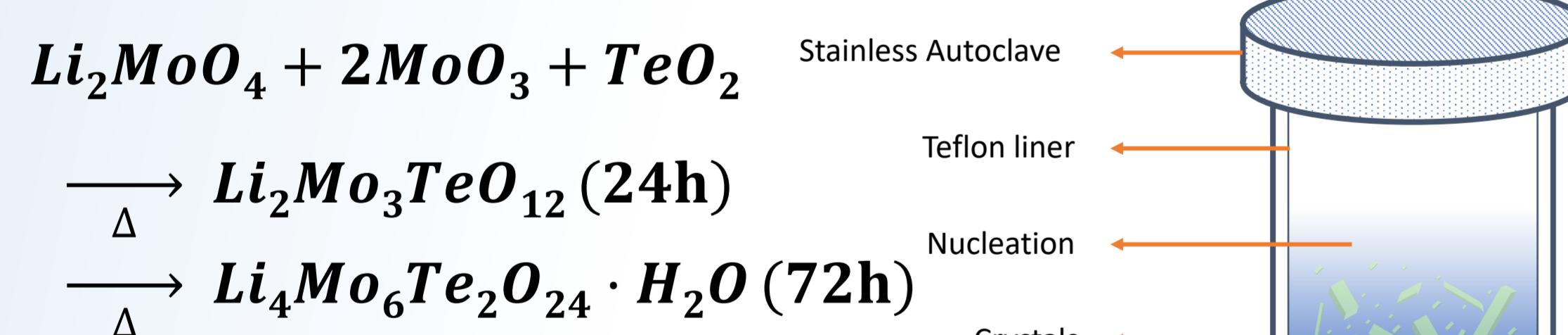
Introduction

- Metal tellurites have been widely discussed due to not only their structural flexibility in making bonds with oxygen atoms, but also stereochemically active lone-pair (SCALP) electrons on Te^{4+} acting as structure-directing agents.
- However, studies on tellurite compounds containing Li^+ cations have been rarely carried out, and therefore the effect of the size of monovalent cations on structure has not been fully understood.
- In-situ* time-resolved powder X-ray diffraction (PXRD) have been widely tried out to elucidate driving forces on the crystallization process.
- We synthesized new lithium contained tellurite with layered structure and induce the structural transformation by ion-exchange reactions.
- The kinetic and thermodynamic data have been modelled using the Avrami-Erofe'ev equation and the Arrhenius equation, respectively.

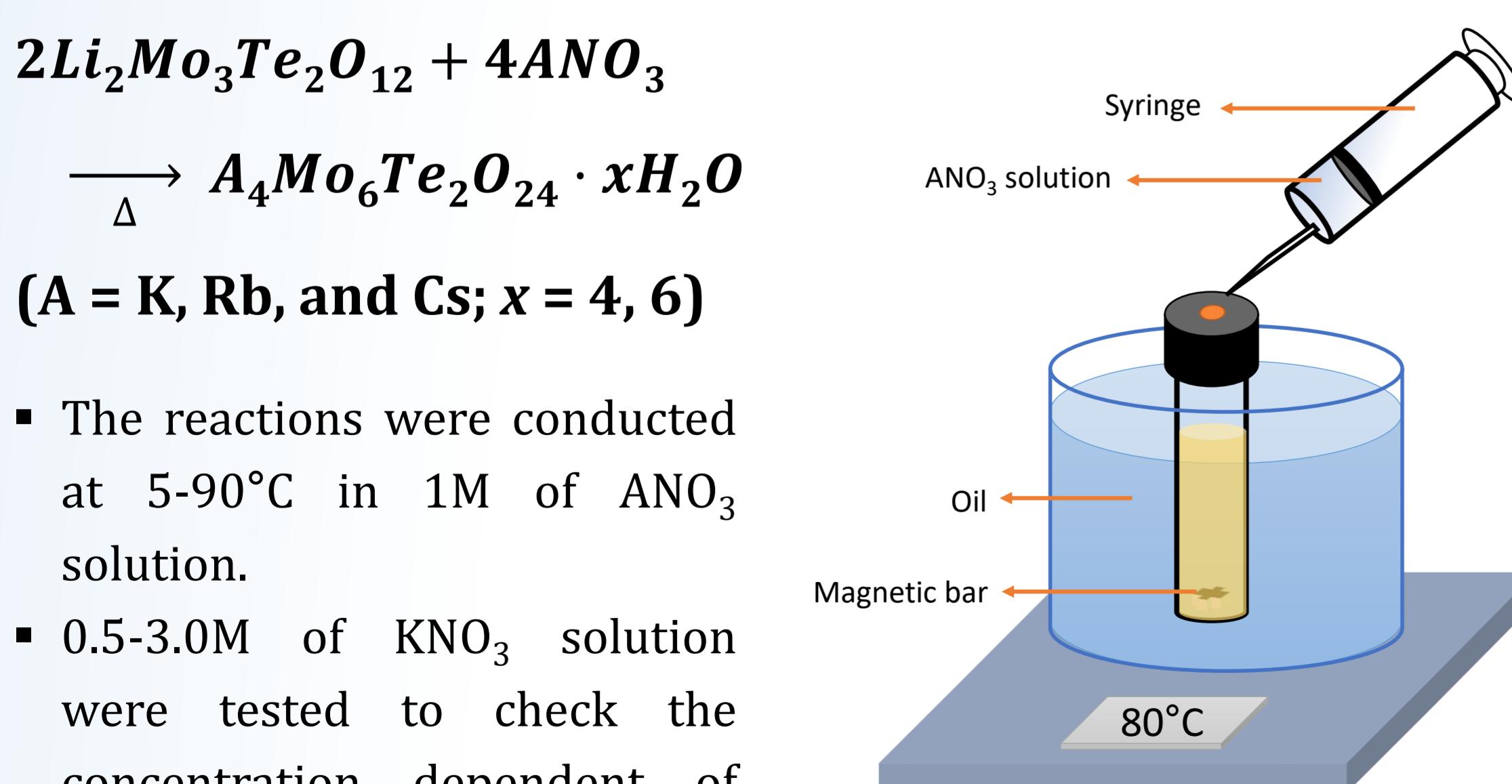
➤ Avrami-Erofe'ev equation: $\alpha(t) = 1 - \exp(-kt^n)$
 ➤ Arrhenius equation: $k = A \exp(-E_a/RT)$

Synthesis

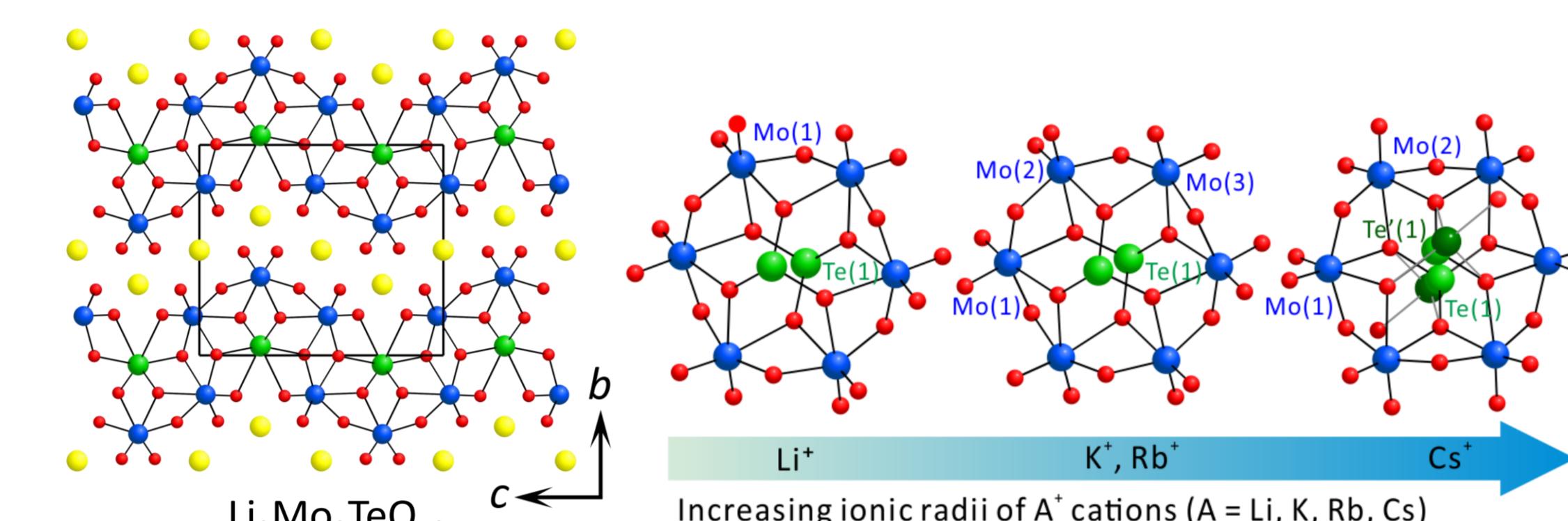
Hydrothermal Reaction



Ion-Exchange Reaction

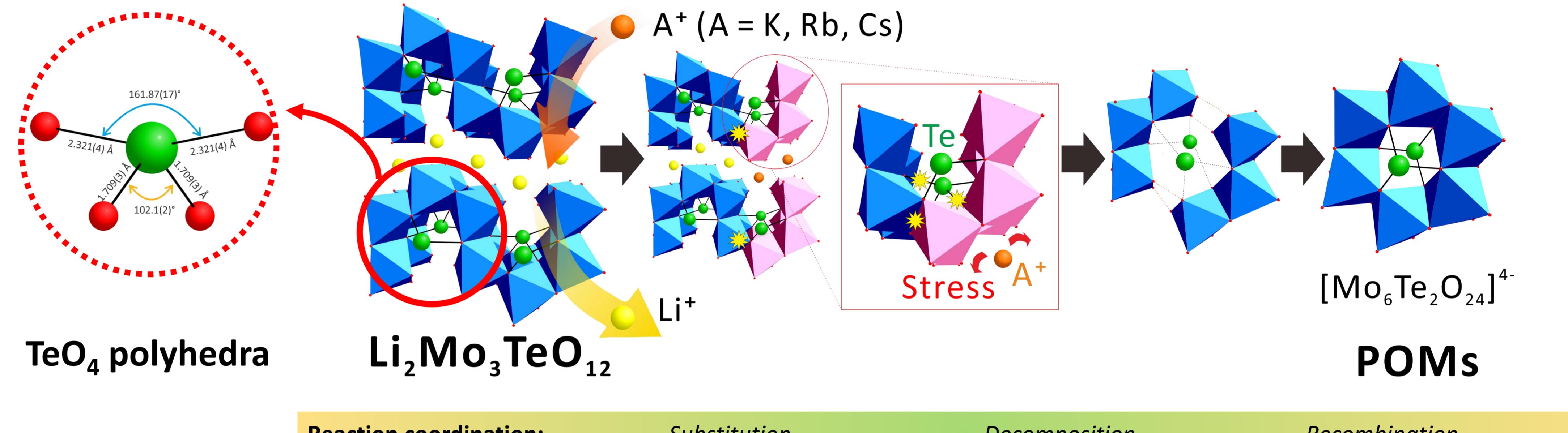


Crystal structures



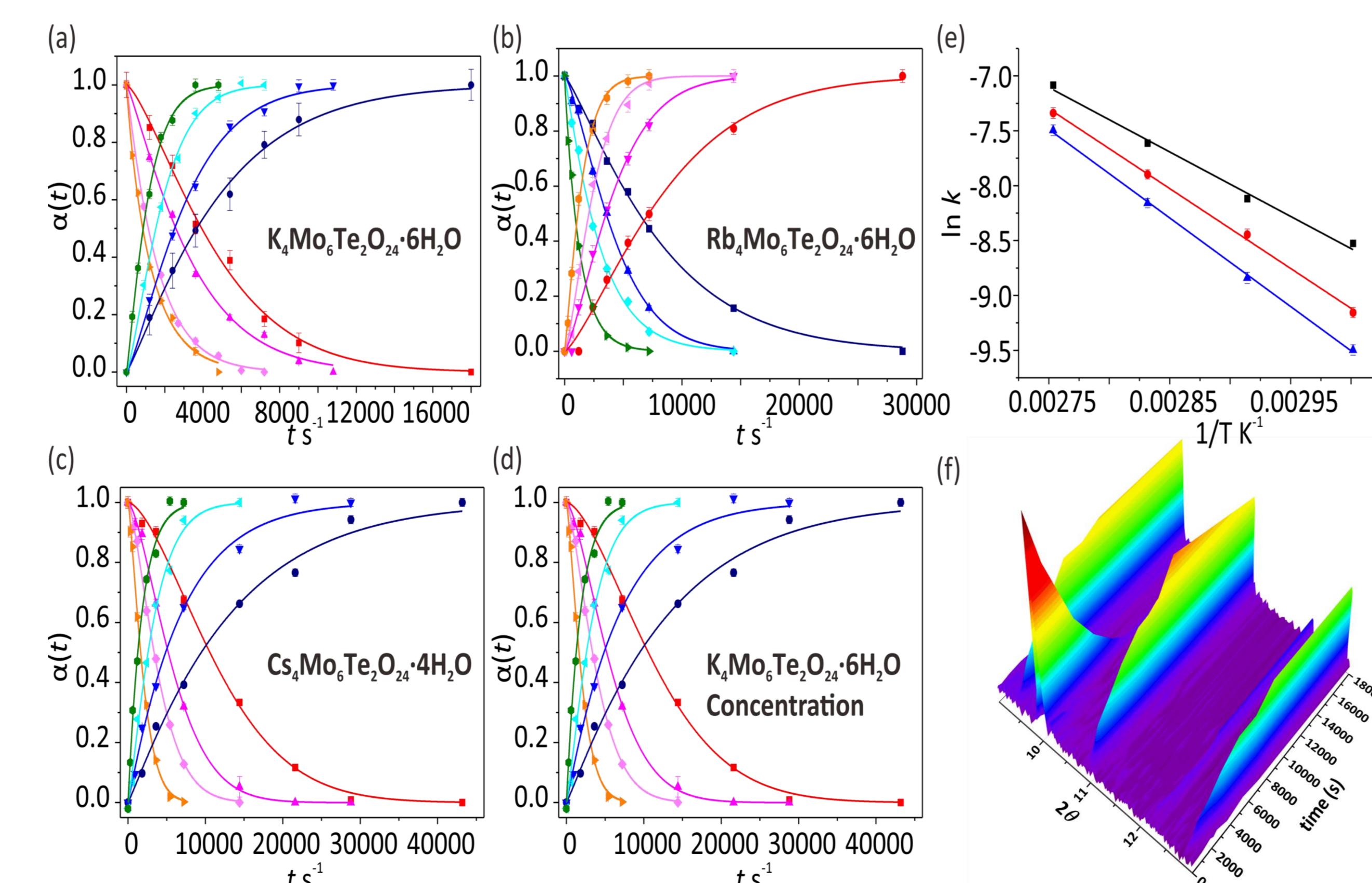
Formula	$\text{Li}_2\text{Mo}_3\text{TeO}_{12}$	$\text{Li}_4\text{Mo}_6\text{Te}_2\text{O}_{24}\cdot\text{H}_2\text{O}$	$\text{Cs}_4\text{Mo}_6\text{Te}_2\text{O}_{24}\cdot 4\text{H}_2\text{O}$
Formula weight	621.30	1260.6	1764.46
Space group	$P2/c$ (No. 13)	$Pa-3$ (No. 205)	$Cmca$ (No. 64)
a (Å)	4.7776(1)	12.50729(10)	21.1903(3)
b (Å)	8.8347(2)	12.50729(10)	14.0510(3)
c (Å)	10.2472(3)	12.50729(10)	9.7460(2)
β (deg)	90.473(2)	-	-
V (Å ³)	432.51(2)	1956.55(5)	2901.82(10)
$R(F)$	0.0251	0.0331	0.0307
$R_w(F_o^2)$	0.0611	0.0795	0.104

Reaction mechanism



- The reaction mechanisms are composed of several steps: substitution, decomposition, and recombination.
- The driving force of the decomposition is structural stress from substituted alkali metal cations between the layer that break the Te-O and Mo-O bonds, forming $[\text{Mo}_3\text{TeO}_{12+8}]^{2-6-}$ fragments.
- The broken part assembled with each other composing $[\text{Mo}_6\text{Te}_2\text{O}_{24}]^{4-}$ structures, polyoxometalates (POMs).
- In consideration of the effect of cationic size on reaction rate, the substitution is the determinant step.

Kinetic & Thermodynamic parameters



System	Condition	k	n	$t_{0.5}$ (s)
K	60°C	0.198 ± 0.005	1.15 ± 0.6	3667
K	70°C	0.298 ± 0.007	1.27 ± 0.06	2513
K	80°C	0.495 ± 0.010	1.32 ± 0.05	1530
K	90°C	0.838 ± 0.019	1.16 ± 0.04	870
Rb	60°C	0.106 ± 0.004	1.32 ± 0.09	7171
Rb	70°C	0.215 ± 0.007	1.35 ± 0.09	3543
Rb	80°C	0.372 ± 0.014	1.39 ± 0.10	2066
Rb	90°C	0.650 ± 0.019	1.180 ± 0.05	1127
Cs	60°C	0.075 ± 0.004	1.08 ± 0.08	9460
Cs	70°C	0.145 ± 0.007	1.04 ± 0.07	4848
Cs	80°C	0.286 ± 0.012	1.21 ± 0.09	2580
Cs	90°C	0.56 ± 0.03	1.02 ± 0.07	1257
K	0.5M (70°C)	0.117 ± 0.002	1.13 ± 0.02	4092
K	1.0M (70°C)	0.298 ± 0.007	1.27 ± 0.06	2513
K	2.0M (70°C)	0.590 ± 0.005	1.37 ± 0.02	1297
K	3.0M (70°C)	0.870 ± 0.013	1.39 ± 0.04	882

- (a)-(d) represent the extent of the reaction for each alkali metal cations with different reaction condition. The results are listed in the Table.
- The gradients of the plot (e) reveal activation energy, E_a , of the substitution with an order of $\text{K}^+ (48.5 \text{ kJ mol}^{-1}) < \text{Rb}^+ (60.42 \text{ kJ mol}^{-1}) < \text{Cs}^+ (67.2 \text{ kJ mol}^{-1})$.
- Ex-situ* time-resolved PXRD pattern (f) for the reaction: $2\text{Li}_2\text{Mo}_3\text{TeO}_{12} + 4\text{KNO}_3 + 6\text{H}_2\text{O} \rightarrow \text{K}_4\text{Mo}_6\text{Te}_2\text{O}_{24}\cdot 6\text{H}_2\text{O} + 4\text{LiNO}_3$ at 70°C.
- The value of Avrami exponent, n , is *ca.* 1, suggesting that one-dimensional diffusion with deceleratory process.

Conclusion

- In summary, we synthesized and characterized the new molybdenum rich tellurium oxides, $\text{Li}_2\text{Mo}_3\text{TeO}_{12}$ and transformed from $\text{Li}_2\text{Mo}_3\text{TeO}_{12}$ to other structures, $\text{A}_4\text{Mo}_6\text{Te}_2\text{O}_{24}\cdot x\text{H}_2\text{O}$, by the decomposition and recombination reaction triggered by cationic substitution.
- The kinetic and thermodynamic factors was investigated by the Avrami-Erofe'ev equation using PXRD patterns.
- The reactions are susceptible to cationic size with corresponding results of E_a for each reaction.

Acknowledgement

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