# University of Siegen

# Synthesis and Characterization of $Li_4P_2Se_6$

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## Introduction

In the course of our investigations on ternary lithium seleno phosphates, we recently synthesized single crystals of **$Li_4P_2Se_6$.** The existence of the compound was first mentioned in 1993 **(only powder investigations)** [1].

## Preparation

All experimental procedures were carried out in a **glove-box** under Argon atmosphere. For the preparation of $Li_4P_2Se_6$, stoichiometric mixtures of lithium selenide, red phosphour and selenium were homogenized, pressed to pellets and transferred into **graphitized quartz glass ampoules.** The reaction at **550 °C** for **5 days** yielded in **air sensitive,** transparent **yellow crystals** sufficient for single crystal X-ray measurements.

$$2\,Li_2Se + 2P + 4\,Se \xrightarrow{550\ °C} Li_4P_2Se_6$$

## Characterization

The title compound was obtained **without any impurity** (see figure 1). The ratio of Se/P was confirmed by **analytical scanning electron microscopy** (EDX, measured/calculated at. **%, Se: 75.65 / 75.0, P: 24.35 / 25**, Li could not be detected due to the limitations of the instrument, see figure 2).

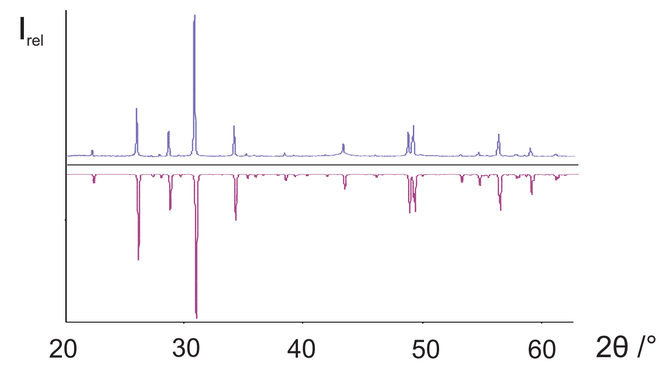


**Figure 1:** Section of X-ray powder diffraction diagrams of $Li_4P_2Se_6$ (top: measured, bottom; calculated).

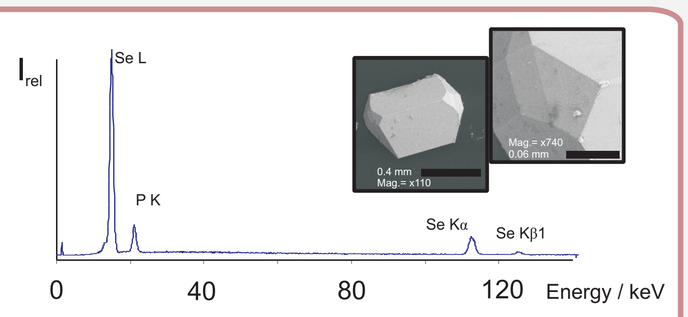


**Figure 2:** EDX spectra of $Li_4P_2Se_6$ and SEM images of a typical crystal.

## Structure

Single crystal measurement was performed with **STOE IPDS.** In agreement with the powder investigation the reflections could be indexed **orthorhombically** (**space group: *Pnma***) with the lattice constants ***a* = 13.882 Å, *b* = 11.219 Å, *c* = 6.455 Å.** $Li_4P_2Se_6$ does not crystallize isostructural with the closely related compound $Li_4P_2S_6$ [2].
The **hexagonal** structure (**space group: *$P6_3/mcm$***) of **$Li_4P_2S_6$** is based on a **hcp of sulfur** in which **4/6 of the octahedral sites** are occupied by **Li**, and the other **2/6** are statistically filled (occupancy: 0.5) by **P-P pairs ($d_{P-P}$= 2.256 Å).** The P-P central bond links two $PS_3$ groups to form **$[P_2S_6]^{4-}$**anions. In contrast to this, the structure of the title compound is characterized by a **mixture of hcp and ccp of selenium** (see figure 3) in which **4/6 of the octahedral sites** is occupied by **Li,** and **1/6 of the octahedral sites** is occupied by **P-P pairs ($d_{P-P}$= 2.243 Å)** in an ordered way forming **$[P_2Se_6]^{4-}$** groups (see figure 4 ).
In the hcp of $Li_4P_2S_6$ every $LiS_6$ octahedron shares two faces with neighbored octahedra. In contrast to this, a mixing of hcp and ccp in $Li_4P_2Se_6$ causes a relaxation of the whole structure. Each $LiSe_6$ octahedron shares only one face with another octahedron (see figure 6).

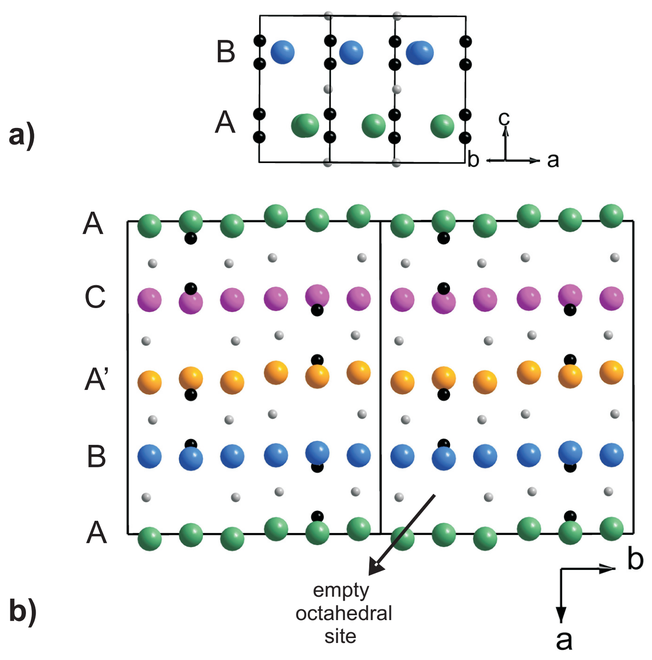


**Figure 3: a)** ABAB sequence of S atoms in **$Li_4P_2S_6$**
**b)** ABA'C sequence of Se atoms in **$Li_4P_2Se_6$**
(black atoms: P, grey atoms: Li, colored atoms: Ch (S, Se)).

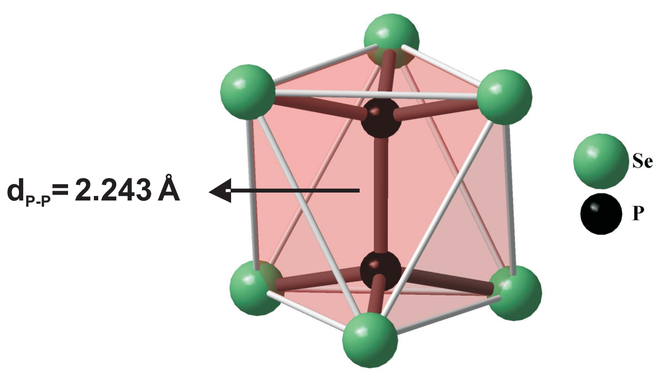


**Figure 4: $P_2Se_6$** units in $Li_4P_2Se_6$.

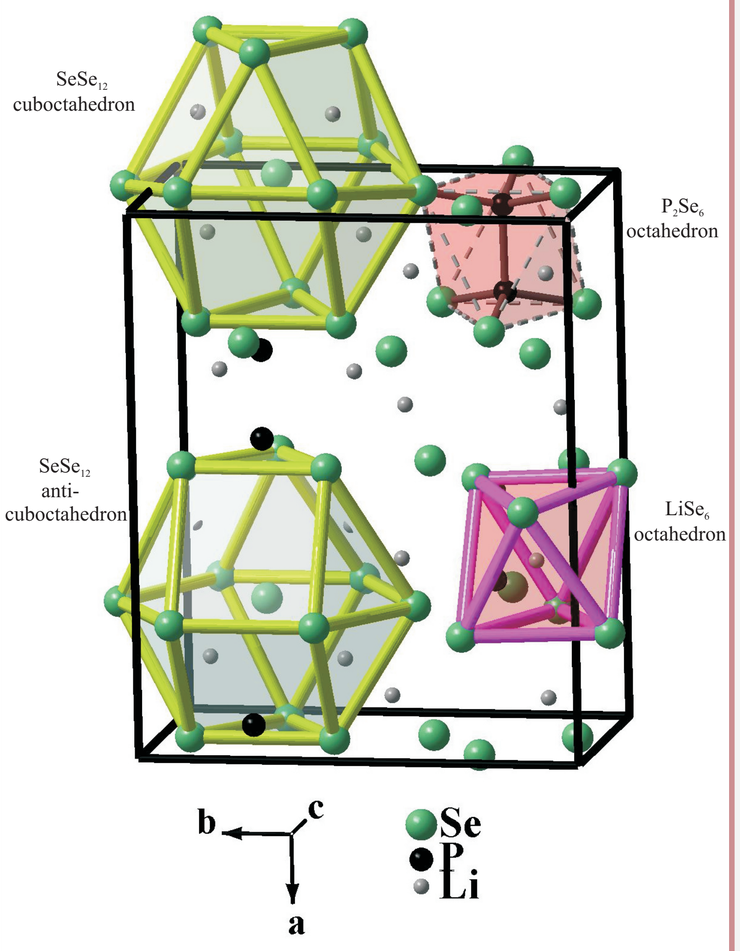


**Figure 5:** Characteristic structural units in $Li_4P_2Se_6$.

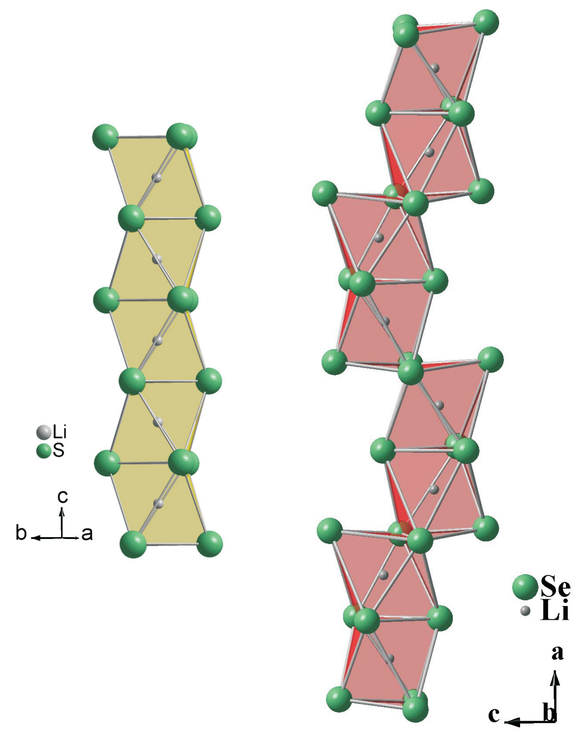


**Figure 6:** Representation of the face-sharing (in $Li_4P_2S_6$) and partly face-sharing (in $Li_4P_2Se_6$) $LiCh_6$ (Ch: S, Se) octahedra.

## Literature

[1] Francisco, R. H. P., Tepe, T., Eckert, H.: J. Solid State Chem. 107 (1993) 452-459.
[2] Mercier, R., Malugani, J. P., Fahys, B., Douglade, J., Robert, G.: J. Solid State Chem. 43 (1982) 151-162.

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