# Low-dimensional materials for high-efficiency/high-power nonlinear optical applications in the infrared

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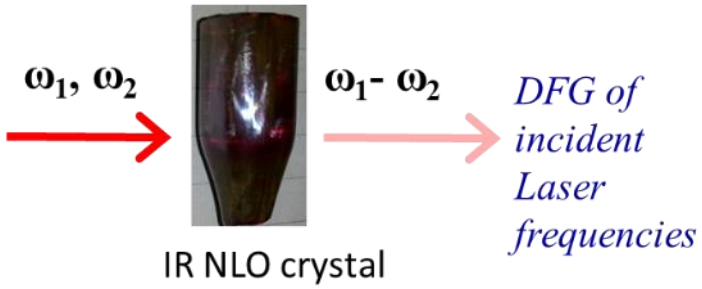
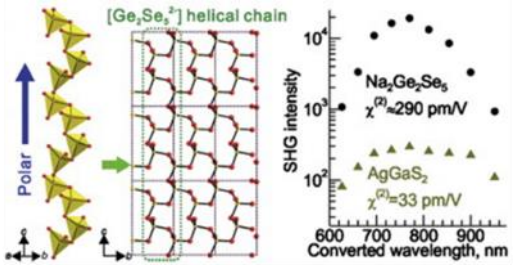
# Overarching goal

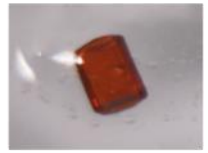
- Next generation of NLO crystals for IR
- Realize a deeper understanding of the relationship between crystal structure, dimensionality and difference frequency generation (DFG), especially in the IR region
- Transform the way high performance NLO materials are designed thereby accelerating future discoveries in the field and enabling associated technologies.
- Leverage the new insights to create a new generation of top performing NLO IR materials with wide optical gaps and high laser damage threshold (LDT).
- Train graduate students and postdocs in the art and science of NLO




IR NLO crystal




$Na_2Ge_2Se_5$ NLO crystal



Flux grown crystal

**Generation of new IR: difference frequency generation ($\omega_1 - \omega_2$)**

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# Project objectives

- Synthesize highly pure chalcogenide materials with non-centrosymmetric structures and strong NLO response,
- Measure all fundamental NLO properties of the crystals
- Demonstrate crystal exhibit excellent wavelength tunability over a very broad IR range (~1 – 20 μm)
- Assess laser damage threshold of most promising materials and down-select to the top one of two best performing materials.
- Provide crystals to the AFRL Dayton group for further evaluation and feedback

# Nonlinear optical phenomena

Taylor series expansion of the dielectric polarization density (electric dipole moment per unit volume) **P**(*t*) at time *t* in terms of the electric field **E**(*t*), $\chi^{(1)}, \chi^{(2)}, \chi^{(3)}$ susceptibilities of the medium

$$\mathbf{P}(t) = \varepsilon_0(\chi^{(1)}\mathbf{E}(t) + \chi^{(2)}\mathbf{E}^2(t) + \chi^{(3)}\mathbf{E}^3(t) + \ldots),$$

where the coefficients $\chi^{(n)}$ are the *n*-th-order susceptibilities of the medium, and the presence of such a term is generally referred to as an *n*-th-order nonlinearity.

**Only non-centrosymmetric crystals have $\chi^{(2)}$**

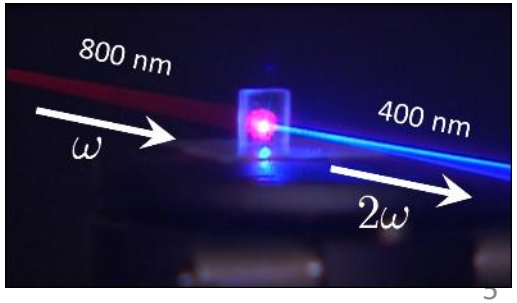
**Generation of new UV: second harmonic generation ($2\omega_1$)**

**sum frequency generation ($\omega_1 + \omega_2$)**

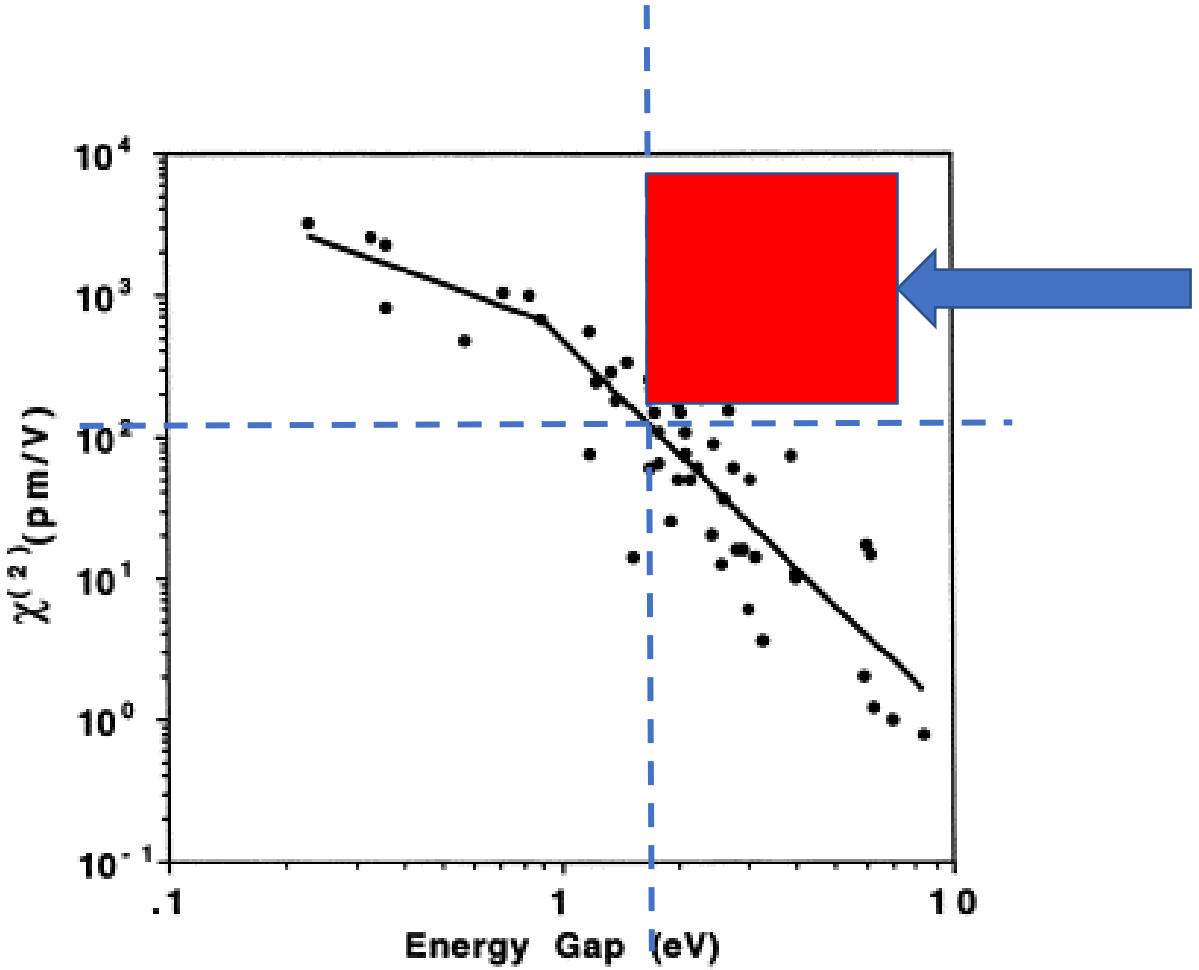
**Generation of new IR: difference frequency generation ($\omega_1 - \omega_2$)**

*Virtual* 2-photon process

in a noncentrosymmetric medium



# Overview Relating $\chi^{(2)}$ to bandgap $E_g$




We seek new materials in this box

Jackson, A. G. et al. *Infrared Phys. Technol.* **1997**, *38*, 233.

**Bandgaps of interest: $E_g$>1.7-2.0 eV**

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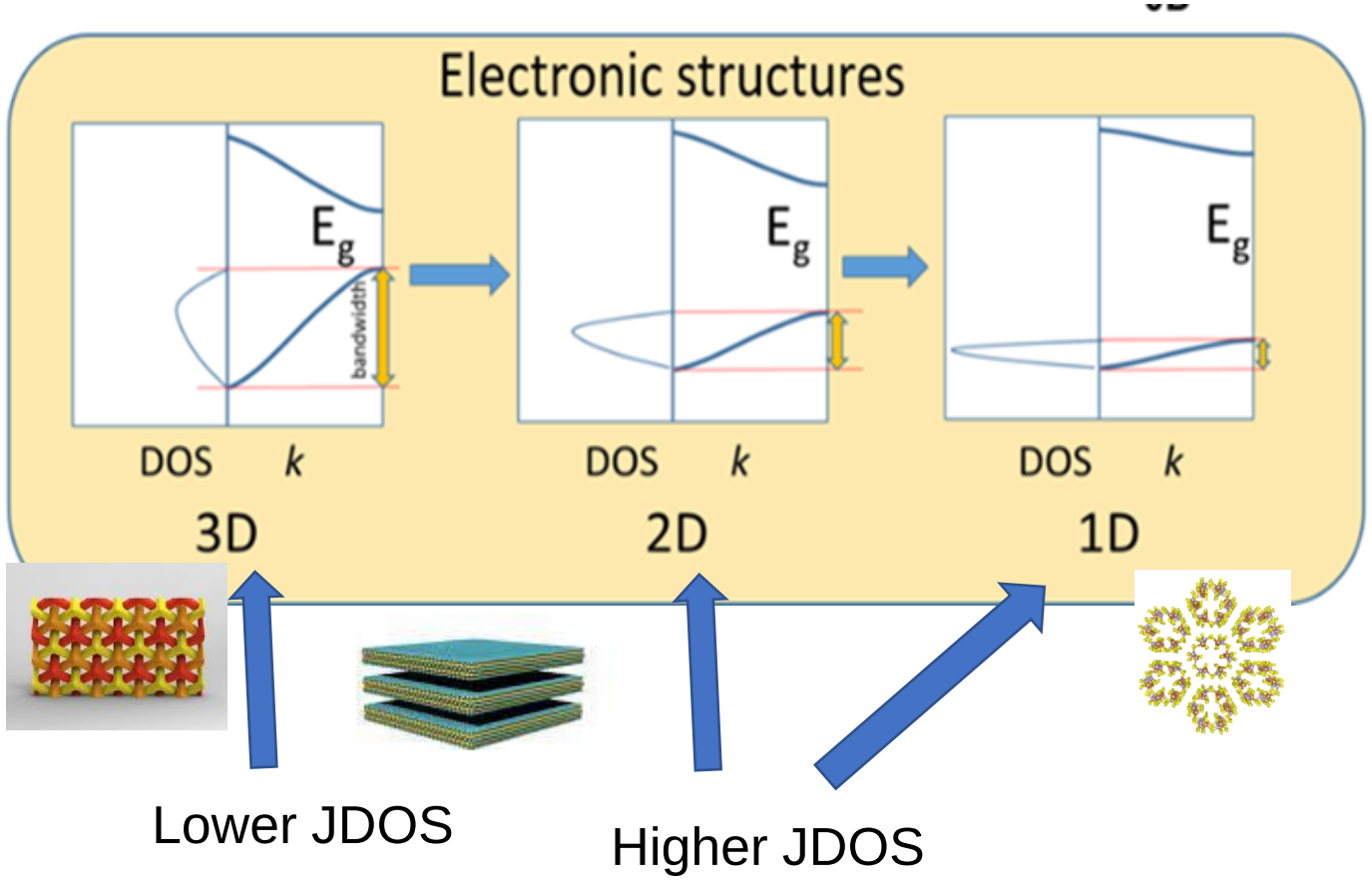
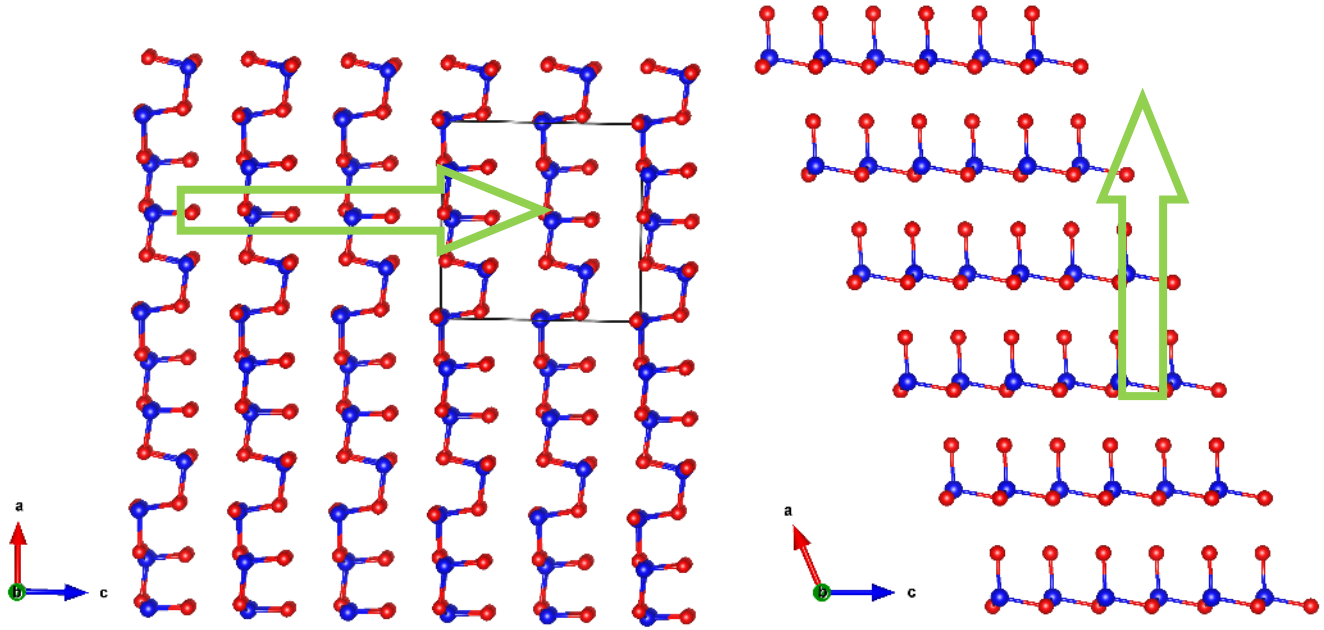
# Our focus is on low-dimensional materials




- Theory predicts:
  - low-dimensional structures with polarizable elements (e.g. chalcogens: S, Se, Te) have higher joint density of states (JDOS) than corresponding three-dimensional (3D) structures
  - Result: higher NLO optical responses.

JH Song, Arthur J. Freeman, TK Bera, I Chung, and MG Kanatzidis, *Phys. Rev. B* **79**, 245203, (2009)

# *Polar crystals:* $A$AsQ$_2$ ($A$ = Li and Na; $Q$ = S, Se)

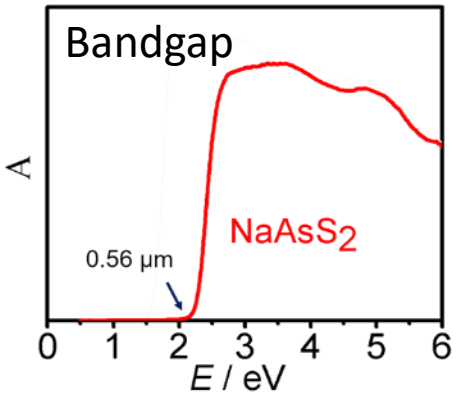


| Sulfide | Space group | Selenide | Space group |
|---|---|---|---|
| $LiAsS_2$ | *Cc* | $LiAsSe_2$ | *Cc* |
| $NaAsS_2$ | $P2_1/b$ | γ-$NaAsSe_2$<br>δ-$NaAsSe_2$ | *Pc*<br>*Pbca* |
| $Li_{0.6}Na_{0.4}AsS_2$ | *Cc* | β-$Li_{0.2}Na_{0.8}AsSe_2$<br>γ-$Li_{0.2}Na_{0.8}AsSe_2$ | *Cc*<br>*Pc* |

**Effect on $NaAsSe_2$ structure due to Li Substitution**

**γ-$NaAsSe_2$**
*Pc* (noncentrosymmetric; NC)
$a$ = 11.682 Å, $b$ = 5.902 Å, $c$ = 11.823 Å
$\beta$ = 90.44°

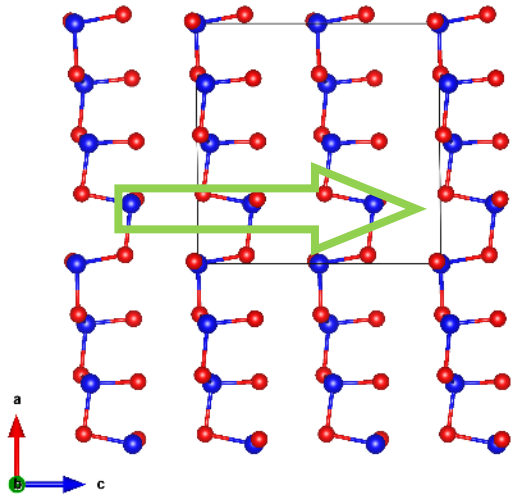
**β-$LiAsSe_2$**
*Cc* (noncentrosymmetric; NC)
$a$ = 12.287 Å, $b$ = 5.541 Å, $c$ = 5.553 Å
$\beta$ = 113.12°



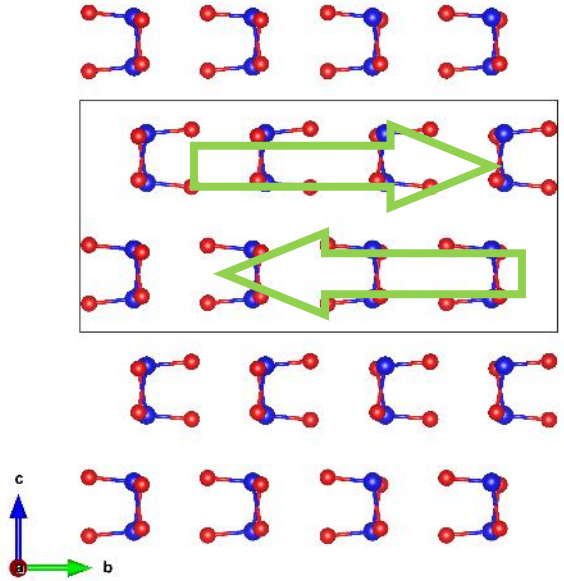

Bera, T. K.; Jang, J. I.; Song, J. H.; Malliakas, C. D.; Freeman, A. J.; Ketterson, J. B.; Kanatzidis, M. G.
*Journal of American Chemical Society* **(2010)** 132, 3484-3495

# Noncentrosymmetric $NaAsSe_2$

## Two Phases of $NaAsSe_2$

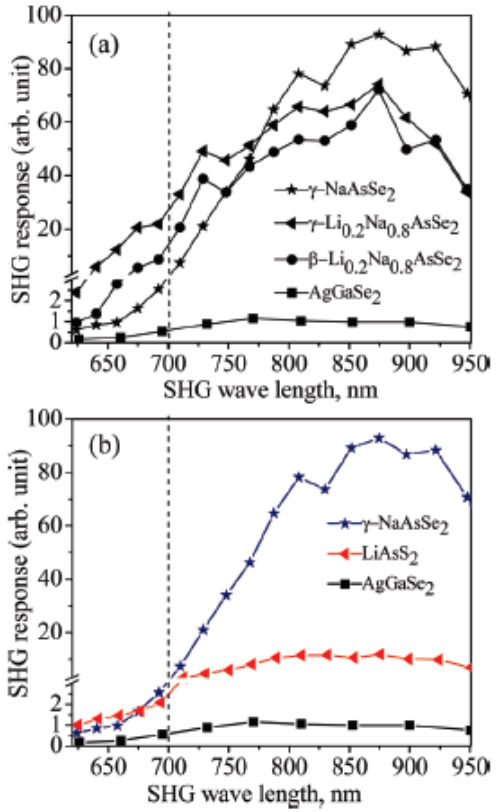



γ-$NaAsSe_2$, *Pc*
Non-centrosymmetric




δ-$NaAsSe_2$, *Pbca*
Centrosymmetric

Na has been removed, for a better understanding of the structure




**SHG intensity**:
**γ-$NaAsSe_2$**
75 x $AgGaSe_2$
**γ-$Li_{0.2}Na_{0.8}AsSe_2$**
65 x $AgGaSe_2$
**β-$Li_{0.2}Na_{0.8}AsSe_2$**
55 x $AgGaSe_2$

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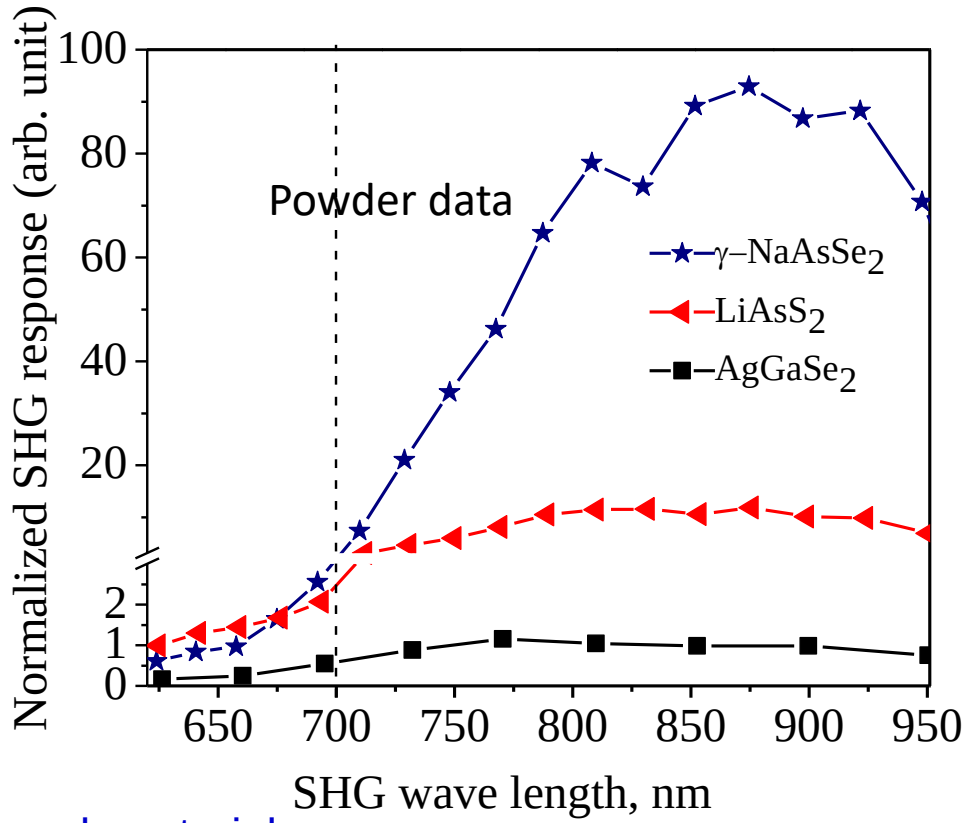
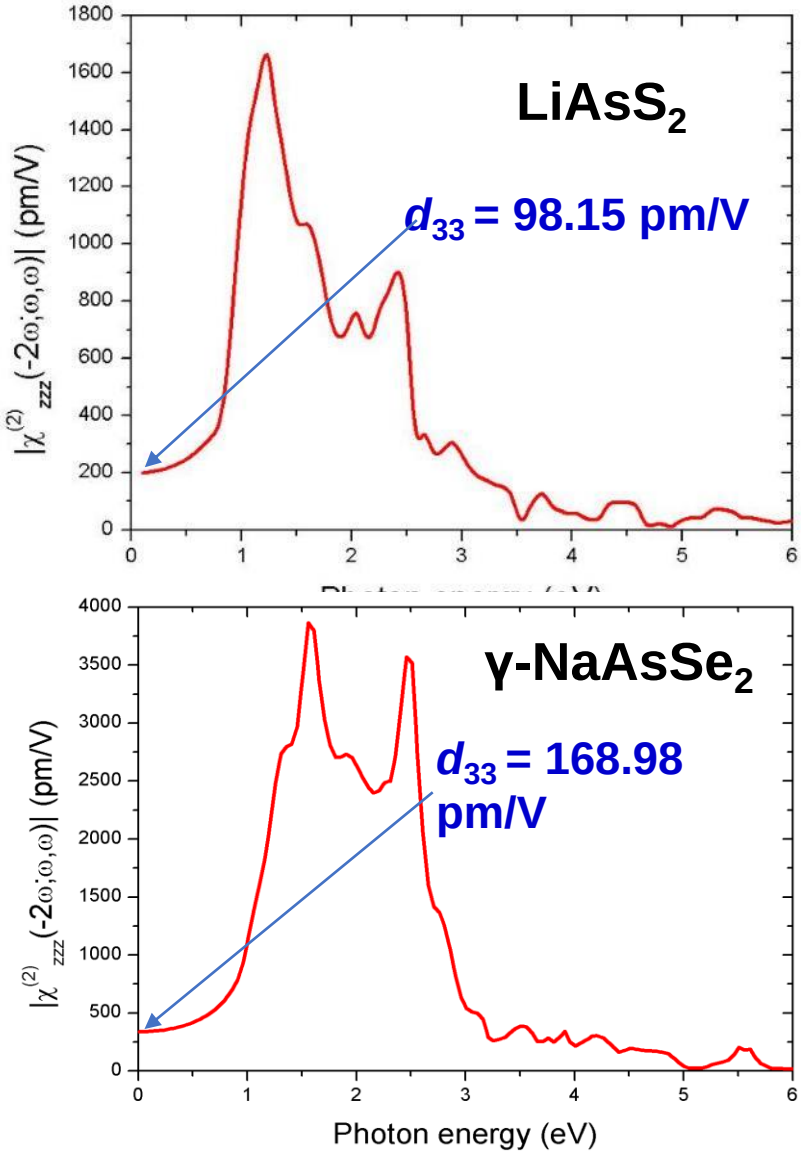
Bera, T. K.; Jang, J. I.; Song, J. H.; Malliakas, C. D.; Freeman, A. J.; Ketterson, J. B.; Kanatzidis, M. G. *Journal of American Chemical Society* **(2010)** 132, 3484-3495

# $AAsS_2$ and $AAsSe_2$: Very promising materials with strong SHG reported by our group



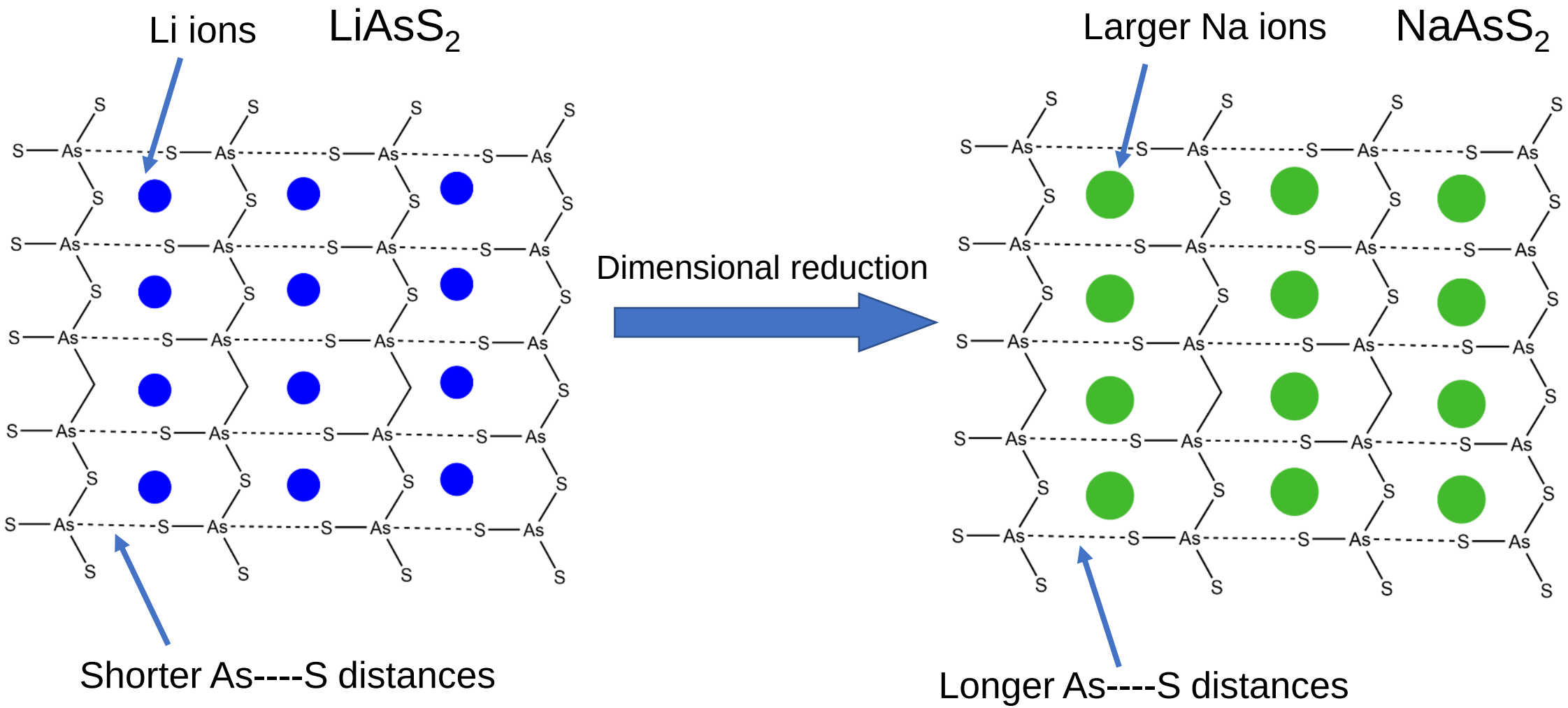

Benchmark materials
$AgGaSe_2$: 32 pm/V
GaAs: 91 pm/V
$ZnGeP_2$ 75 pm/V

**Highest SHG susceptibility (χ)**
(with band-gap >1.5 eV)

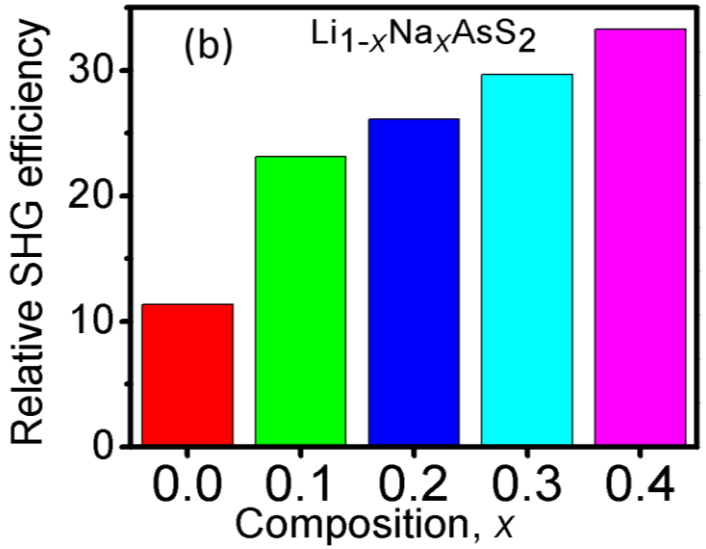


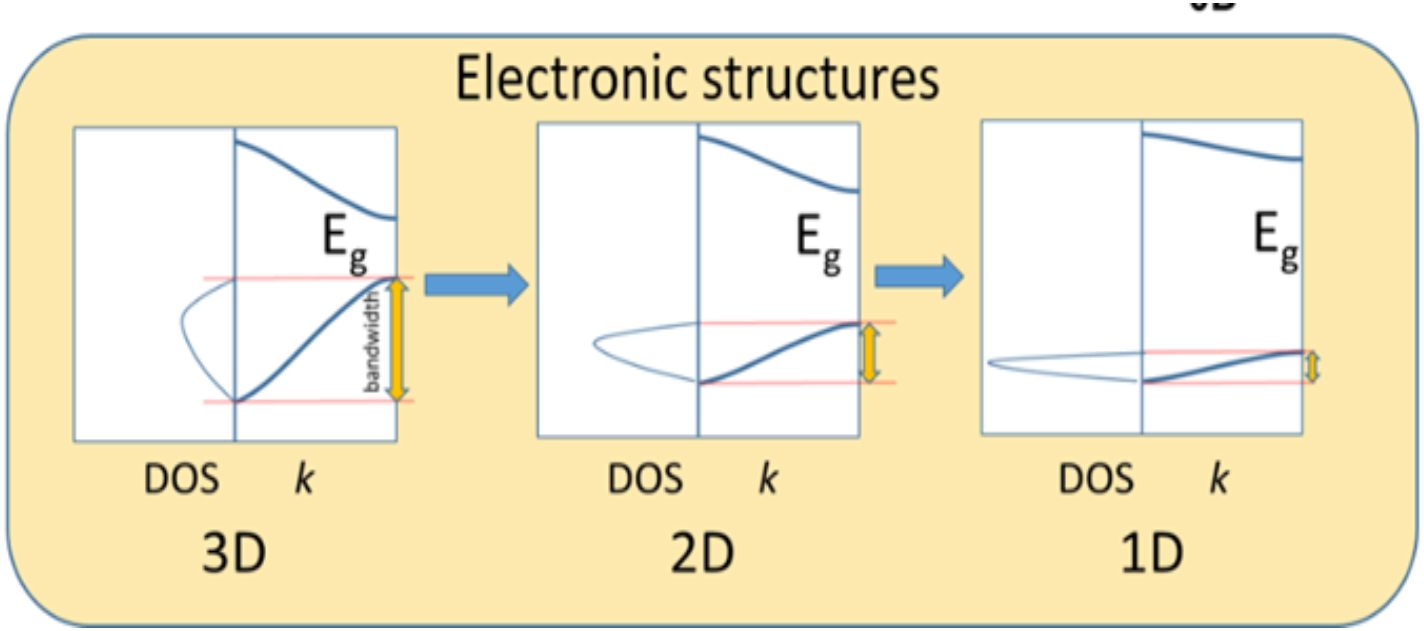

Song, Bera, Chung, Freeman, Kanatzidis, *Phys. Rev. B., 79*, **2009**, 245203

# $Li_{1-x}Na_xAsS_2$: Na addition reduces interchain $[AsS_2]^1$ interactions…



# $Li_{1-x}Na_xAsS_2$: Na addition reduces interchain $[AsS_2]^{1-}$ interactions…




- The SHG intensity of powder $LiAsS_2$ is ~10 times larger than that of the benchmark $AgGaSe_2$ at 790 nm.
- The resulting $Li_{0.6}Na_{0.4}AsS_2$ is isostructural to $LiAsS_2$ and exhibits 30 times stronger SHG response than $AgGaSe_2$, a large enhancement over $LiAsS_2$ itself.
- We believe this enhancement is due to the small (fine tuning) of *Dimensional Reduction* occurring when larger Na is added raising the JDOS and enhancing the SHG.

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# Synthesis of $Na_{1-x}K_xAsQ_2$

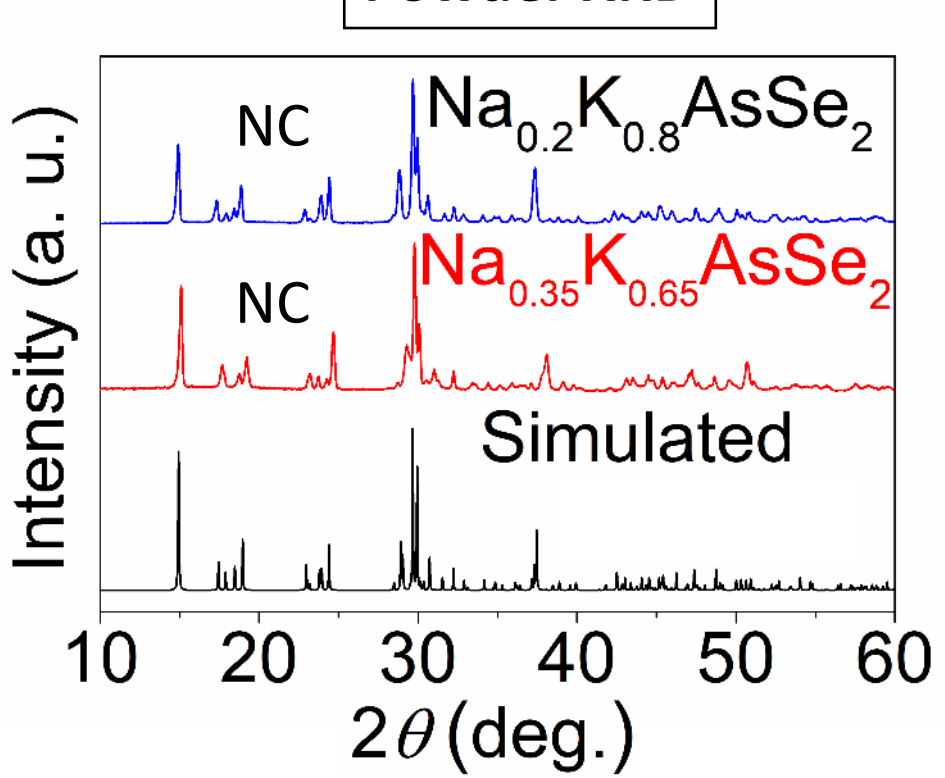
$0.1Na_2Se + 0.4K_2Se + As + 1.5Se \longrightarrow Na_{0.2}K_{0.8}AsSe_2$

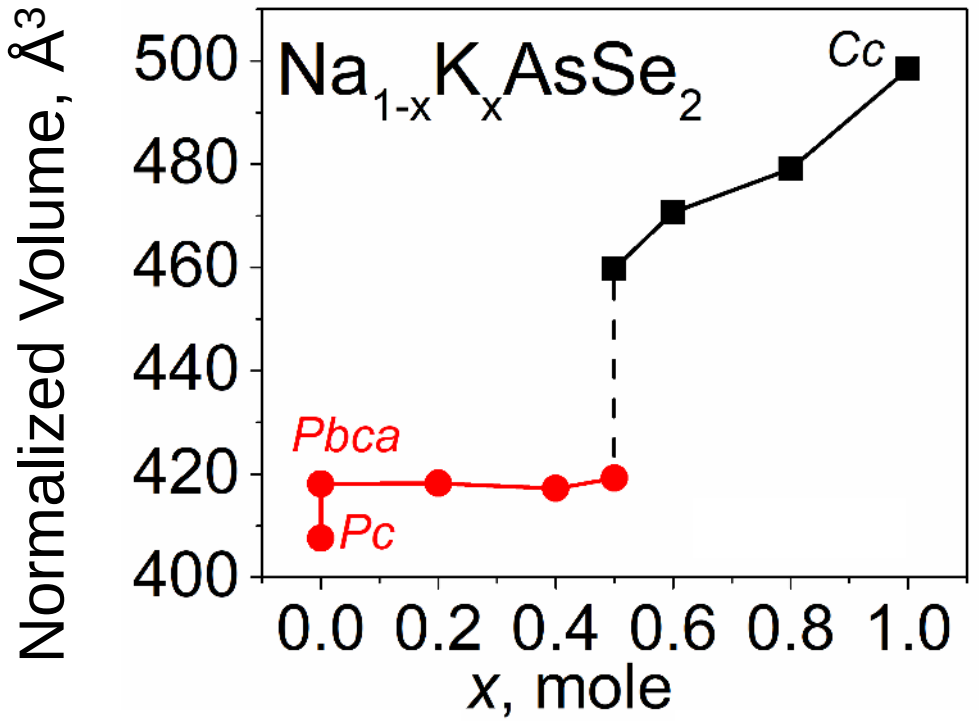
Similarly reactions were performed for $x$ = 0.65 and 0.5 and $Na_{0.1}K_{0.9}AsS_2$

**Standardized Temperature Profile**

RT —(12 h)→ 500 ° C —(48 h)→ 500 ° C —(96 h)→ 250° C —(4 h)→ RT

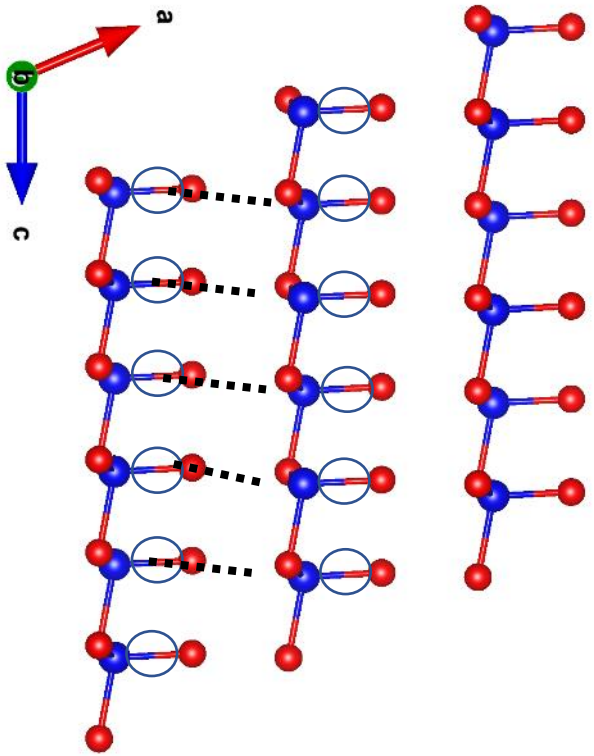
**Powder XRD**



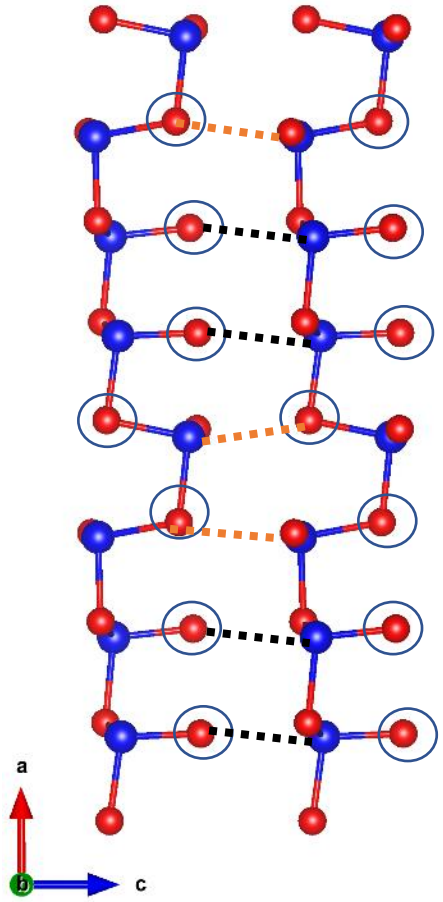




- NC = noncentrosymmetric; C = centrosymmetric

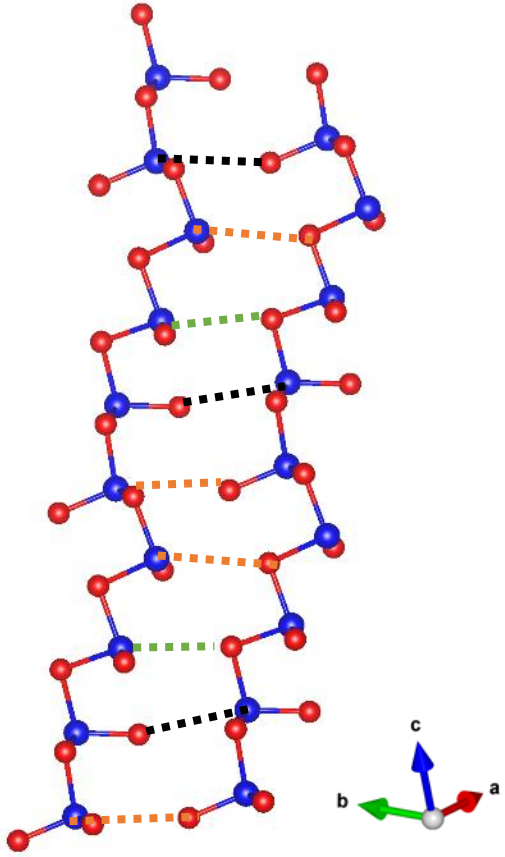
# Change in interchain $[AsQ_2]^-$ interactions due to *A* cation




**LiAsSe$_2$** (*Cc*)
Interchain distance
3.37 Å



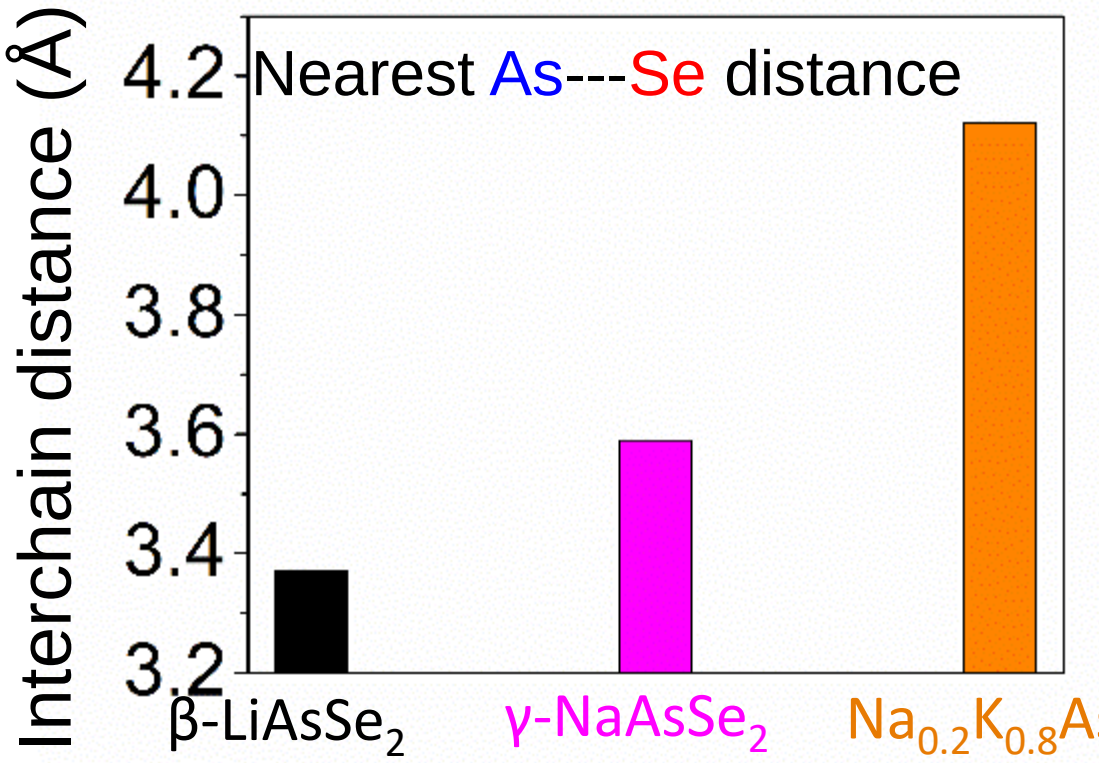

**NaAsSe$_2$** (*Pc*)
Interchain distance
3.59 Å, 3.64 Å

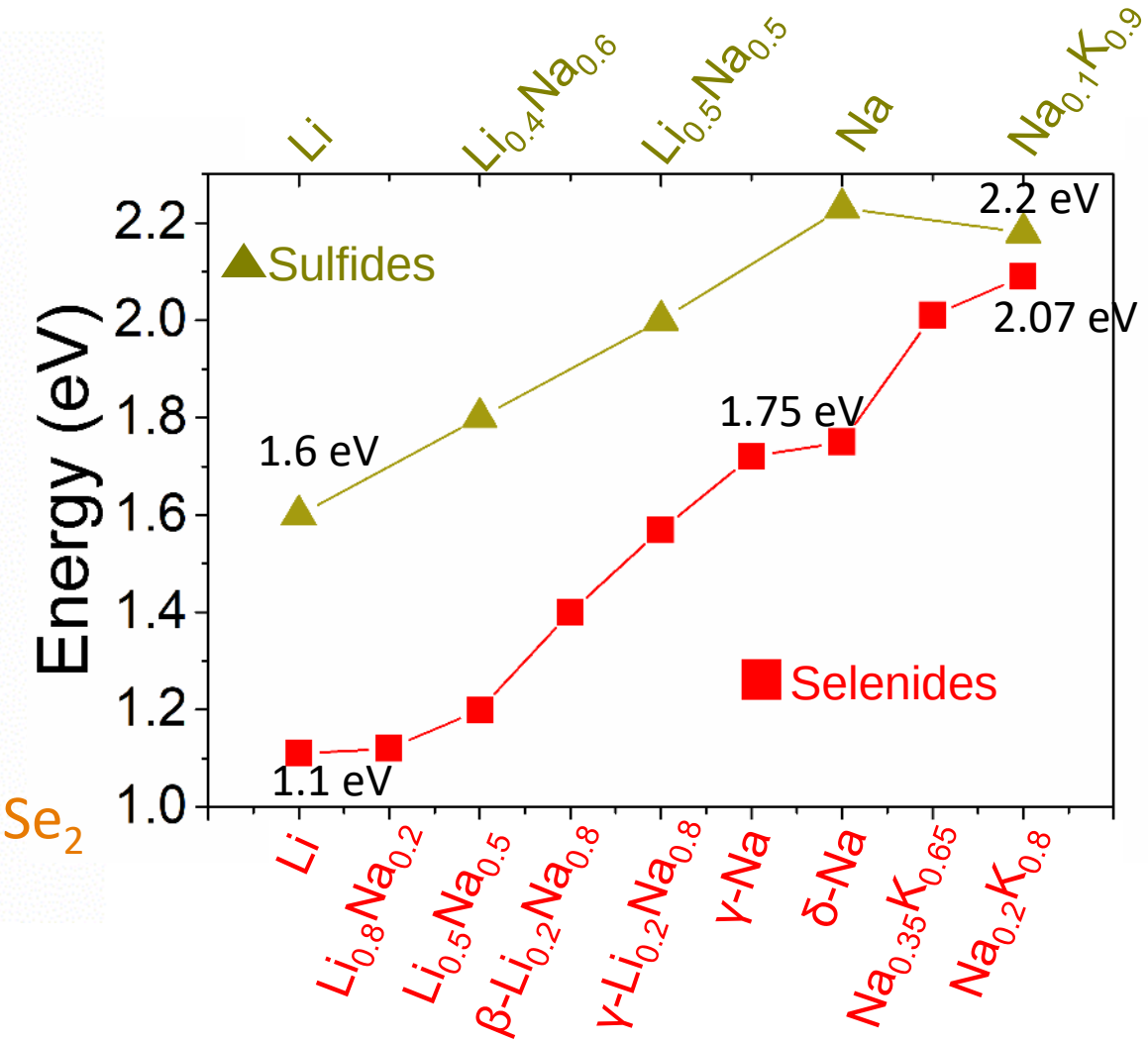



$Na_{0.2}K_{0.8}AsSe_2$ (*Cc*)
Interchain distance
4.12 Å, 4.29 Å, 4.41 Å

**As-Se Van der Waals distance ~ 4.64 Å**

# Bandgap comparison between $AAsQ_2$ structures




**Experimental bandgap**

1.11 eV 1.75 eV 2.07 eV

$LiAsSe_2$< γ-$NaAsSe_2$<$Na_{0.2}K_{0.8}AsSe_2$

Bandgap increases when larger *A* cations are added

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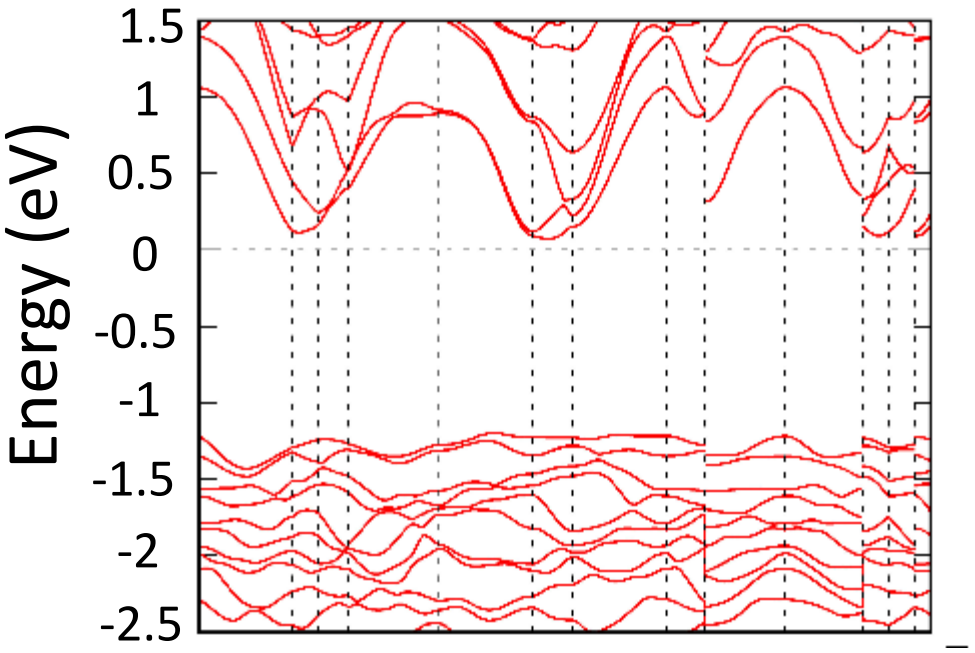
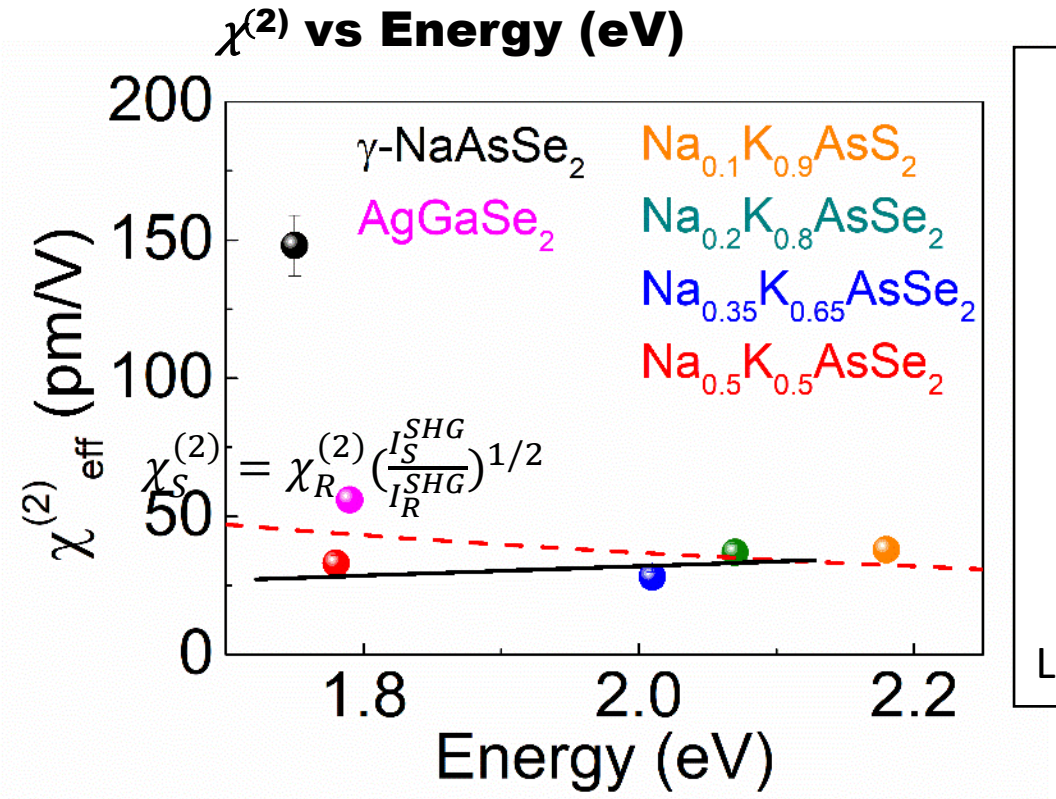
# $KAsSe_2$ has flat bands like γ-$NaAsSe_2$ but γ-$NaAsSe_2$ has greater anisotropy along the chain direction




| Effective mass direction | $KAsSe_2$ | γ-$NaAsSe_2$ |
|---|---|---|
| | Electrons | |
| a* | 0.179 $m_0$ | 0.219 $m_0$ |
| b* | 0.154 $m_0$ | 0.517 $m_0$ |
| c* | 0.238 $m_0$ | 4.961 $m_0$ |
| | Holes | |
| a* | 0.820 $m_0$ | 1.360 $m_0$ |
| b* | 0.522 $m_0$ | 2.159 $m_0$ |
| c* | 0.715 $m_0$ | 2.370 $m_0$ |

γ-$NaAsSe_2$ has larger electron and hole mass along the chain direction.
γ-$NaAsSe_2$ has flatter bands compared to $KAsSe_2$ and its analogous compounds.
γ-$NaAsSe_2$ has greater anisotropy.

# Low SHG response but high LIDT for $Na_{1-x}K_xAsSe_2$




**Theoretical $d_{ij}$**

**γ-$NaAsSe_2$**

$d_{11}$ = 168.9 pm/V

**$Na_{0.5}K_{0.5}AsSe_2$**

$d_{26}$ = 48.3 pm/V

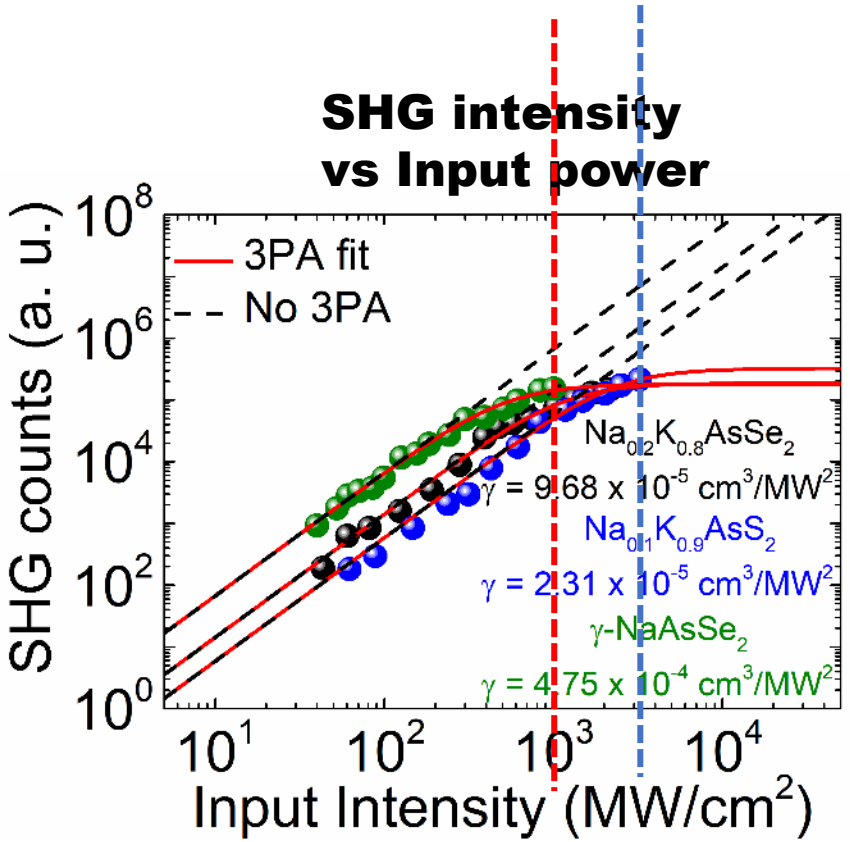
**Experimental LIDT**

**γ-$NaAsSe_2$**

LIDT = 60MW/cm$^2$

**$Na_{0.2}K_{0.8}AsSe_2$**

LIDT = 303 MW/cm$^2$




All samples undergo 3 Photon Absorption (3PA)

$\chi_S^{(2)}$: SHG coefficient for the sample

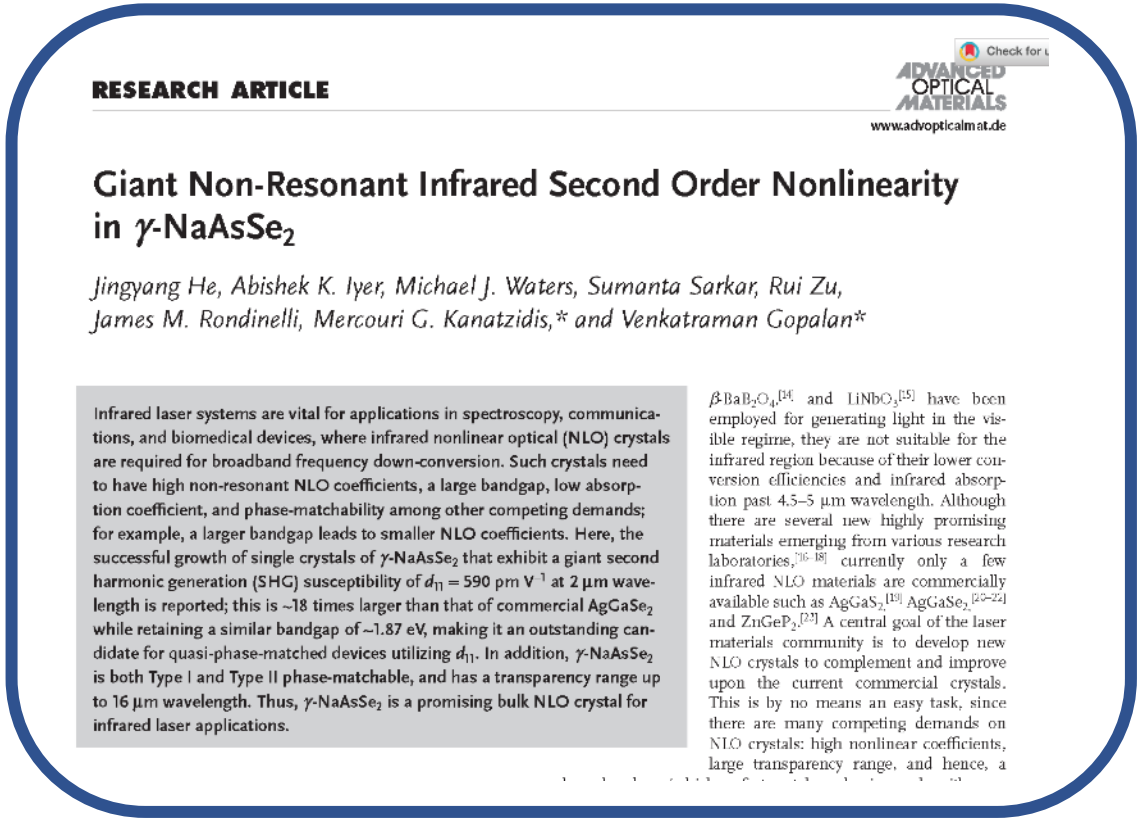
$\chi_R^{(2)}$ SHG coefficient for the reference ($AgGaSe_2$)

Thanks to Hye Ryung Byun, Jang Group Sogang University for SHG measurements
Thanks to Michael J. Waters, Rondinelli Group Northwestern University for theoretical calculations

# Grow Single crystal of $NaAsSe_2$

- Challenge:
- A phase transition from *Pc* to *Pbca* *exists that may complicate our crystal growth efforts*

- Approach: Understand the nature phase transition from *Pc* to *Pbca* and control it.



RESEARCH ARTICLE

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## Giant Non-Resonant Infrared Second Order Nonlinearity in $\gamma$-$NaAsSe_2$

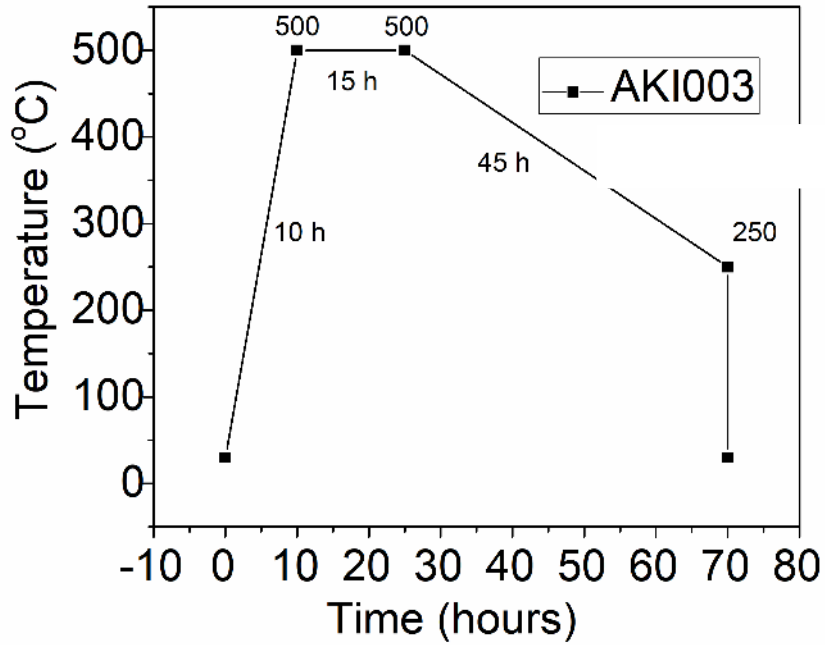
*Jingyang He, Abishek K. Iyer, Michael J. Waters, Sumanta Sarkar, Rui Zu, James M. Rondinelli, Mercouri G. Kanatzidis,* and Venkatraman Gopalan**

Infrared laser systems are vital for applications in spectroscopy, communications, and biomedical devices, where infrared nonlinear optical (NLO) crystals are required for broadband frequency down-conversion. Such crystals need to have high non-resonant NLO coefficients, a large bandgap, low absorption coefficient, and phase-matchability among other competing demands; for example, a larger bandgap leads to smaller NLO coefficients. Here, the successful growth of single crystals of $\gamma$-$NaAsSe_2$ that exhibit a giant second harmonic generation (SHG) susceptibility of $d_{11} = 590$ pm $V^{-1}$ at 2 µm wavelength is reported; this is ~18 times larger than that of commercial $AgGaSe_2$ while retaining a similar bandgap of ~1.87 eV, making it an outstanding candidate for quasi-phase-matched devices utilizing $d_{11}$. In addition, $\gamma$-$NaAsSe_2$ is both Type I and Type II phase-matchable, and has a transparency range up to 16 µm wavelength. Thus, $\gamma$-$NaAsSe_2$ is a promising bulk NLO crystal for infrared laser applications.

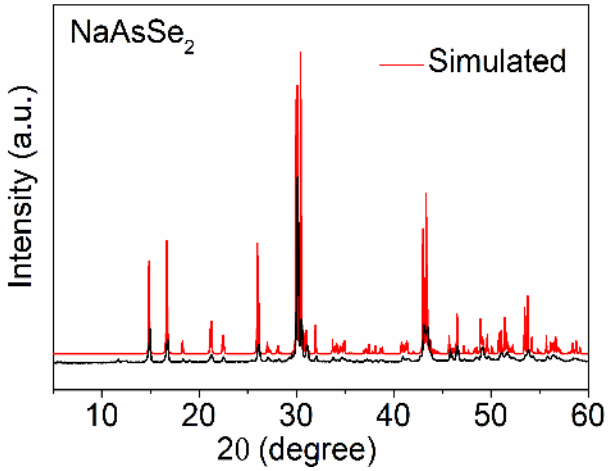
$\beta$-$BaB_2O_4$,[14] and $LiNbO_3$[15] have been employed for generating light in the visible regime, they are not suitable for the infrared region because of their lower conversion efficiencies and infrared absorption past 4.5–5 µm wavelength. Although there are several new highly promising materials emerging from various research laboratories,[16–18] currently only a few infrared NLO materials are commercially available such as $AgGaS_2$,[19] $AgGaSe_2$,[20–22] and $ZnGeP_2$.[23] A central goal of the laser materials community is to develop new NLO crystals to complement and improve upon the current commercial crystals. This is by no means an easy task, since there are many competing demands on NLO crystals: high nonlinear coefficients, large transparency range, and hence, a

# Synthesis of γ-$NaAsSe_2$

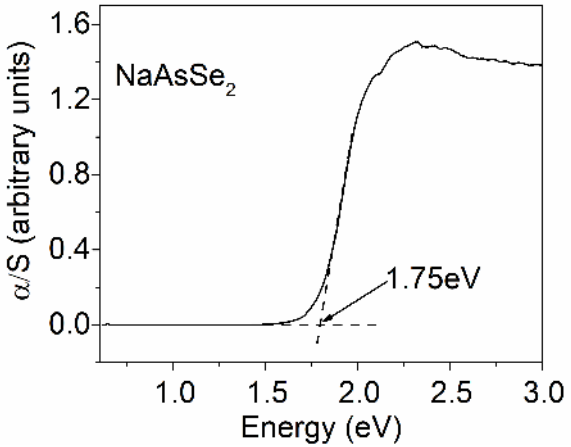
$Na_2Se + As + 3Se \rightarrow 2NaAsSe_2$




Powder XRD




Optical absorption



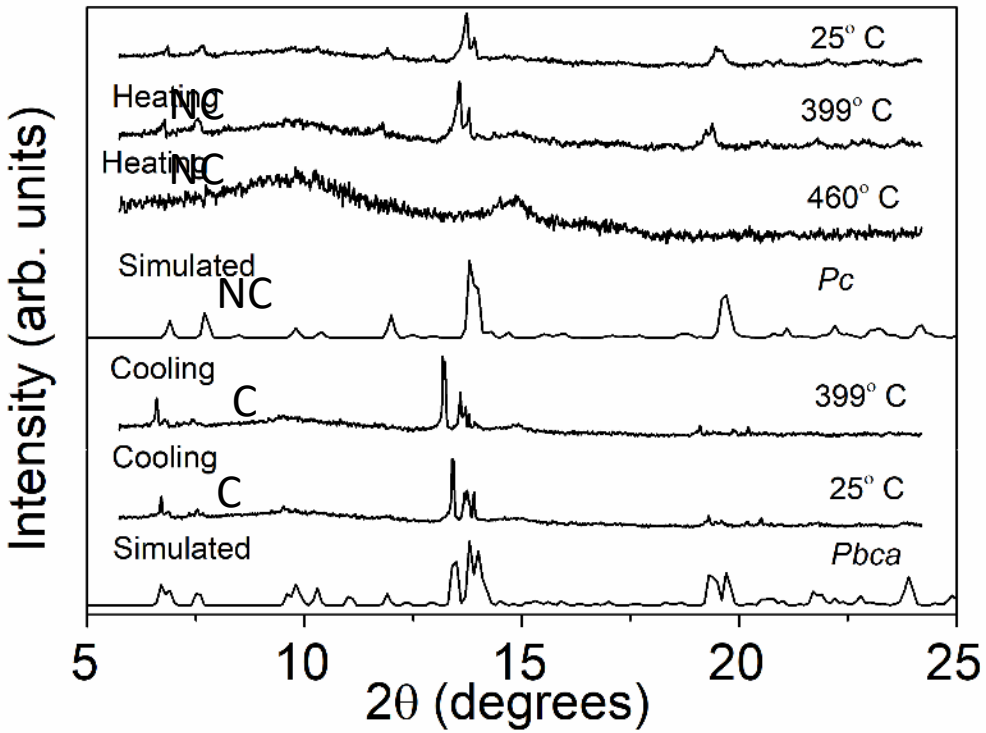

γ-$NaAsSe_2$, *Pc*
melts congruently, melting point is 444 °C
*Means large crystal growth possible*

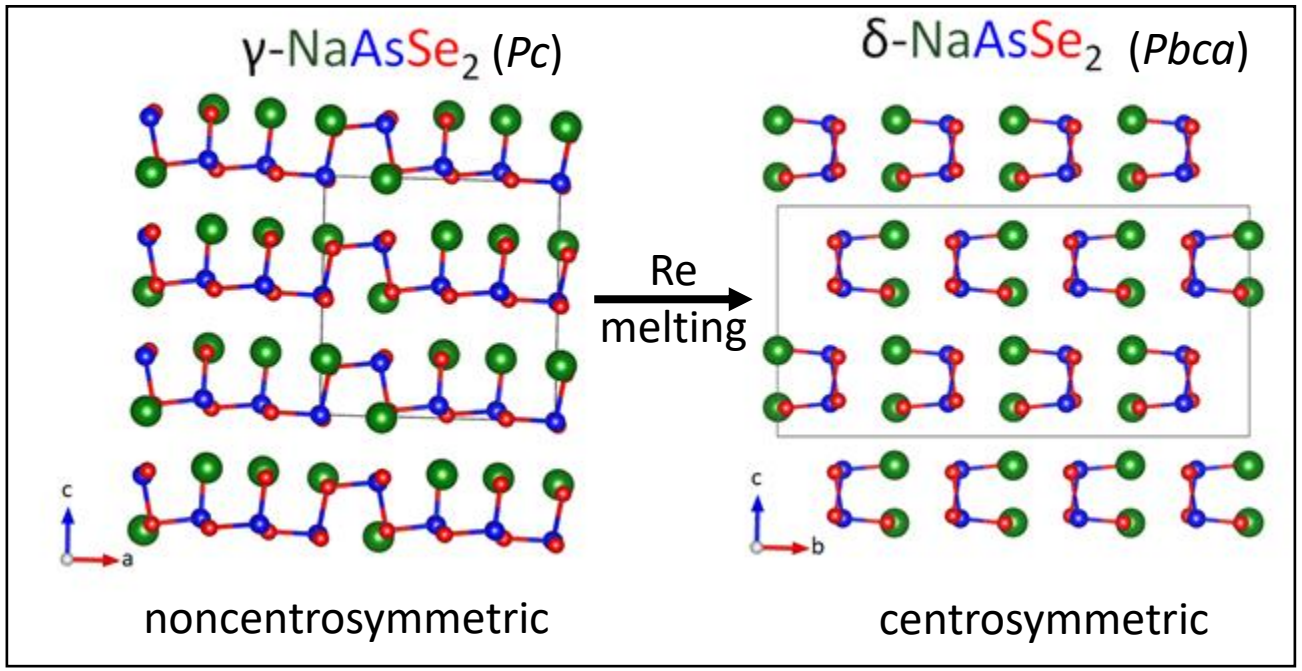
**Structure information**
Space Group: *Pc* (Non-centrosymmetric)
*a* = 11.682 Å, *b* = 5.9021 Å, *c* = 11.8231 Å;
*β* = 90.446˚
Band gap: 1.75 eV

Challenge: Re-melting the γ-$NaAsSe_2$ (NC) sample changes to δ-$NaAsSe_2$ upon cooling

# Synthetic Challenge:
# γ-$NaAsSe_2$ (NC) to δ-$NaAsSe_2$ (C) phase transition at 450°C

**Variable temperature PXRD**




Ramp rate: 10°C/min, Mo Kα

C = centrosymmetric
NC = noncentrosymmetric

# γ-$NaAsSe_2$ Single Crystals Grown by the Bridgman Method: first try

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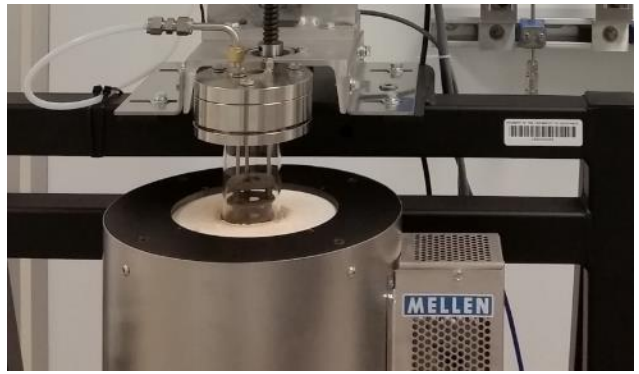
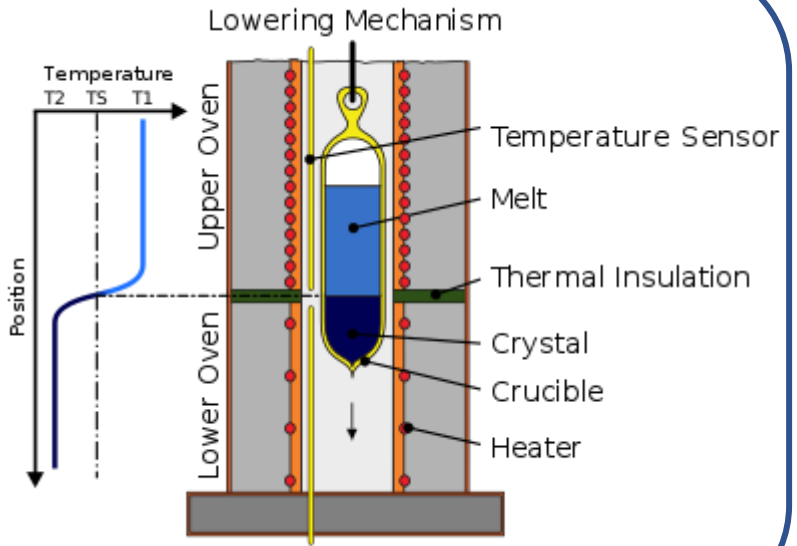
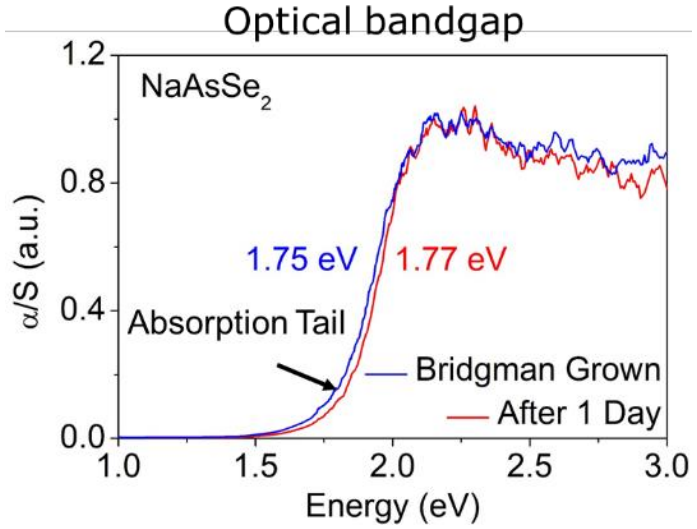
Bridgeman furnace




Single Crystals of γ-$NaAsSe_2$

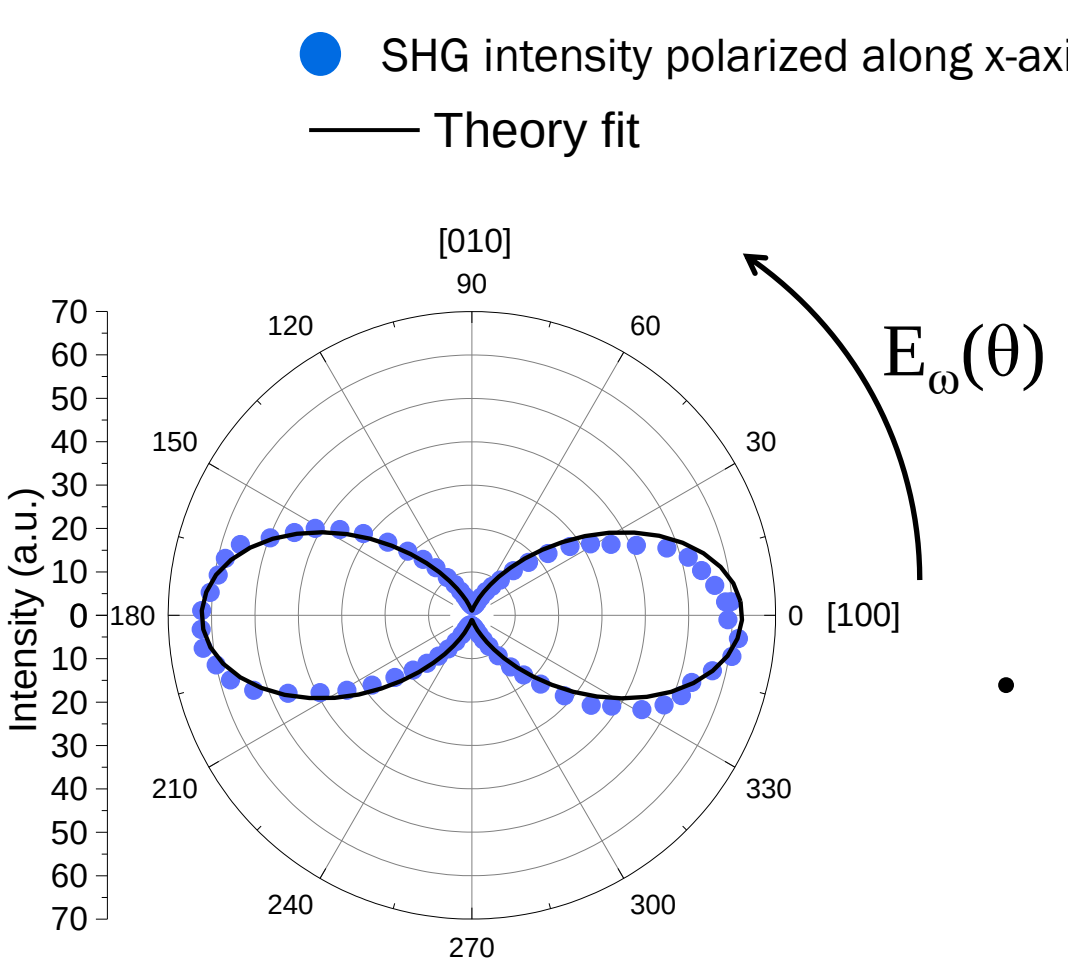
Ingot of γ-$NaAsSe_2$

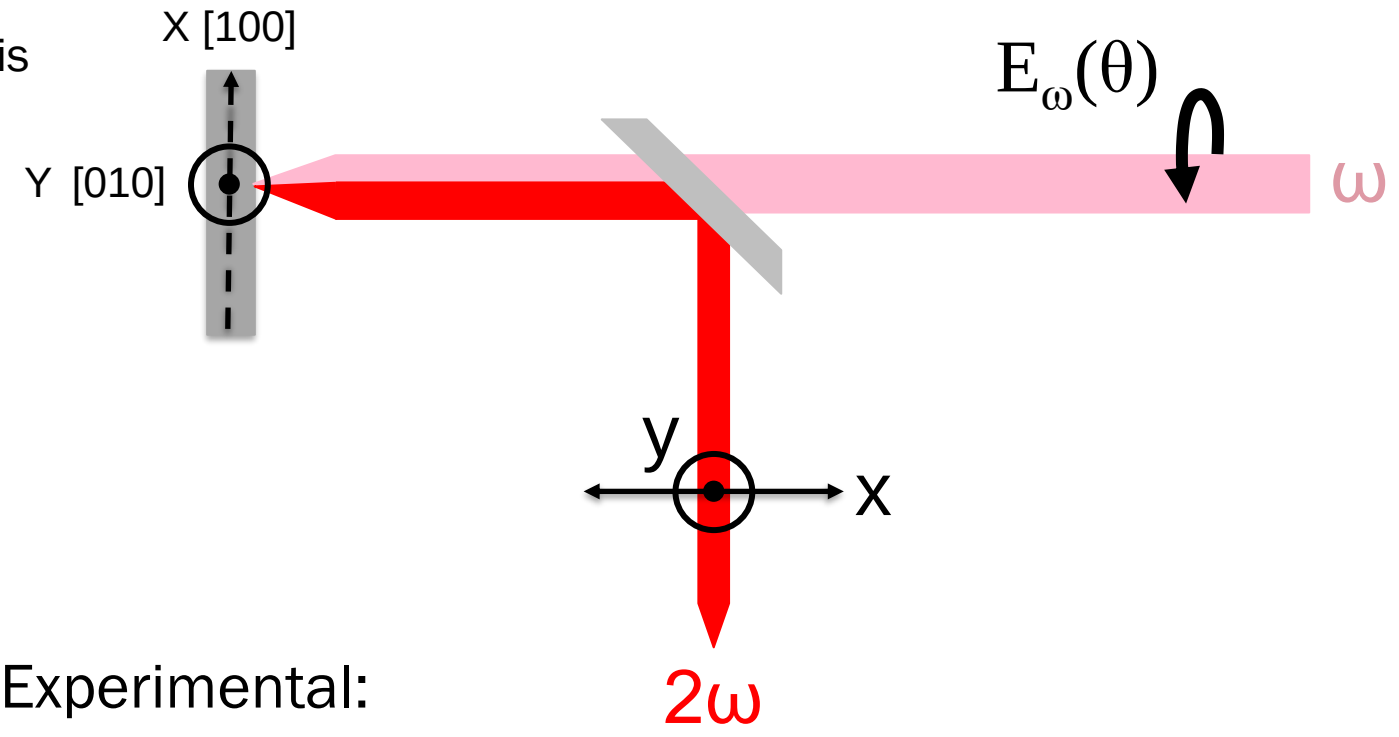



Temperature 520°C
Cold side: 300°C
Dropping rate: 0.5 mm/h

# Nonlinear Optical Properties of γ-$NaAsSe_2$

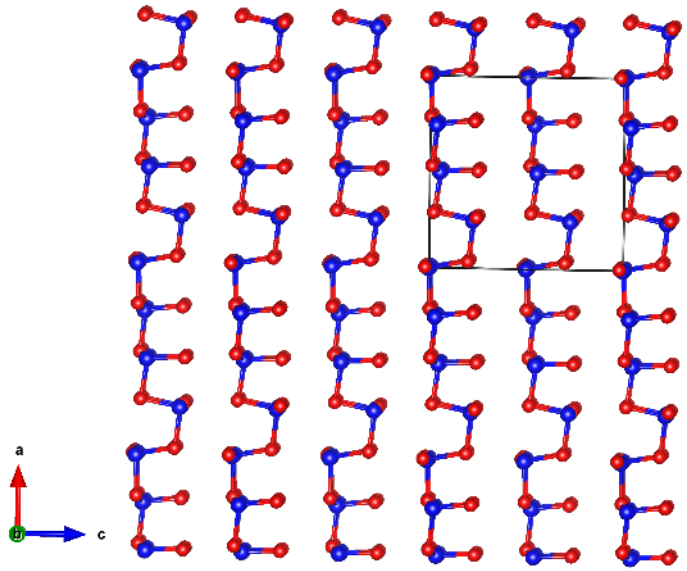


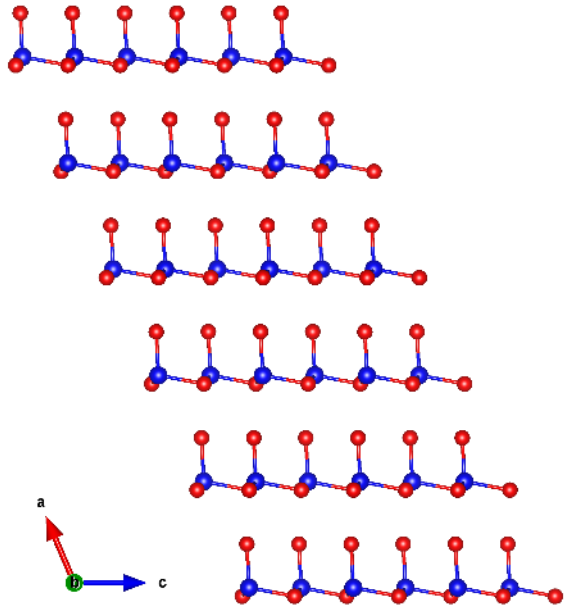




- Experimental:
  - $d_{11}/d_{12}$=7.8
  - $d_{11}$~354pm/V ($\chi^{(2)}=2d_{11}$~708 pm/V)

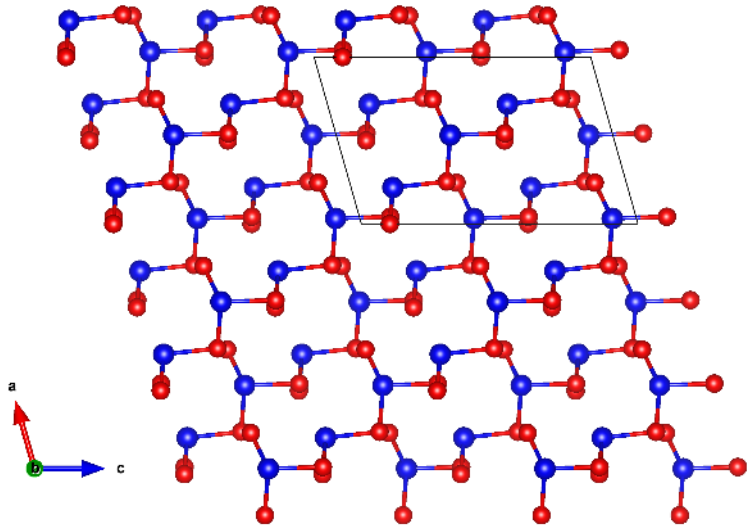
(compared to $LiNbO_3$: $d_{33}$=23.7pm/V at 1550nm)

# How do we stabilize *Cc* γ-$NaAsSe_2$?




New structure type!




**$NaAsSe_2$**, ***Pc***
*a* = 11.682 Å, *b* = 5.902 Å, *c* = 11.823 Å
*β* = 90.44°

**$LiAsSe_2$**, ***Cc***
*a* = 12.287 Å, *b* = 5.541 Å, *c* = 5.553 Å
*β* = 113.12°

**$K_{0.8}Na_{0.2}AsSe_2$**, ***Cc***
*a* = 7.764 Å, *b* = 10.164 Å,
*c* = 12.403 Å, *β* = 105.87°

Na, Li and K atoms removed, for a better understanding of the structures

# Challenge: Can the γ-$NaAsSe_2$ be stabilized through chemical substitution?

Alkali-metal substitution

δ-$K_{0.2}Na_{0.8}AsSe_2$

Centrosymmetric (*Pbca*)

γ-$Li_{0.2}Na_{0.8}AsSe_2$

Non-Centrosymmetric

**But melts incongruently**

γ-$Na_{0.95}Ag_{0.05}AsSe_2$

Non-Centrosymmetric

**But melts incongruently**

γ-$NaAsSe_2$

Sb substitution?

Chalcogen substitution

δ-$NaAsSe_{1.8}S_{0.2}$

Centrosymmetric (*Pbca*)

# γ-$NaAs_{0.95}Sb_{0.05}Se_2$ crystallizes in γ-$NaAsSe_2$ (*Pc*)

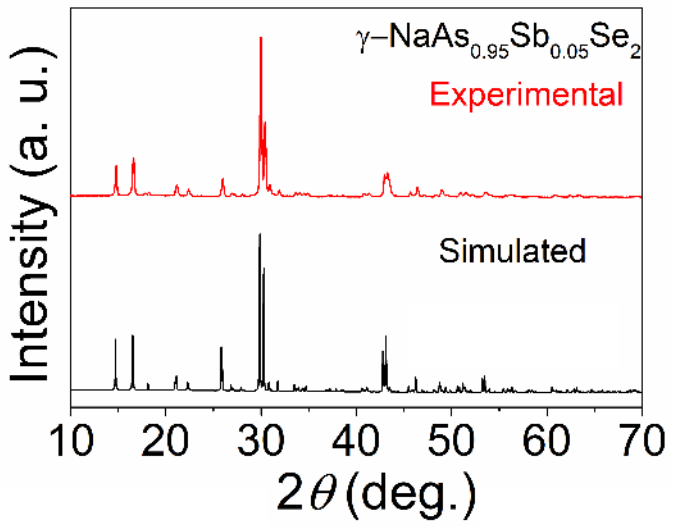
**Synthesis of γ-$NaAs_{0.95}Sb_{0.05}Se_2$**

$0.5Na_2Se + 0.05Sb + 0.95As + 1.5Se \rightarrow NaAs_{0.95}Sb_{0.05}Se_2$

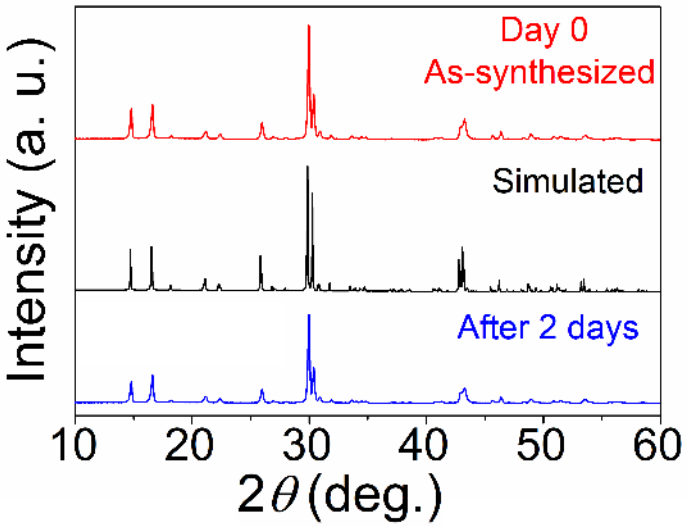
**Standardized Temperature Profile**

RT —(12 h)→ 500 ° C —(24 h)→ 500 ° C —(24 h)→ 250° C —(4 h)→ RT

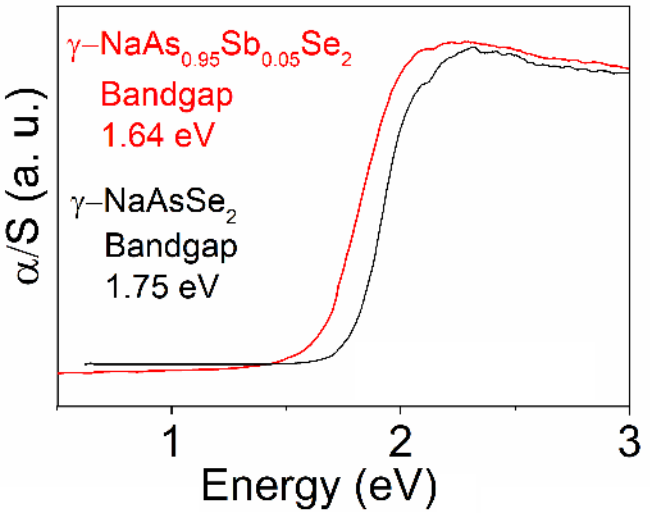
Powder x-ray diffraction




Sample stability in air

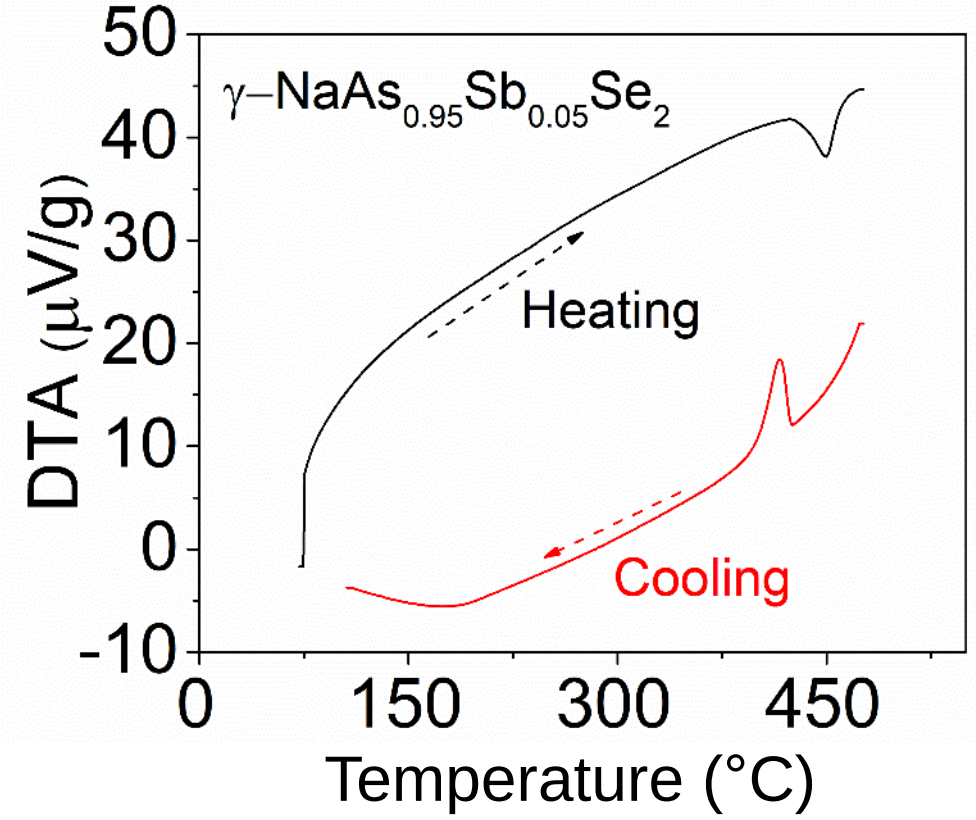


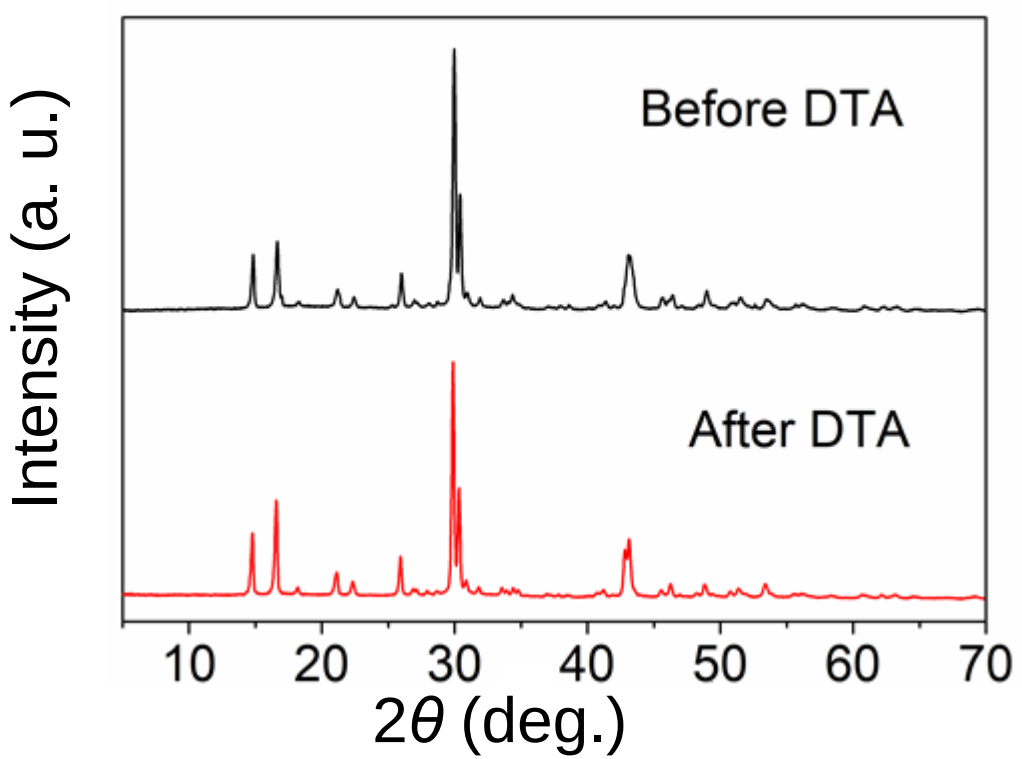

Diffuse Reflectance Spectrum



# Differential Thermal Analysis confirms γ-$NaAs_{0.95}Sb_{0.05}Se_2$ remains noncentrosymmetric

## Good News!



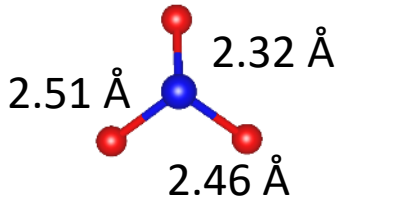




γ-$NaAsSe_2$ is stabilized by doping with Sb

Rate of heating and cooling: 10°C/min

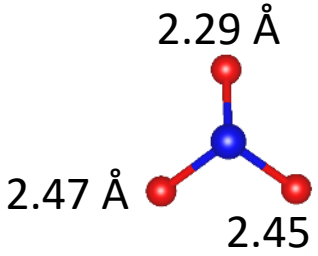
# As-Se bond length in the different $AAsSe_2$ structures

Substitution of As with Sb offers bond flexibility to keep the chain

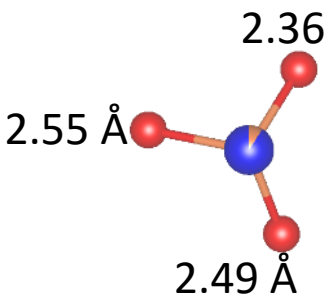



γ-$NaAsSe_2$ (*Pc*)

Melts incongruently

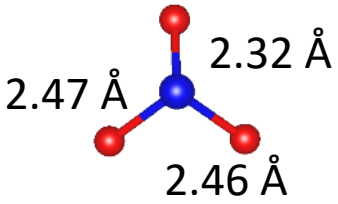



δ-$NaAsSe_2$ (*Pbca*)



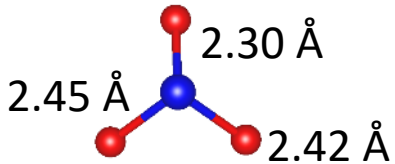

γ-$NaAs_{0.95}Sb_{0.05}Se_2$

Melts congruently



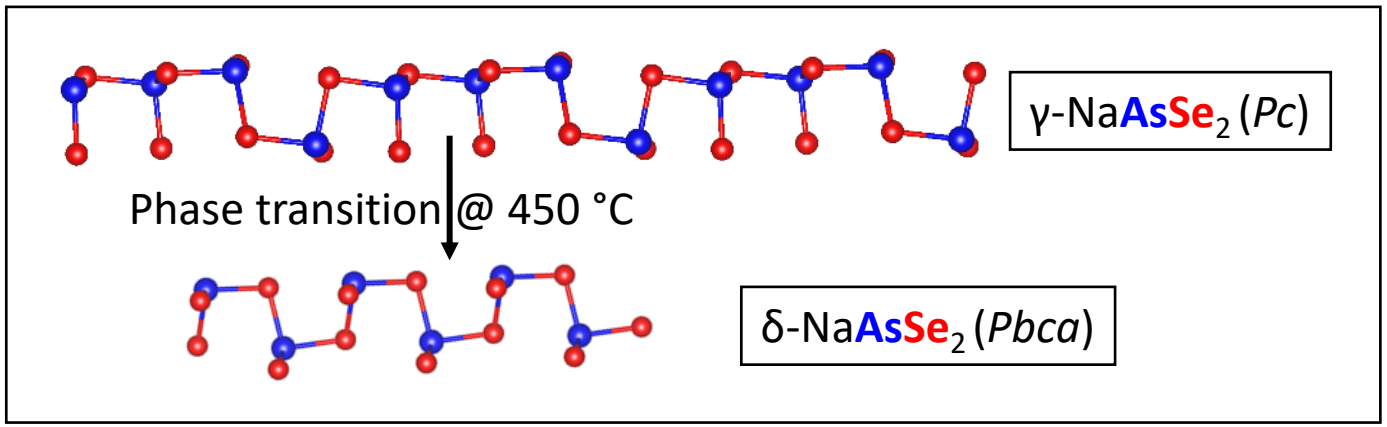

β-$LiAsSe_2$

Melts congruently

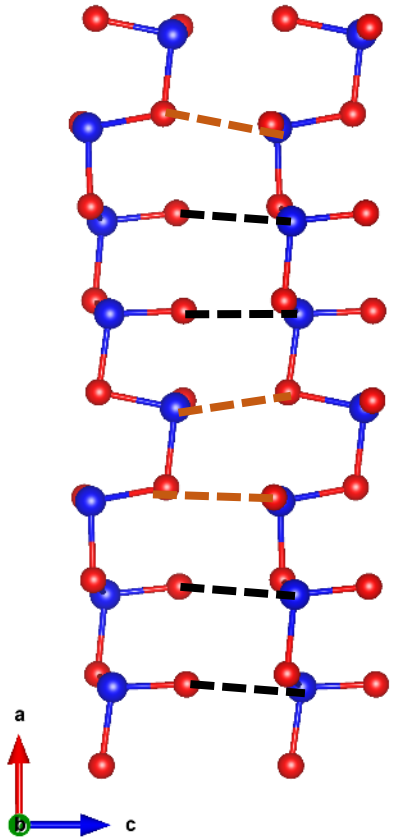


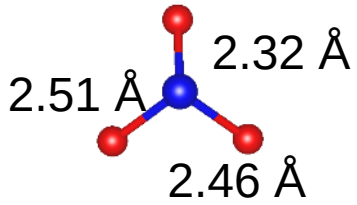

$K_{0.8}Na_{0.2}AsSe_2$

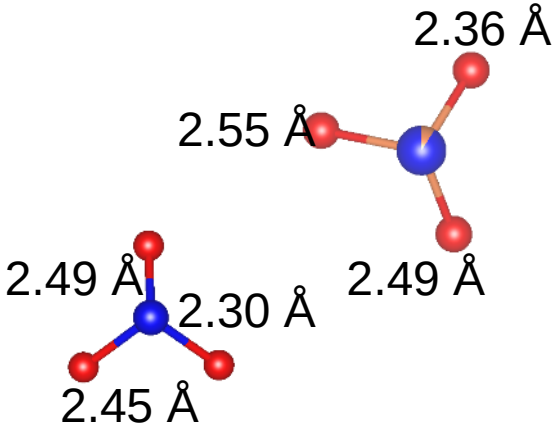
Melts congruently



# Structural differences between γ-$NaAsSe_2$ and $NaAs_{0.95}Sb_{0.05}Se_2$

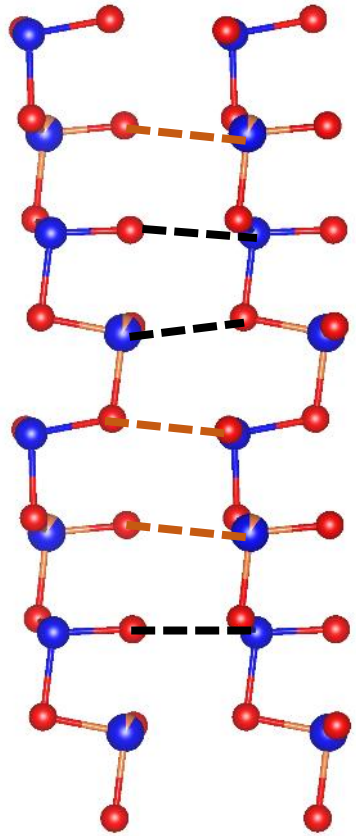



| γ-$NaAsSe_2$<br>Space Group: *Pc* | $NaAs_{0.95}Sb_{0.05}Se_2$<br>Space Group: *Pc* |
|---|---|
| *a* = 11.726(2) Å<br>*b* = 5.932(1) Å<br>*c* = 11.866(2) Å<br>*β* = 90.39(3)°<br><br>**V: 825.5 (3) Å³** | *a* = 11.761(2) Å<br>*b* = 5.958(7) Å<br>*c* = 11.928(2) Å<br>*β* = 90.34(3)°<br><br>**V: 835.9 (3) Å³** |

**γ-NaAsSe$_2$** (*Cc*)
Interchain distance
3.59 Å, 3.64 Å



**γ-$NaAs_{0.95}Sb_{0.05}Se_2$** (*Cc*)
Interchain distance
3.63 Å, 3.67 Å

*Na removed to understand the change in structure better

# Bridgman growth of γ-$NaAs_{0.95}Sb_{0.05}Se_2$

5mm x 4mm x 2mm

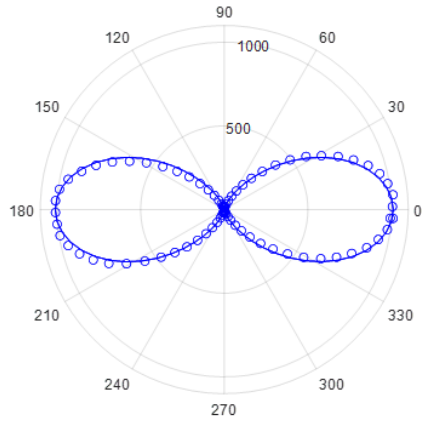
Polished Crystals

Temperature 520°C
Cold side: 350°C
Dropping rate: 1 mm/h
Kept at 350 °C for 54 hours
Dropped to RT at 10 mm/h

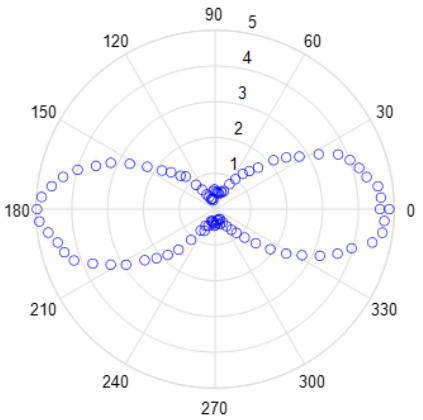
Purity of the starting material
3N $Na_2Se$, 5N As, 5N Sb and 5N Se

**Preliminary SHG data at 2 µm on the single crystal of γ-$NaAs_{0.95}Sb_{0.05}Se_2$**

γ-$NaAs_{0.95}Sb_{0.05}Se_2$




$LiNbO_3$

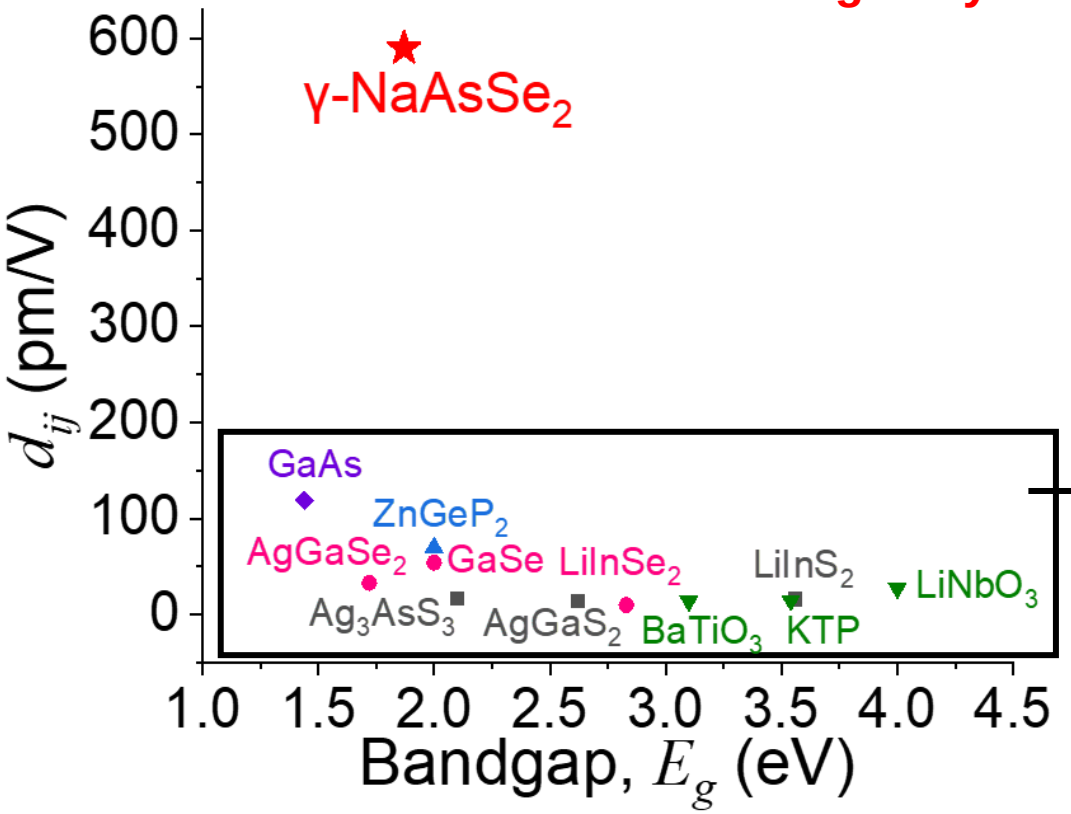



$LiNbO_3$ $d_{33}$: 18 pm/V
γ-$NaAs_{0.95}Sb_{0.05}Se_2$ $d_{11}$: 592 pm/V

The SHG data is comparable to γ-$NaAsSe_2$

# Comparison of γ-$NaAsSe_2$ with other NLO materials

**Single crystal of γ-$NaAsSe_2$ has a $d_{11}$ = 590 pm/V @ 2 µm**




Comparison with SHG response to all other commercially used NLO crystals

**$AgGaSe_2$: $d_{36}$: 33 pm/V (2 µm)**

**$ZnGeP_2$: $d_{36}$: 75 pm/V (2 µm)**

These results clearly suggest that stabilizing the γ –$NaAsSe_2$ is worth exciting!