Synthesis of nonlinear optical material $Ag_5PS_4Cl_2$ crystals

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Why Nonlinear Optical Materials?

- Crystallize in the noncentrosymmetric space group (NCS)
- High second harmonic generation (SHG) response, which only occurs in NCS crystals
- Withstand infrared (IR) laser damage (high threshold)
- Resistant to chemical change[1]
- Used to halve wavelength and double frequency of IR lasers

Hypothesis: Using varying synthesis methods, an ideal phase match of Pentasilver Tetrathiophosphate Dichloride, $Ag_5PS_4Cl_2$, can be produced as a crystal with nonlinear optical (NLO) properties.

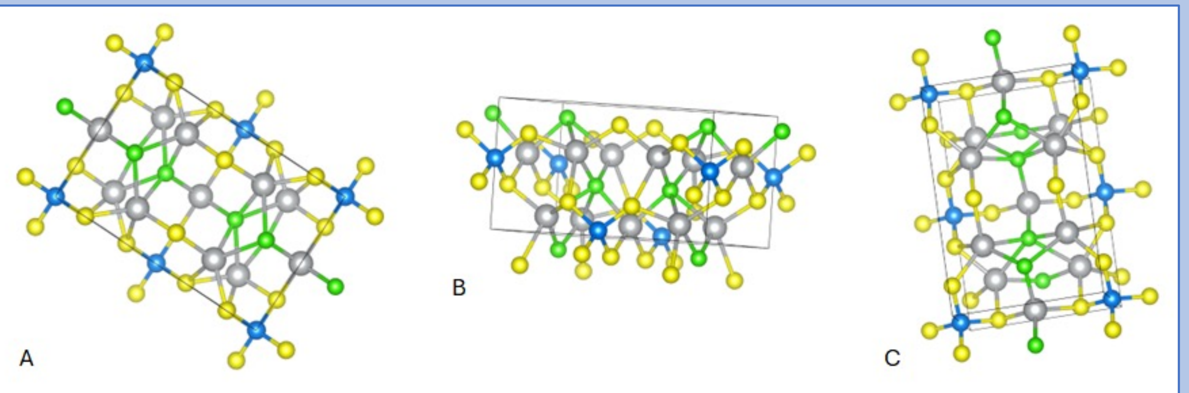

Figure 1. Three-dimensional unit cell structure of Pentasilver Tetrathiophosphate Dichloride, $Ag_5PS_4Cl_2$. The three points of view (A-C) of this non-centrosymmetric crystal show the complex bonds between Silver (grey), Phosphorus (blue), Sulfur (yellow), and Chlorine (green).

Materials and Methods

- 9 mm Glass Quartz Tubing for Test Tubes
- Argon-gas compacted elements stored and extracted from a sealed glove box
- Vacuum pump and torch for sealing tubes procedure
- Synthesis via furnace based on percentage weight of solid-state compound, compound mass to flux mass ratio, and temperature profile
- Solid-State Elements and Compound: Silver (Ag), Phosphorus (P), Sulfur (S), and Silver Chloride (AgCl)

Table 1. Summary of $Ag_5PS_4Cl_2$ Synthesis Methods and Conditions

Sample Number	Compound	Total Compound Mass	Synthesis Temperature (°C)	Additional Conditions
KB001	$Ag_5PS_4Cl_2$	0.95 g	800°C	
KB002	$Ag_5PS_4Cl_2$	0.95 g	800°C	0.4 g AgCl flux
KB003	$Ag_5PS_4Cl_2$	0.95 g	800°C	0.9 g AgCl flux, centrifuge
KB014	$Ag_5PS_4Cl_2$	0.4 g	800°C	0.4 g AgCl flux
KB015	$Ag_5PS_4Cl_2$	0.4 g	800°C	0.2 g AgCl flux
KB016	$Ag_5PS_4Cl_2$	0.4 g	800°C	0.4 g AgCl flux
KB017	$Ag_5PS_4Cl_2$	0.4 g	800°C	0.2 g AgCl flux
KB018	$Ag_5PS_4Cl_2$	0.4 g	800°C	0.4 g AgCl flux + $ZnCl_2$, centrifuge
KB028	$Ag_5PS_4Cl_2$	0.95 g	800°C	0.4 g AgCl flux

Results

- Powder X-Ray Diffraction (PXRD) performed on all samples
- Analysis of PXRD results via comparison with target Inorganic Crystal Structure Database (ICSD) patterns reveals the accuracy of synthesis methods.
- Correlating with one another, the percentage weight of compound, compound mass to flux mass ratio, and synthesis duration effected the ideal synthesis of $Ag_5PS_4Cl_2$
- Found KB002 and KB017 to have phase-matched best with $Ag_5PS_4Cl_2$ due to their similarities with the three main peaks of $Ag_5PS_4Cl_2$
- Ideal focus on KB002 because its lack of the two primary peaks that occur in AgCl flux and were present in all other samples
- KB002 included a 2:1 ratio of compound mass to flux mass synthesized at 800°C, dwelling for 120 hours and cooling to 25°C for 48 hours

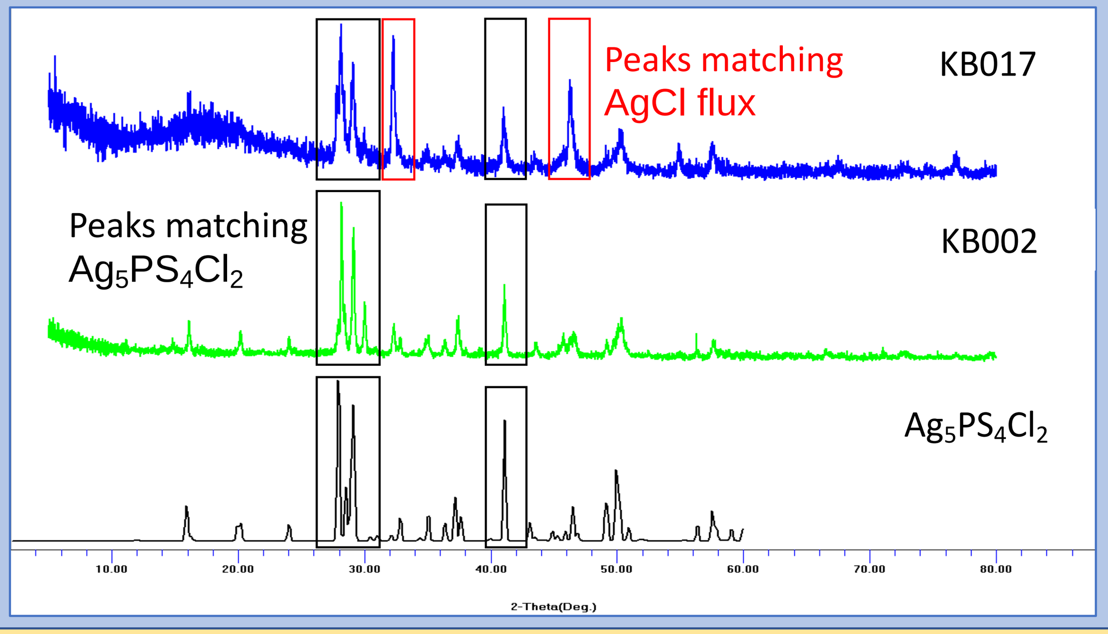

Figure 2. Comparison of PXRD Results From KB002 and KB017 with $Ag_5PS_4Cl_2$ ICSD File

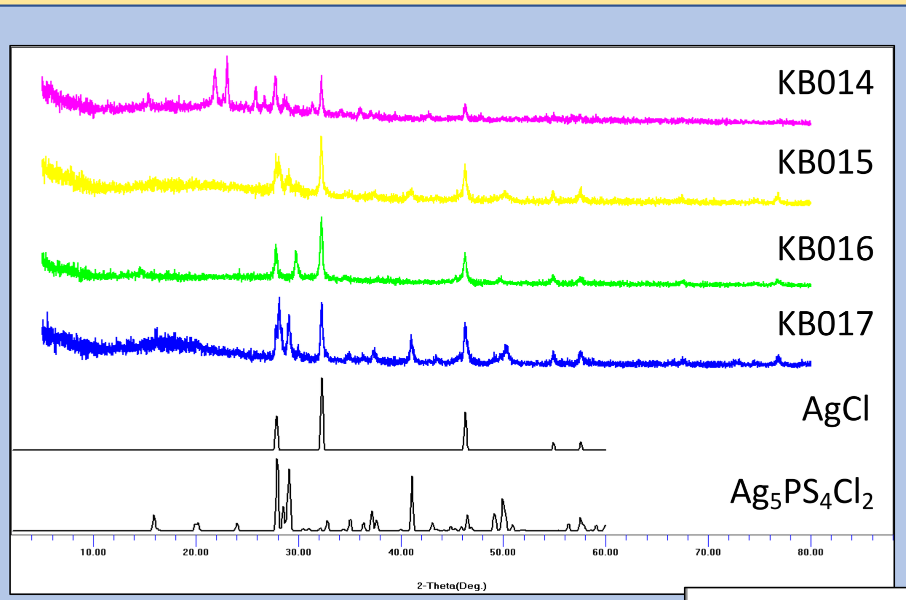

Figure 3. Comparison of PXRD Results From KB014-KB017 with $Ag_5PS_4Cl_2$ and AgCl ICSD Files

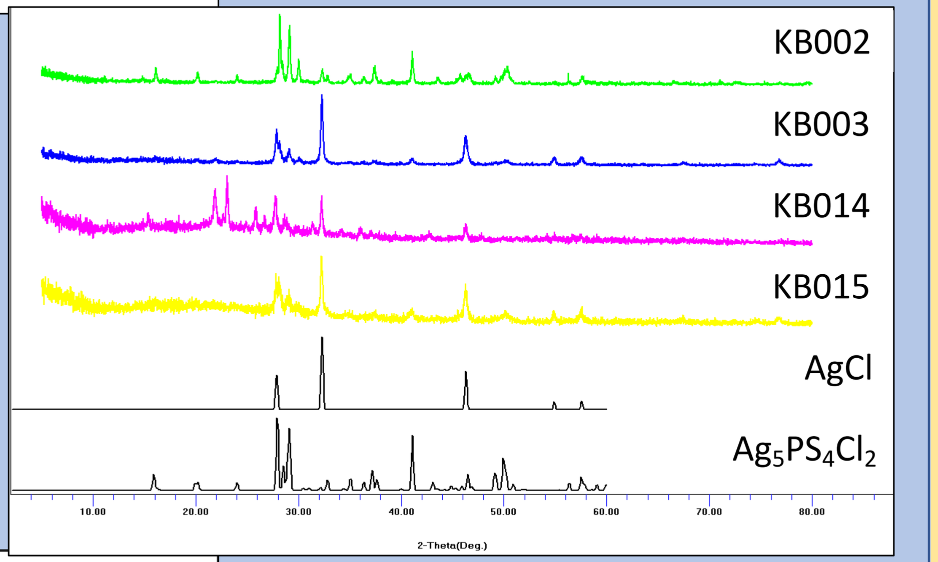

Figure 4. Comparison of PXRD Results From KB002, KB003, KB014, and KB015 with $Ag_5PS_4Cl_2$ and AgCl ICSD Files

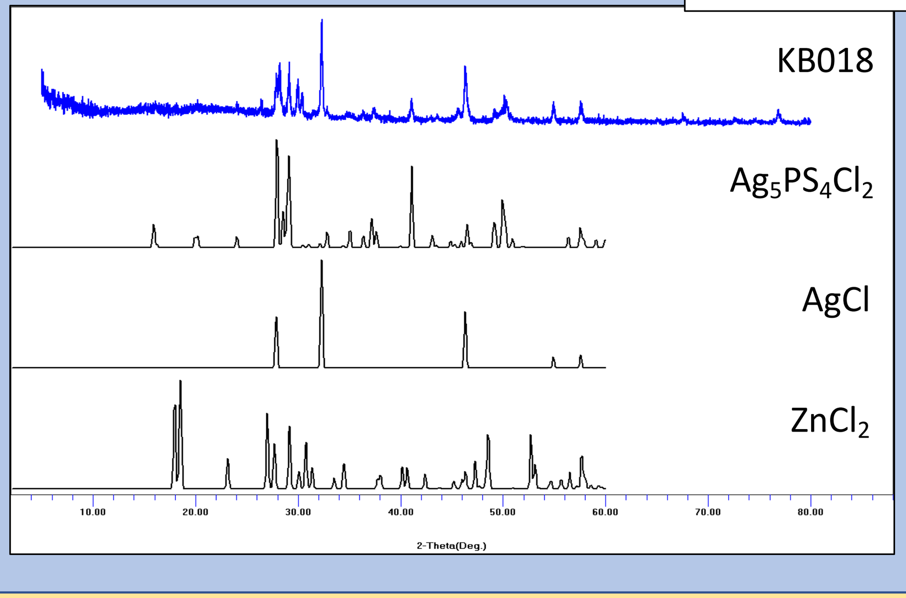

Figure 5. Comparison of PXRD Results From KB018 with $Ag_5PS_4Cl_2$, AgCl, and $ZnCl_2$ ICSD Files

References

[1] Aslam, H. Z.; Doane, J. T.; Yeung, M. T.; Akopov, G. Advances in Solid-State Nonlinear Optical Materials: From Fundamentals to Applications. ***ACS Applied Optical Materials*** **2023**, *1* (12), 1898–1921. DOI:10.1021/acsaom.3c00352.

[2] Jörgens, S.; Mewis, A. AG5PS4CL2 and AG15(PS4)4CL3 – Crystal Structures and Their Relation to AG3PS4. ***Solid State Sciences*** **2007**, *9* (2), 213–217. DOI:10.1016/j.solidstatesciences.2006.09.003.

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Conclusions

- Nonlinear Optical (NLO) materials produce new photons via second harmonic generation (SHG), resulting in noncentrosymmetric (NCS) crystals like Pentasilver Tetrathiophosphate Dichloride, $Ag_5PS_4Cl_2$.
- An ideal $Ag_5PS_4Cl_2$ crystal was synthesized by a 2:1 compound mass to flux mass ratio and a temperature profile of 800 °C.

Future Directions/Plans

- Reproduce an abundance of the ideally phase-matched crystal, KB002
- Remove the excess AgCl flux via additional $ZnCl_2$ flux synthesis and centrifuge
- Run PXRD analysis of newly synthesized crystal(s)