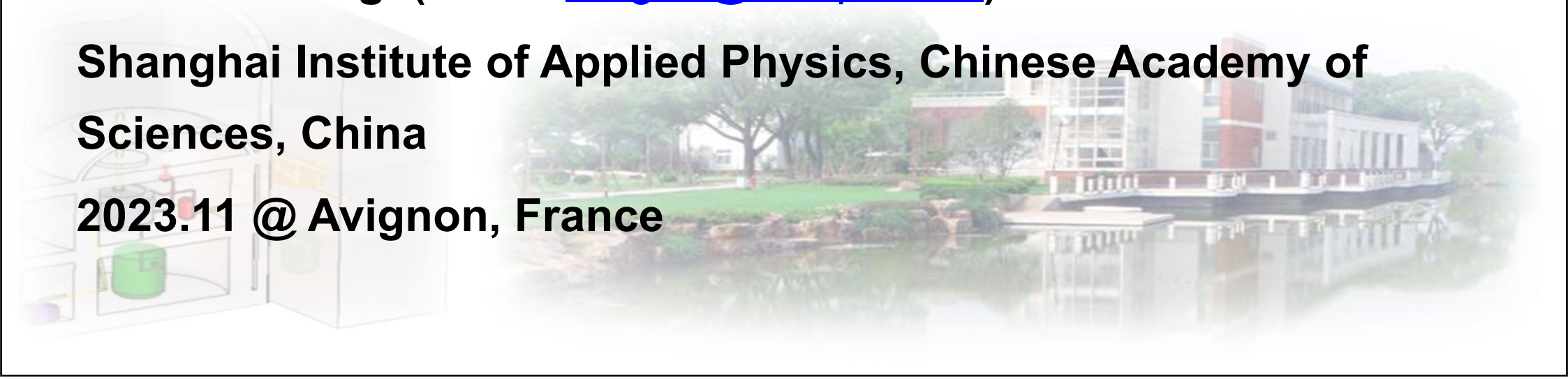
Research progress on microstructure and interfacial chemical behavior of molten salt

Prof. Rui Tang (Email: tangrui@sinap.ac.cn)

Shanghai Institute of Applied Physics, Chinese Academy of Sciences, China

2023.11 @ Avignon, France

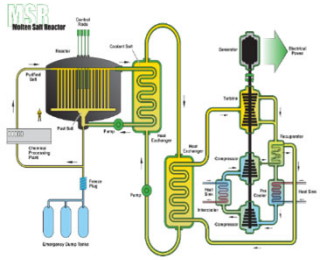


Presentation Outline

- **Background**
  - ◎ The Influence of Water and Oxygen on Molten Salt Reactor (MSR)
  - ◎ Key Factors of controlling Water and Oxygen in MS
- **Microstructure and Interfacial Chemical Behavior of Molten Salt**
  - ◎ Introducing of High-Temp in-situ Study Platform: NMR & Spectroscopic
  - ◎ Experimental study on microstructure of High Temp. molten salt
  - ◎ Experimental investigation into interface between metal and liquid MS
  - ◎ Theoretical exploration of water decomposition in liquid MS
- **Chemical and Engineering Issues in Molten Salt Production**
  - ◎ Strategy and Process of Preparing Nuclear Purity Level Molten Fluorides
- **Future Prospects**

Molten Salt Reactor

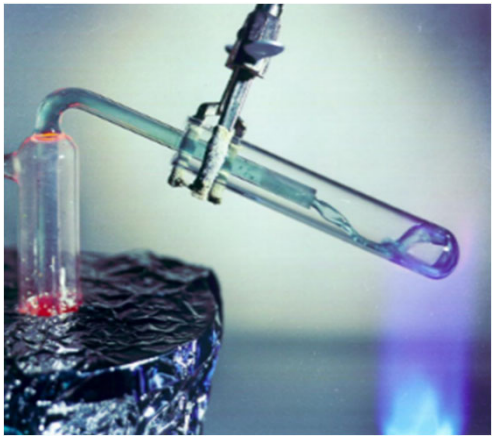
Suitable for generate electricity, comprehensive utilization and modular design



- **Th utilization**: Physical features applicable for Th fuel
- **Online refueling**: Refueling and reprocessing of fuel
- **Inherent safety**: Intrinsic safety features, can be built underground
- **Water-free cooling**: Applicable for inland arid area

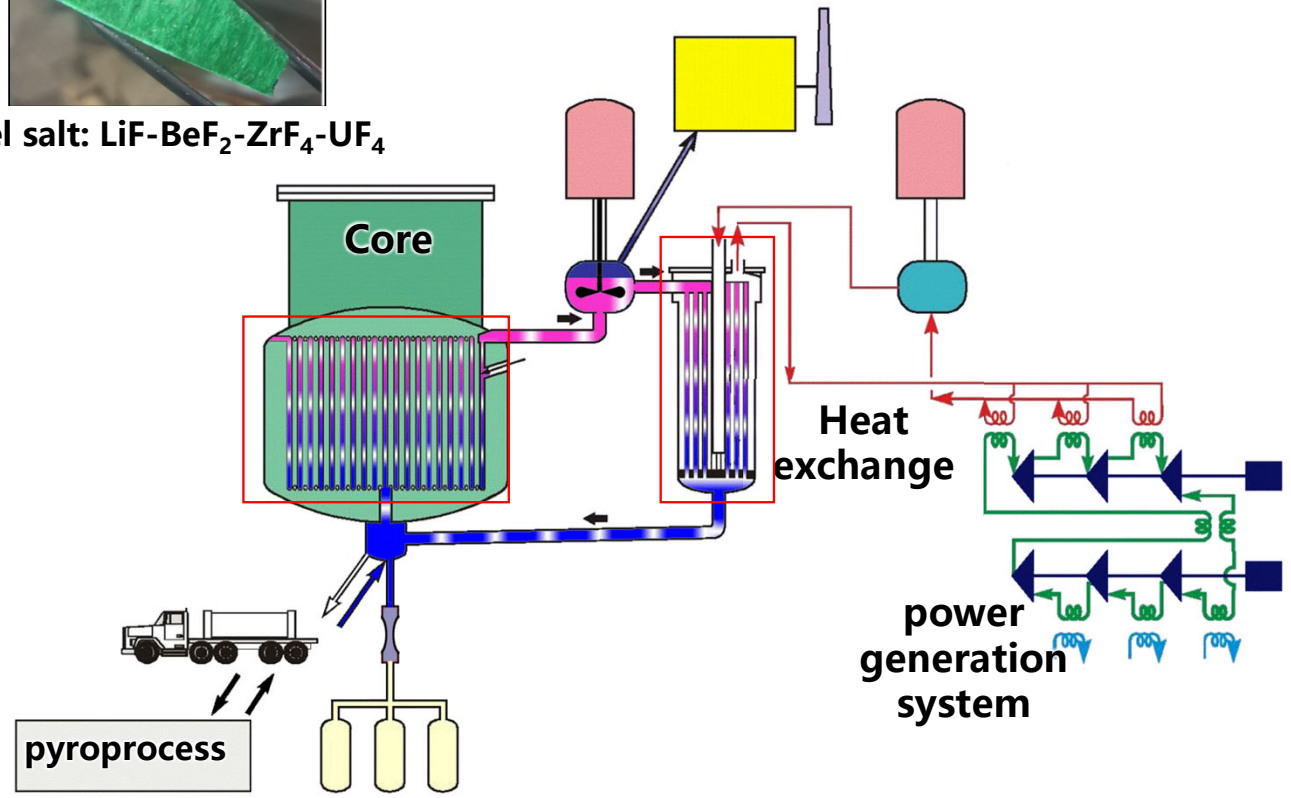
MS was performance excellent combination properties

	Outlet-Temp (℃)	Pressure (atm)	Heat Capacity (kJ/m³℃)	Materials Compatibility
Molten salt	**1000**	**~2**	**4670**	**Good**
Water	320	~150	4040*	Excellent
Sodium	545	~2	1040	Medium
Helium	1000	~70	20*	Excellent



Molten fluoride systems used in MSR

fuel salt: $LiF\text{-}BeF_2\text{-}ZrF_4\text{-}UF_4$



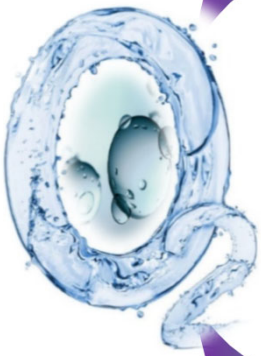
FLiBe, $LiF\text{-}BeF_2$

FLiNaK,LiF-NaF-KF

The key problem of molten salt application in MSR

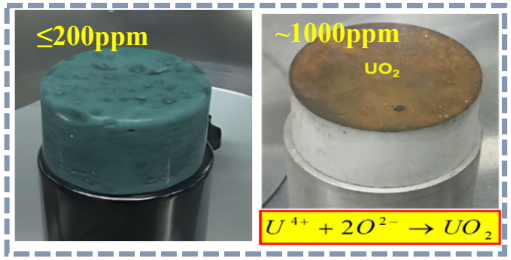
Fluorides for MSR

Control of trace water and oxygen



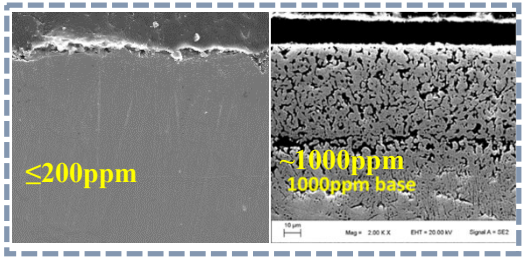
Homogeneous liquid fuel

The Effect of Trace Water & Oxygen on Fuel

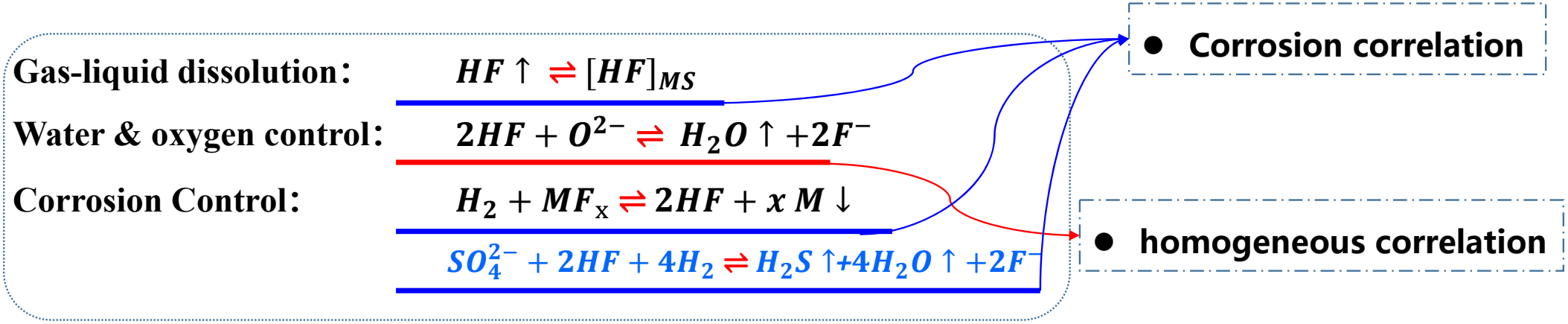


Corrosion control

The Effect of Trace Water & Oxygen on Material Corrosion



How to control Water & Oxygen in MS from chemistry



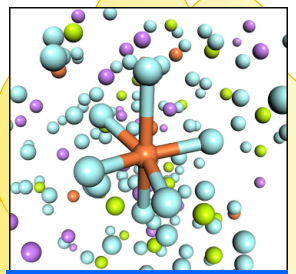
The chemical reaction is simple. However, the challenge is controlling the direction of the reaction. This required a full understanding of the microscopic processes of chemical reactions in molten salt

Presentation Outline

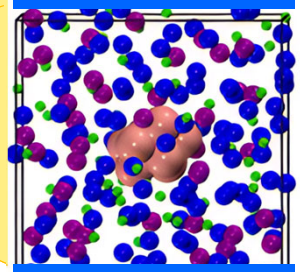
- Background
  - ◎ The Influence of Water and Oxygen on Molten Salt Reactor (MSR)
  - ◎ Key Factors of controlling Water and Oxygen in MS
- **Microstructure and Interfacial Chemical Behavior of Molten Salt**
  - ◎ Introducing of High-Temp in-situ Study Platform: NMR & Spectroscopic
  - ◎ Experimental study on microstructure of High Temp. molten salt
  - ◎ Experimental investigation into interface between metal and liquid MS
  - ◎ Theoretical exploration of water decomposition in liquid MS
- **Chemical and Engineering Issues in Molten Salt Production**
  - ◎ Strategy and Process of Preparing Nuclear Purity Level Molten Fluorides
- **Future Prospects**

Method of controlling reaction direction

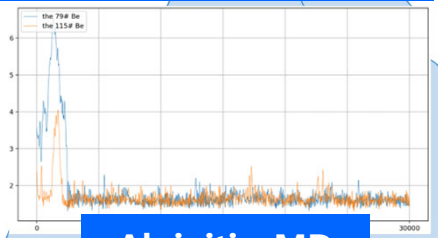
Understanding micro



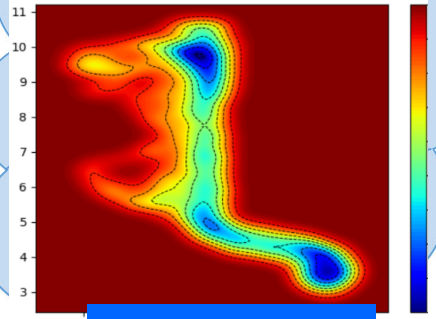
microstructure



microinterface



Ab initio-MD

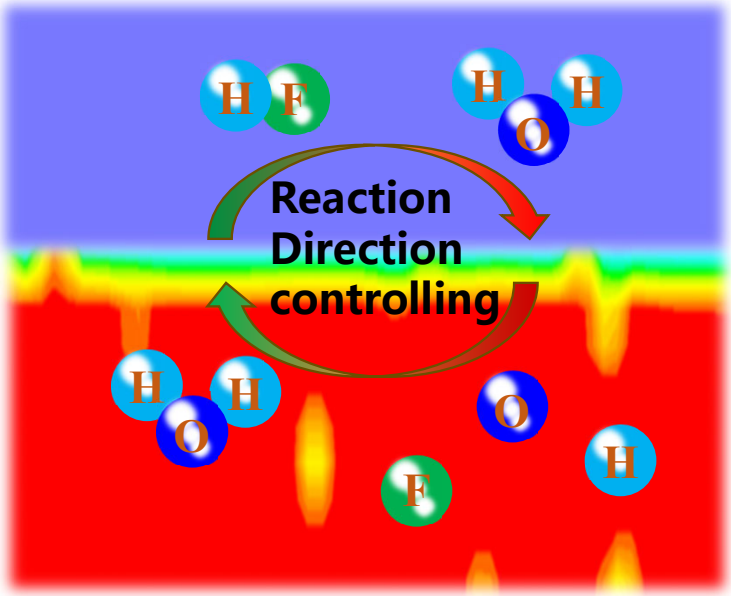


Meta-dynamic

Experimental perspective

simulation view

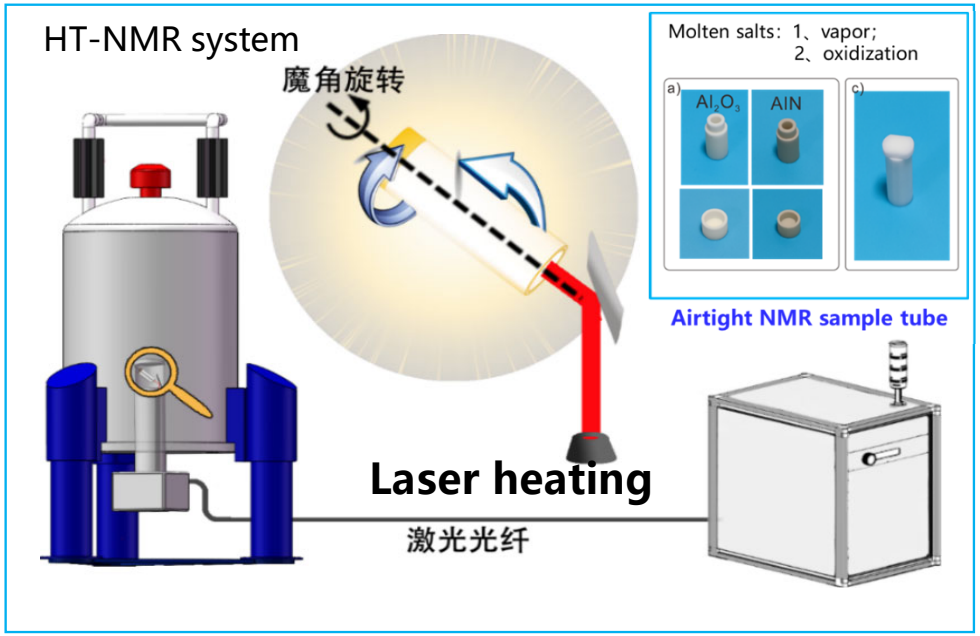
Improving macro



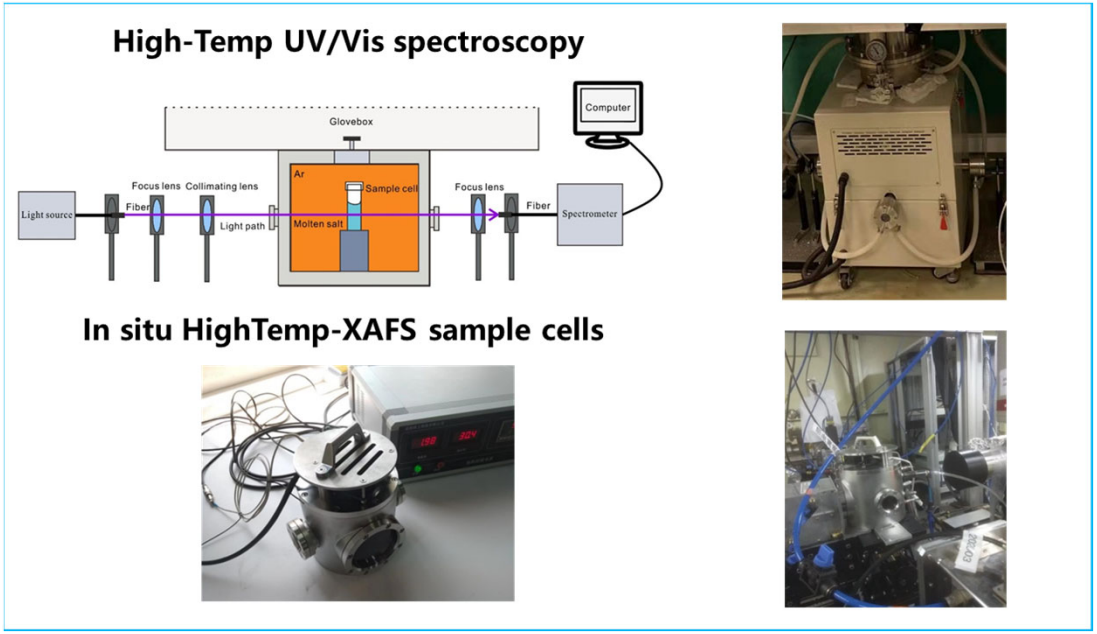
Controlling reaction direction

Molten salt microstructure research platform

The difference between the molten salt microstructure of liquid and solid, the challenge is how to view the phenomenon of liquid MS in high-temp.



In situ NMR detection at 700 ℃



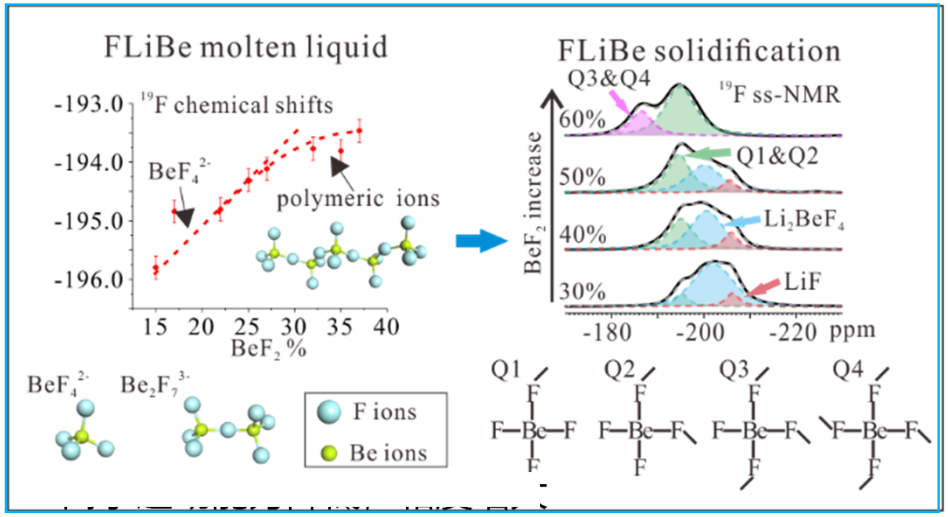
In situ High-temp UV/Vis, FTIR, XAFS detection at 900 ℃

In situ equipment of HT-NMR & spectroscopic were constructed

Understanding the MS FLiBe microstructure

As we all know, the strong covalent interactions of Be^{2+} ions can facilitate the coordination between Be-F, but how is the detail of the structure?

^{19}F HT-NMR chemical shift evolution of $LiF\text{-}BeF_2$ melts



PCCP back cover

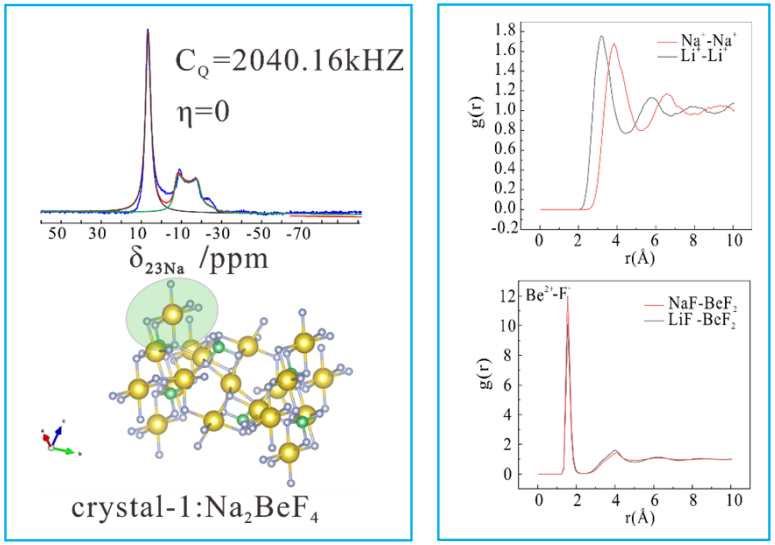
Formation of polymeric ions and networks will slow down the ionic dynamics

Phys. Chem. Chem. Phys., 2023, 25, 19446

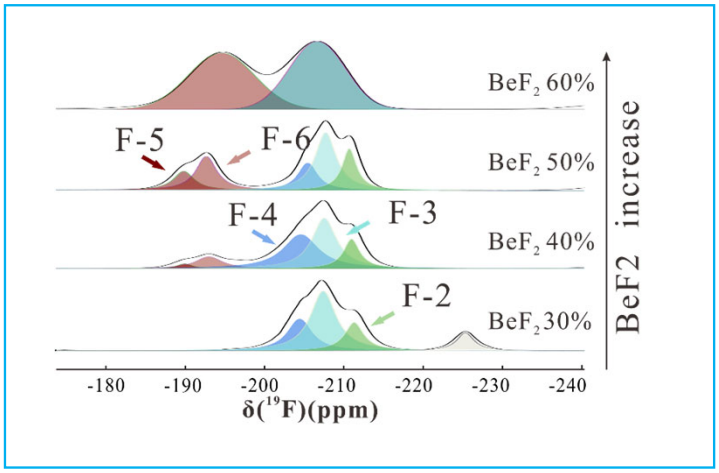
Understanding the MS FNaBe microstructure

The Be-F coordination structure also exist in FNaBe, whether the Na ion had an effect on the form of the Be-F coordination structure?

Be-F coordination structure



^{19}F NMR of FNaBe and signal decomposition



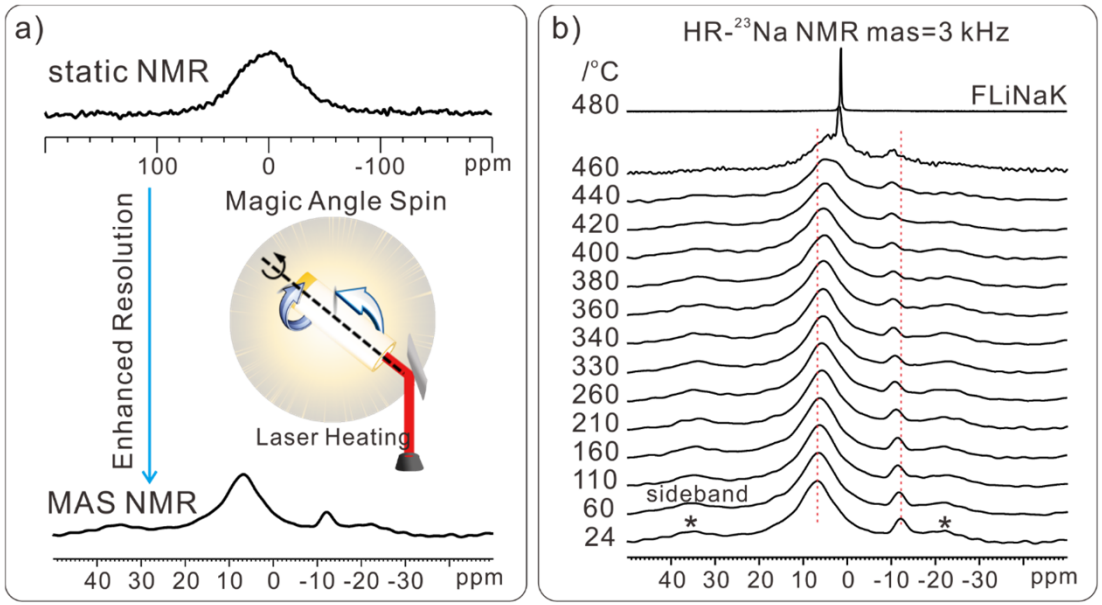
Similarities: Structure of FNaBe is quite similar as FLiBe, which is consisted of 4-fold tetrahedron coordination structure.

Differennce: More Be-F networks could be formed in FNaBe at a lower BeF concentration.

Understanding the MS FLiNaK microstructure

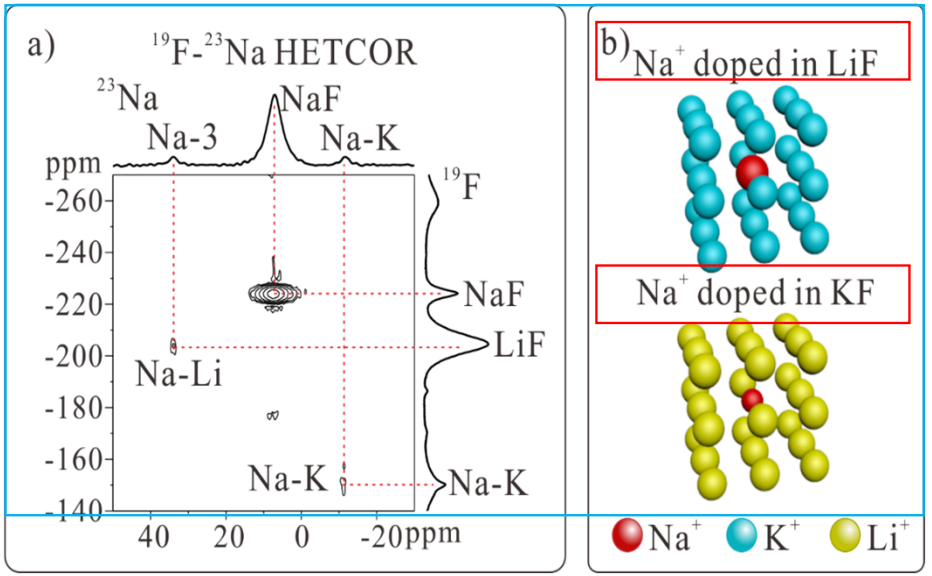
What happened in FLiNaK without strong covalent interactions?

^{23}Na HT NMR spectra of FLiNaK from 480 to 24 °C.



Formaion process of the ionic dopping *

Na^+ ion could be doped into LiF and KF crystals to form different ionic doped crystals during FLiNaK solidication.

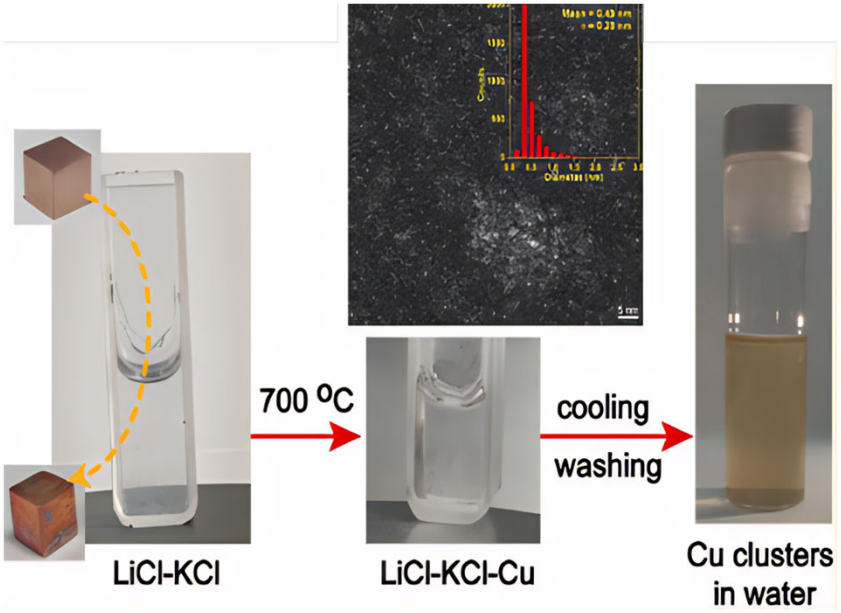


Ionic dopping in FLiNaK solidified salts **

* J. Phys. Chem. C 2021, 125:4704-4709. ** J. Phys. Chem. C 2023, 127:8687-8694.

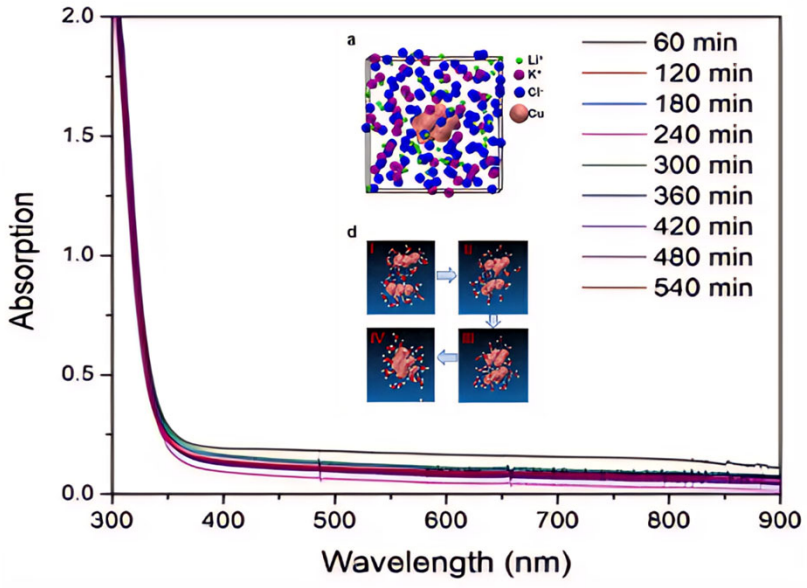
Micro interface in MS: Metallic nanoclusters

Whether the metal in molten salt was a traditional solid-liquid interface? Take the copper for example, The bulk Cu was partially dissolved and uniformly dispersed in the molten salt as small nanoclusters with only a few atoms. metal cluster and MS interface



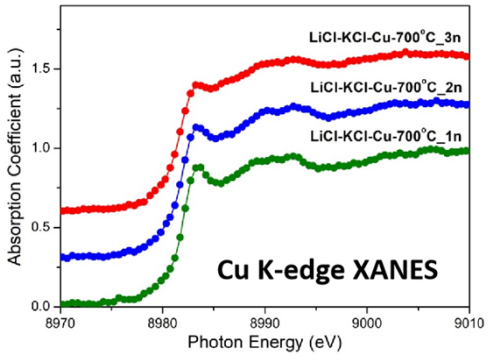
Reaction phenomena of metallic Cu in salt melts

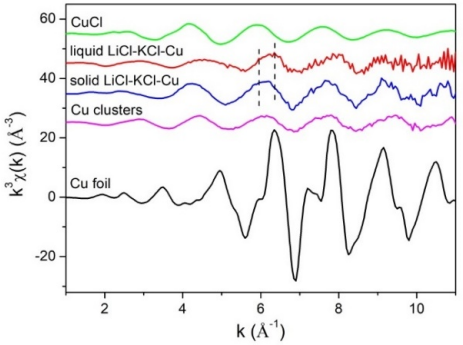
Chem. Mater., 2023, 35, 5832-5837.

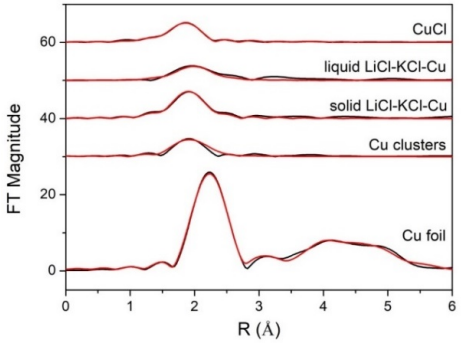


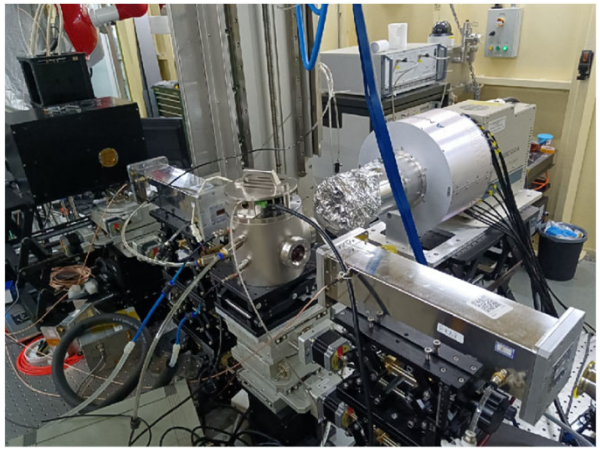
UV-vis spectra of the LiCl-KCl-Cu at 700°C with different heating time

The structure of copper nanocluster







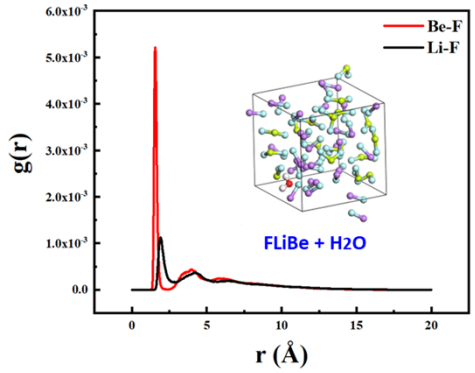


beamline 14W1 at the Shanghai Synchrotron Radiation Facility (SSRF)

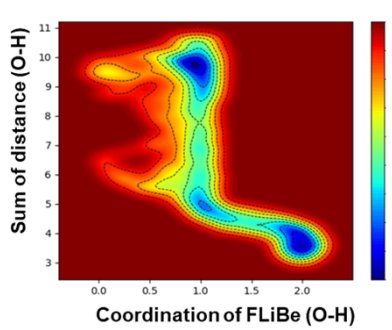
Sample	Paths	*CN*	*R* (Å)
CuCl	Cu-Cl	4.1 ± 0.2	2.30 ± 0.01
liquid LiCl-KCl-Cu	Cu-Cl	1.3 ± 0.4	2.28 ± 0.02
	Cu-Cu	2.0 ± 0.8	2.52 ± 0.03
solid LiCl-KCl-Cu	Cu-Cl	2.1 ± 0.3	2.36 ± 0.01
	Cu-Cu	2.9 ± 0.5	2.43 ± 0.02
Cu clusters	Cu-Cu	3.0 ± 0.3	2.42 ± 0.02

Effect of MS microstructure on water decomposition reaction

Different molten salts（FLiBe & FLiNaK）affects the decomposition energy barrier of water.



RDF analysis of FLiBe-H_2O & FLiNaK-H_2O



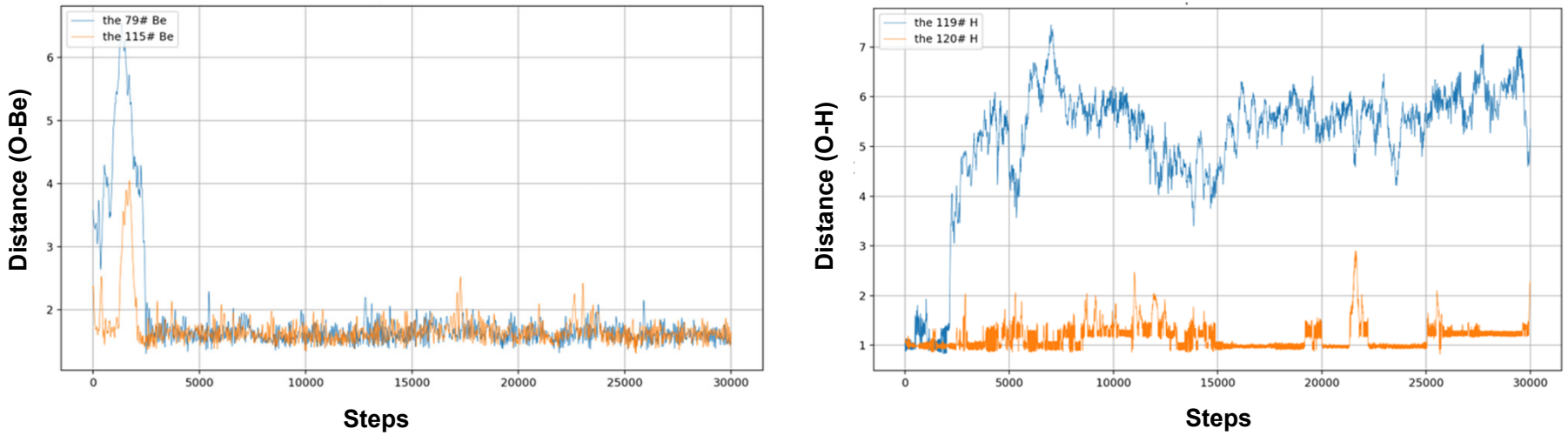
- hard to OH^-
- Easy to O^{2-}
- easy to OH^-
- hard to O^{2-}

Energy barrier of FLiBe-H_2O & FLiNaK-H_2O clusters

unpublished work

Why were decomposition energy barrier of water different

Beryllium captures oxygen result in reducing the energy barrier for the decomposition of OH into O, but increasing the energy barrier for the decomposition of H2O into OH



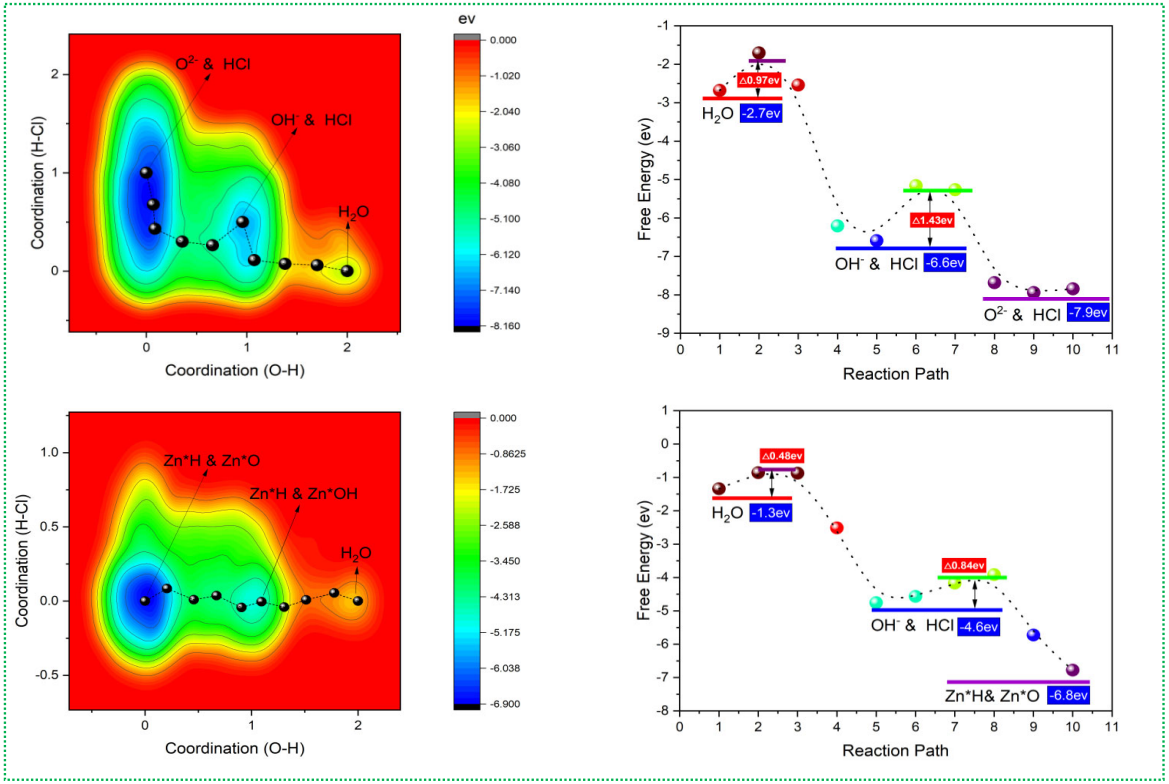
Distance(O-Be) and Distance(O-H) vs. Time Steps in the process for decomposition of H_2O in FLiBe& FLiNaK

79 # and 115 # Be get close to the O atom within 1.2 ps, , while 119 # H goes far away from O, resulting in the O-H coordination number changed from 2 to 1, and the complexation between Be and O leads a change in the energy barrier.

unpublished work

Effect of metal clusters on H_2O decomposition in molten salts

Take the Zinc for example, the clusters changed the decomposition path of water in molten salt.



- Melt nanocluster can exist stably in liquid MS
- A micro-interface was formed between MS and nanocluster
- The water molecules were adsorbed and the decomposition path of water were changed

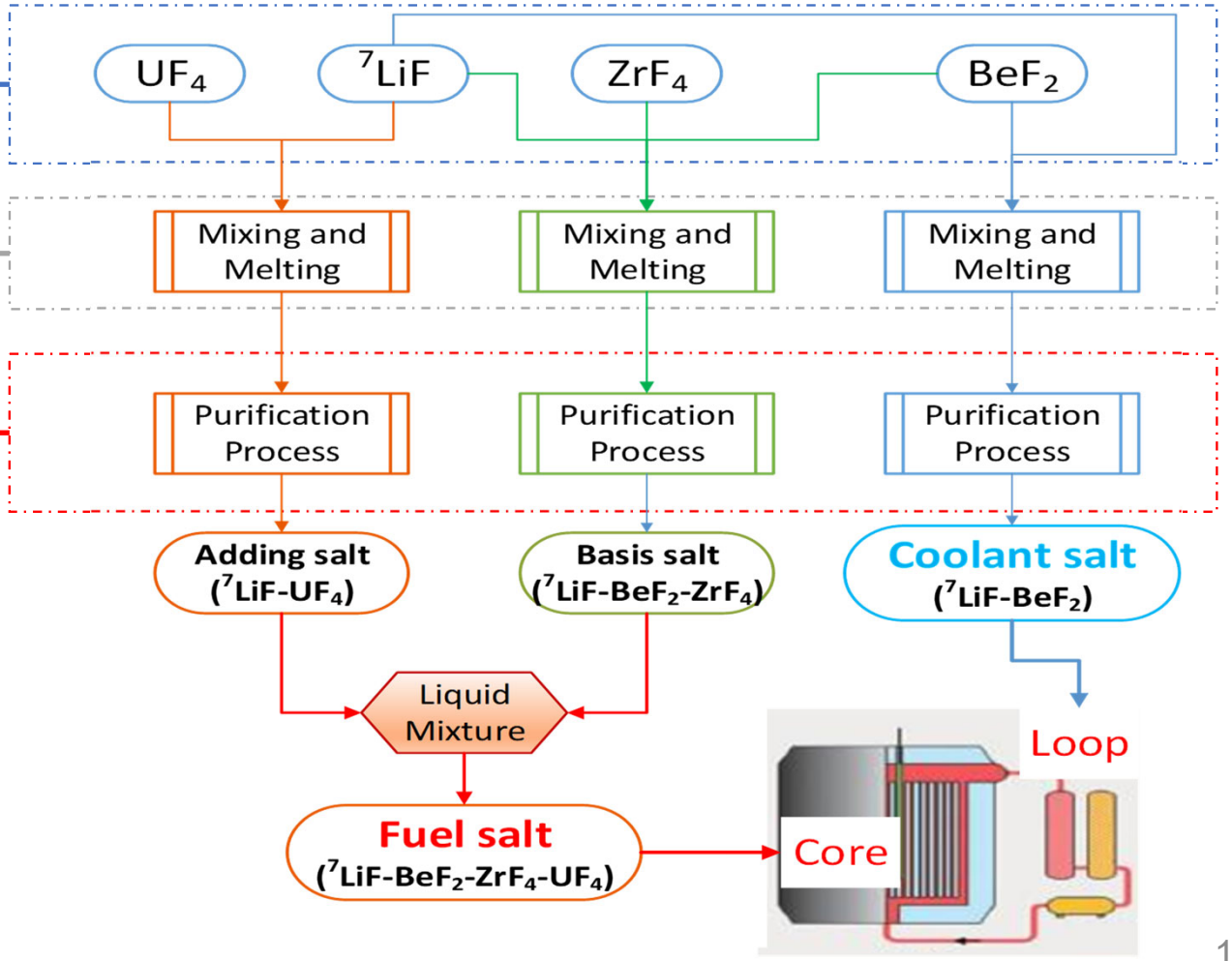
unpublished work

Presentation Outline

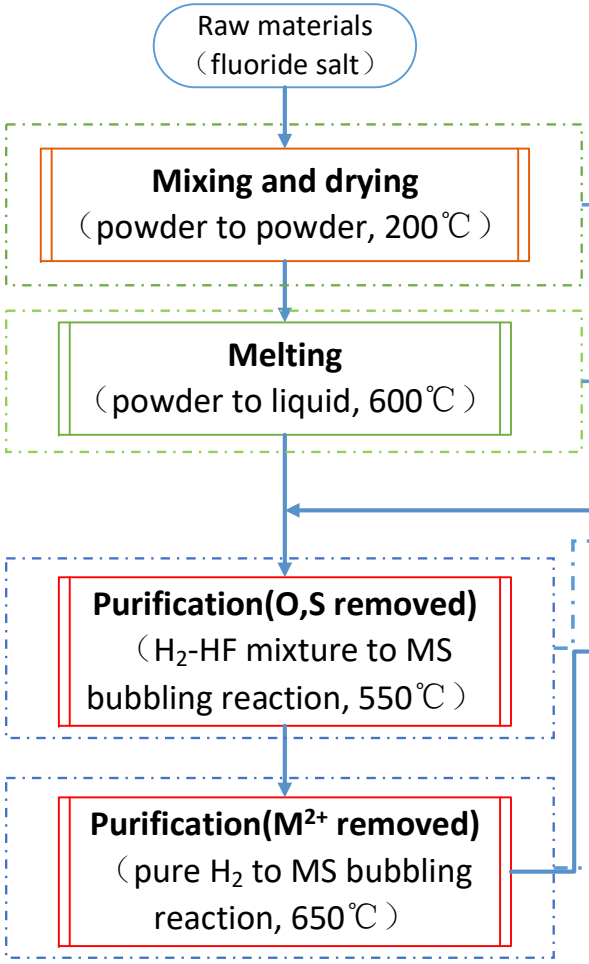
- Background
  - ◎ The Influence of Water and Oxygen on Molten Salt Reactor (MSR)
  - ◎ Key Factors of controlling Water and Oxygen in MS
- Microstructure and Interfacial Chemical Behavior of Molten Salt
  - ◎ Introducing of High-Temp in-situ Study Platform: NMR & Spectroscopic
  - ◎ Experimental study on microstructure of High Temp. molten salt
  - ◎ Experimental investigation into interface between metal and liquid MS
  - ◎ Theoretical exploration of water decomposition in liquid MS
- **Chemical and Engineering Issues in Molten Salt Production**
  - ◎ Strategy and Process of Preparing Nuclear Purity Level Molten Fluorides
- **Future Prospects**

Strategy of preparing molten salt for FMSR

- **Raw materials:**
  - Controlling (CoNP) according to quality standard built on the basis of analysis reactor neutron economy
- **Molten salt design:**
  - Forming eutectic fluoride salt on the basis of phase diagram analysis and physicochemical experiment
- **Purification of fluoride salt:**
  - Controlling (CoOI) on the basis of analysis chemical reaction and process investigative experiment



Reaction process of preparing nuclear grade molten salt



- **Step 1:**
  - Mixing the powder of the fluoride salt and removing the water adsorbed on powder
- **Step 2:**
  - Converting the powder to eutectic molten salt in high temperature condition
- **Step 3:**
  - Removing the [O^{2-}] and [SO_4^{2-}] ion dissolved in MS using H_2-HF mixture bubbling reaction
- **Step 4:**
  - Removing the [M^{2+}] ion dissolved in MS using H_2 mixture bubbling reaction

Reaction process of preparing nuclear grade molten salt

High purity fluorine salt for reactor was successfully obtained, and the engineering of the process has been realized

Fuel solute
(addition salt-FLiU)

Fuel solvent
(basic salt-FLiBeZr)

Liquid fuel
(fuel salt-FLiBeZrU)

Based on the study of microstructure and interface behavior of molten salt, the preparation process of molten salt was designed, the reaction direction was controlled, and the total amount of oxgen was less **than 200ppm**

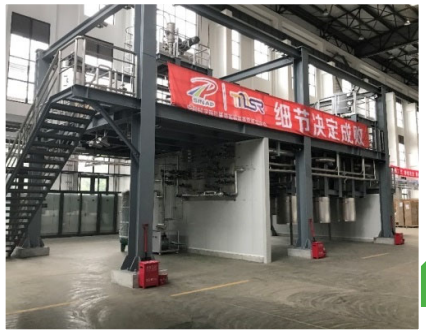
Presentation Outline

- Background
  - ◎ The Influence of Water and Oxygen on Molten Salt Reactor (MSR)
  - ◎ Key Factors of controlling Water and Oxygen in MS
- Microstructure and Interfacial Chemical Behavior of Molten Salt
  - ◎ Introducing of High-Temp in-situ Study Platform: NMR & Spectroscopic
  - ◎ Experimental study on microstructure of High Temp. molten salt
  - ◎ Experimental investigation into interface between metal and liquid MS
  - ◎ Theoretical exploration of water decomposition in liquid MS
- Chemical and Engineering Issues in Molten Salt Production
  - ◎ Strategy and Process of Preparing Nuclear Purity Level Molten Fluorides
- **Future Prospects**

Progress and future plans of preparing molten salt applied in MSR

Laboratory research (500g/batch)

Bench scale production (5Kg/batch)



Pilot scale production (10t/year)

Demo scale production (100t/year)

2012 2015 2020 2030

Thank you very much!