❖ 2016 KCS Inorganic Chemistry Division Summer Symposium

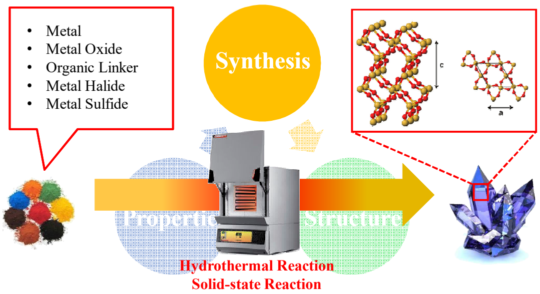
Crystal Growth, Structure, and Characterization of an Organic-Inorganic Hybrid 1D-Chain Compound: $(i\text{-}Pr)_2NH_2PbBr_3$

Seung-Jin Oh, Ho Yong Jung, Jung Joo Kim, Jong Ho So, Eun Jung Cho, Kang Min Ok*

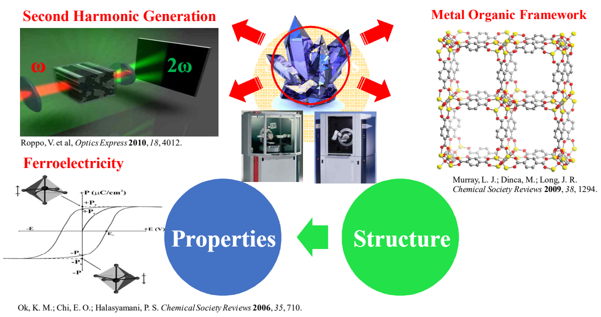
Department of Chemistry, Chung-Ang University, Seoul, 156-756, Republic of Korea.

❖ **Structure-Property Relationships**

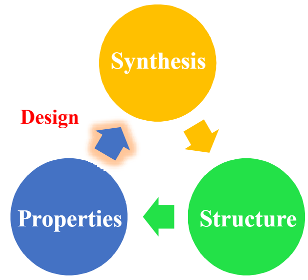
- Metal
- Metal Oxide
- Organic Linker
- Metal Halide
- Metal Sulfide



❖ **Structure-Property Relationships**

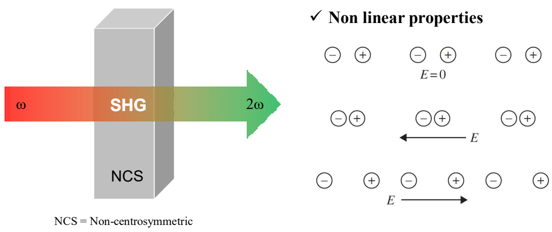


❖ **Structure-Property Relationships**



❖ **What is second harmonic generation (SHG)?**

✓ **Non linear properties**



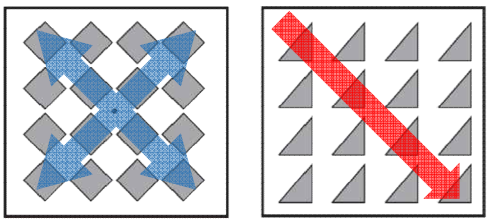
NCS = Non-centrosymmetric

- $\vec{P} = \epsilon_0\chi^{(1)}\vec{E}$

$= \epsilon_0[\chi^{(1)}\vec{E}(t) + \chi^{(2)}\vec{E}^2(t) + \cdots]$ $\quad \vec{E} = Ee^{-iwt} + c$ $\quad$ 2ω frequency

$= \vec{P}^{(1)}(t) + \vec{P}^{(2)}(t) + \cdots \rightarrow \vec{P}^{(2)}(t) = 2\epsilon_0\chi^{(2)}EE^* + \epsilon_0\chi^{(2)}E^2e^{-i2wt} + c$

❖ **What is Non-centrosymmetric (NCS) materials?**



Centrosymmetric | Non-centrosymmetric

No SHG produced | **SHG produced**

❖ **How to make NCS?**

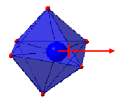
➢ **Asymmetric building unit**

- Second-order Jahn-Teller distortion

(1) Octahedrally Coordinated d^0 Transition Metals: MO_6

Ti^{4+}, Nb^{5+}, Ta^{5+}, V^{5+}, Mo^{6+}, W^{6+}, etc.

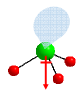
Out-of-Center Intra-Octahedral Distortion



(2) Lone Pair Cations

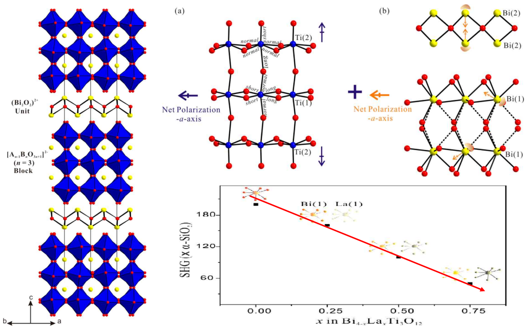
Tl^{+}, Pb^{2+}, Sn^{2+}, Sb^{3+}, Bi^{3+}, Se^{4+}, Te^{4+}, etc.

Stereochemically Active



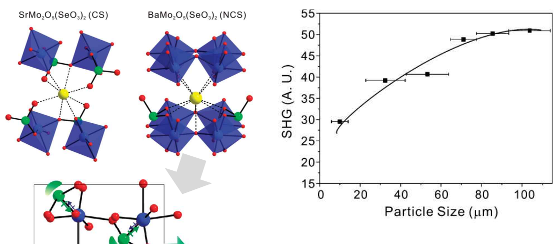
P. S. Halasyamani, K. R. Poeppelmeier, *Chem. Mater.*, (1998) ***10***, 2753.

➢ **Structure−Property Relationships in Solid Solutions of Noncentrosymmetric Aurivillius Phases, $Bi_{4-x}La_xTi_3O_{12}$ (x = 0−0.75)**



S.-J. Oh, Y. Shin, T. T. Tran, D. W. Lee, A. Yoon, P. S. Halasyamani and K. M. Ok, *Inorganic Chemistry* **2012**, *51*, 10402-10407.

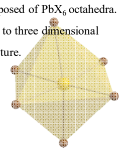
➢ **Influence of the Cation Size on the Centricities in $AMo_2O_5(SeO_3)_2$ (A = Sr, Pb, and Ba)**



S.-J. Oh, D. W. Lee and K. M. Ok, *Inorganic Chemistry* **2012**, *51*, 5393-5399.

Inorganic Frameworks → **Hybrid-Halometallates** ← **Organic** Asymmetric units

- PbX_2 (X = F, Cl, Br, and I).
- Anionic frameworks composed of PbX_6 octahedra.
- Zero to three dimensional structure.

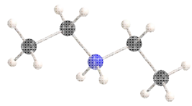


- Induced arrangement of Ammonium cations

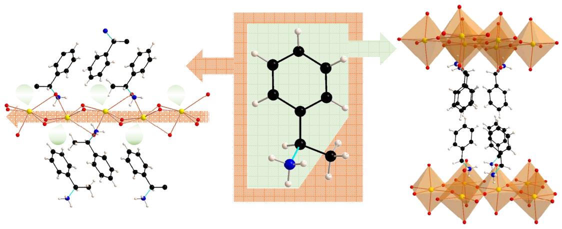
→ Aligned asymmetric unit

→ **NCS structure & High performance**

- Organic cations: Ammonium.
- Asymmetric cations
- Hydrogen bondings



(S-β-phenethylammonium) Pb Cl_3 (benzylammonium)$_2$ Pb Cl_3

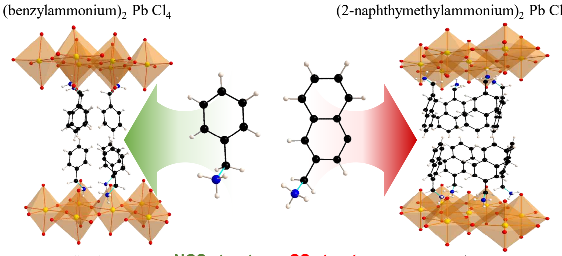


$P2_12_12_1$ **1D Structure** | **Dimension** | $Cmc2_1$ **2D Structure**

D. G. Billing and A. Lemmerer, *CrystEngComm* **2006**, *8*, 686-695.

W. Q. Liao et al., *Nat Commun* **2015**, *6*, 7338.

(benzylammonium)$_2$ Pb Cl_4 (2-naphthymethylammonium)$_2$ Pb Cl_3

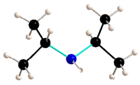


$Cmc2_1$ **2D Structure** | **NCS structure** | **CS structure** | *P*bma **2D Structure**

W. Q. Liao et al., *Nat Commun* **2015**, *6*, 7338.

M. Braun, W. Frey, *Z. Kristallogr. NCS* **1999**, *214*, 333.

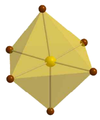
- **Ammonium cations**
  - Secondary ammonium **cations**



Diisopropylammonium (DIPA)

a. Large cone-angle: restrict the H-bonds.
b. Few study about secondary ammonium.
c. Few study for aliphatic functional group R

- **Frameworks**
  - Lead Bromide

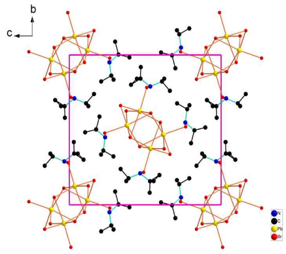


$PbBr_6$ octahedra
Anionic frameworks

a. Rare study for Bromide
b. Easy to synthesize the ammonium salts
: Diisopropylammonium bromide (DIPAB)

❖ Single-Crystal X-ray Diffraction

- Synchrotron light source: 2D-SMC at Pohang Accelerator Laboratory (PAL), Korea.
- Temperature: 100K
- Wavelength: 0.63000 Å



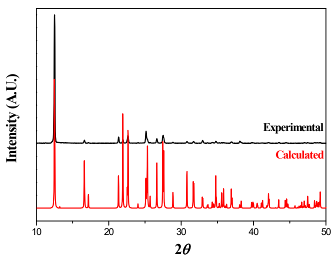
Formula sum	$C_{12}H_{32}N_2Br_6Pb_2$
Formula weight	1098.22
Crystal system	monoclinic
Space group	$P2_1/c$ (no. 14)
Unit cell dimensions	a = 8.2950(17) Å
	b = 16.9110(3) Å
	c = 18.3850(3) Å
	β = 91.90(3) °
Z	4
Cell volume	2577.6(9) $Å^3$
Density, calculated	2.819 g/cm^3
$R(F)^a$	0.043
$R_w(F_o^2)^b$	0.073

$^aR(F) = \sum||F_o| - |F_c|| / \sum|F_o|$. $^bR_w(F_o^2) = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\right]^{1/2}$.

❖ Synthesis

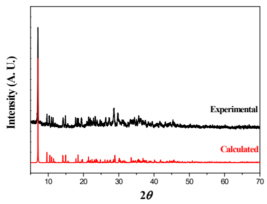
Preparations of reagents: DIPAB

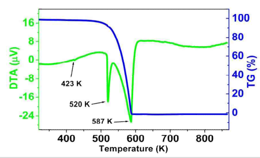
- DIPA + conc. HBr solution + Acetone in ice-bath.



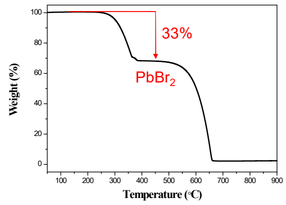
Powder X-ray diffraction pattern of synthesized DIPAB and compared data with simultaneously calculated pattern.

❖ Powder X-ray Diffraction





❖ Temperature Gravimetric Analysis



The organic compound, DIPAB, undergo 100% weight loss in a single step at 247 ºC.

*Da-wei Fu at al., *SCIENCE*, **2013**, 339, 425

DIPAB are to be stabilized in the hybrid inorganic organic compounds

❖ Synthesis

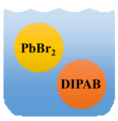
Synthesize the halometallates: $(DIPA)PbBr_3$

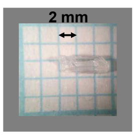
[redacted]

- **Solution methods**

I. DIPAB + $PbBr_2$ + Solvent with stir at 50ºC for 1day.
   - solvent: DMF, DMSO, or conc. HBr

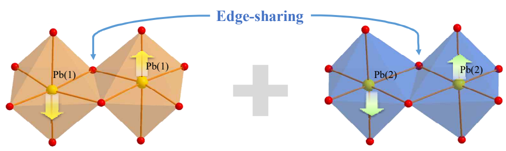
II. Slow evaporation until crystalized.





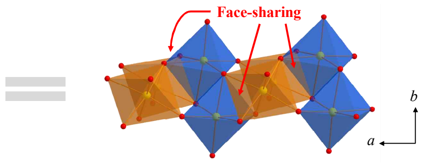
Transparent crystal obtained

❖ Structure

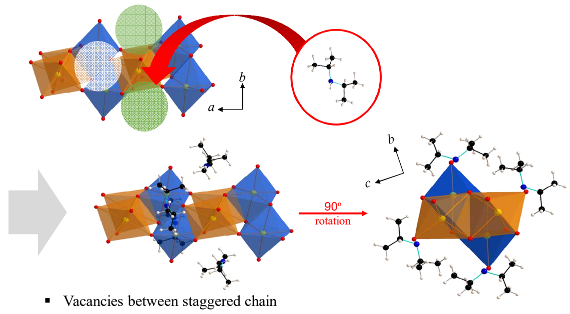


Pb_2Br_{10} dimer

Pb_2Br_{10} dimer



❖ **Structure**



- Vacancies between staggered chain

➡ Each chain units surrounded by the four DIPA cations

Plan

1 Change Br to F, Cl, and I

- Control the distance of H-bonds.

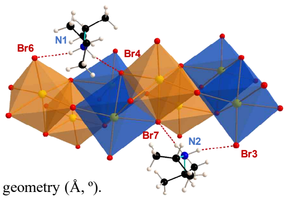
2 Change ammonium

- Asymmetric secondary or tertiary ammonium.

3 Conductivity

- Along the *a*-axis.

❖ **Structure**



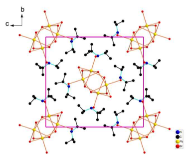
Hydrogen-bonding geometry (Å, °).

N-H···Br	N-H	H···Br	N···Br	N-H···Br
N1-H1A···Br6	0.970(4)	2.457(5)	3.401(1)	164.29(2)
N1-H1B···Br4	0.970(1)	2.606(3)	3.547(4)	163.51(1)
N2-H2A···Br7	0.970(3)	2.446(3)	3.390(1)	164.14(2)
N2-H2B···Br3	0.970(1)	2.525(2)	3.491(1)	173.47(2)

Strong H-bonds can be found between H-Br.

Crystal Growth

Hydrogen bonding

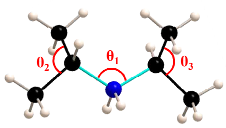


$(i\text{-Pr})_2NH_2PbBr_3$

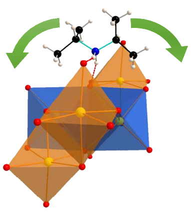
1D structure

Structure -Property relation

❖ **Structure**



	C-C bonds	N-C bonds	θ_1	θ_2	θ_3
DIPAB	1.496(2), 1.524(1) 1.515(1), 1.513(5)	1.509(1) 1.497(4)	119.13(3)	112.13(2)	112.35(3)
DIPA-Pb-Br_3	1.520(2), 1.523(4) 1.510(2), 1.527(1)	**1.512(2)** **1.517(4)**	117.50(4)	**110.73(5)**	113.10(5)



Obstruct the composition of 2D-layer

➡ **1D-chain structure**

Acknowledgements

지도 교수: 옥강민

Research Pf. Min Feng Lu
Post doc. Guohong Zou
Graduate Student 황차환, 조홍일
김형구, 송승윤
김봉수, 정호용

❖ 중견 연구자지원산업 (핵심 연구)

NRF 한국연구재단

❖ 비중심대칭 소재은행