



Quaternary Lithium Seleno Halide Argyrodites

Ö. Gün, C. Reiner, H.J. Deiseroth

Universität Siegen, Anorganische Chemie, 57068 Siegen

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Introduction

Ternary argyrodite compounds with the general formula $A_{(12-n)}BCh_6$ (A = Cu, Ag; B = P, As, Ge, Si; Ch = S, Se, Te, n = charge of the cation B) are derived from the mineral Ag_6GeS_6 [1]. In many argyrodite type compounds it is possible to substitute a small part ($\delta \leq 1$) of the chalcogenides by halides resulting in quaternary formulas. The **anionic substructure** of these compounds form a **tetrahedral close packing**, which is topologically related to the arrangement of Mg and Cu atoms in the cubic **Laves phase $MgCu_2$** [2]. In the course of our investigations on lithium seleno argyrodites, we obtained quaternary compounds with the composition $Li_{7-3}PSe_{6-x}X_3$ (X = Cl, Br, I) and $Li_{7-3}AsSe_{6-x}I_3$.

Preparation

All experimental procedures were carried out in a **glove-box** under Argon atmosphere. In typical experiments **carbon coated**, evacuated and sealed quartz ampoules loaded with Li_2Se , P_2Se_6 and LiX (X = Cl, Br, I) in stoichiometric proportions were heated for **5 days at 550 °C**. For the preparation of $Li_{7-3}AsSe_{6-x}I_3$, **elemental As and Se** were used instead of P_2Se_6 . After the reaction, the ampoules were cooled to room temperature with a rate of **30 °C/h**.

Characterization

All samples crystallize in the **cubic system** (Figure 1). The title compounds do not have a defined composition (the lattice constants range obtained from different samples are given in Table 1).

Table 1: Some properties of the compounds.

compound	color	lattice constants range obtained from different samples	lattice constants for the measured crystals
$Li_{7-3}PSe_{6-x}Cl_3$	orange	10.348- 10.383 Å	10.374 Å
$Li_{7-3}PSe_{6-x}Br_3$	orange	10.379-10.395 Å	not measured
$Li_{7-3}PSe_{6-x}I_3$	orange	10.484-10.562 Å	10.540 Å
$Li_{7-3}AsSe_{6-x}I_3$	dark pink	10.647(1) Å (only one sample)	not measured

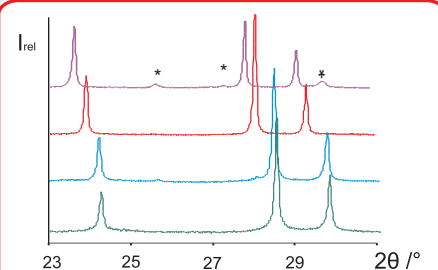
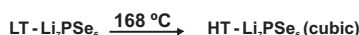


Figure 1: Sections of X-ray powder diagrams of the title compounds (from top to down): $Li_{7-3}AsSe_{6-x}I_3$, $Li_{7-3}PSe_{6-x}I_3$, $Li_{7-3}PSe_{6-x}Br_3$, $Li_{7-3}PSe_{6-x}Cl_3$ (reflections resulting from impurities are indicated).

Thermal Measurements

The pure ternary compound Li_7PSe_6 crystallize at room temperature **orthorhombically**.



Because the title compounds crystallize at RT in the **HT structures**, LT DSC (for the phosphorus compounds) and LT single crystal X-ray measurement (only for $Li_{7-3}PSe_{6-x}I_3$) were performed. **DSC experiments (from RT to -100 °C) did not indicate a phase transition**. During the LT single crystal measurement (at **-50 °C, -100 °C and -150 °C**) of the iodine compound the symmetry of the crystal did not change.

DTA measurements showed decomposition temperatures of the compounds (Table 2).

Table 2: Decomposition temperatures of the compounds

compound	decomposition temperature	powder pattern after DTA experiment
$Li_{7-3}PSe_{6-x}Cl_3$	691 °C	some additional impurities from released educts
$Li_{7-3}PSe_{6-x}Br_3$	670 °C	some additional impurities from released educts
$Li_{7-3}PSe_{6-x}I_3$	683 °C	split

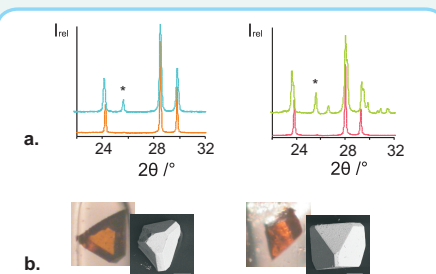


Figure 2: a. Section of X-ray powder diagrams of $Li_{7-3}PSe_{6-x}Cl_3$ (left), and $Li_{7-3}PSe_{6-x}I_3$ (right) before (bottom) and after (top) DTA experiments (reflections resulting from Li_2Se are indicated). b. Optical and SEM images of $Li_{7-3}PSe_{6-x}Cl_3$ (left) and $Li_{7-3}PSe_{6-x}I_3$ (right).

Structure Description-NMR

Single crystals of $Li_{7-3}PSe_{6-x}Cl_3$ and $Li_{7-3}PSe_{6-x}I_3$ were measured on a STOE IPDS. In agreement with the powder investigations the reflections could be indexed cubically (**space group: $F\bar{4}3m$**). Although the quaternary title compounds are not isostructural with the unsubstituted Li_7PSe_6 [3], they are isostructural with the quaternary sulphur compounds [4]. Because of the **small X-ray contrast for Se and Br atoms**, the exact value of δ **can not be given** for the bromine compound. In many quaternary argyrodites the chalcogen atoms occupy 2 of the 3 crystallographically independent positions (Ch1 and Ch2) and the halide ions are located on the third position (e.g. in Li_6PS_4) [4]. For another group of argyrodites a mixed occupancy of the chalcogen and halogen atoms on 2 of the 3 positions (Ch2 and Ch3) which are not connected directly to phosphorus is observed (e.g. Li_6PS_4Br) [4]).

$Li_{6.69}PSe_{5.69}Cl_{0.31}$ belongs to the second group. The group refinement Se/Cl results in a **chlorine ratio of about 15% on Ch2 and Ch3 positions** while Ch1 is fully occupied by selenium (Figure 3). Unlike $Li_{6.69}PSe_{5.69}Cl_{0.31}$ a **mixed occupancy of chalcogen and halogen atoms is found only on the third selenium position (Ch3)** in $Li_{6.25}PSe_{5.25}I_{0.75}$. Ch1 and Ch2 positions are fully occupied by selenium atoms.

Table 3: Some crystallographic properties of the measured chlorine and iodine compounds.

compound	lattice constant	δ	resulting formula	position of halide atoms
$Li_{7-3}PSe_{6-x}Cl_3$	10.374 Å	0,31	$Li_{6.69}PSe_{5.69}Cl_{0.31}$	Ch2 and Ch3
$Li_{7-3}PSe_{6-x}I_3$	10.540 Å	0,75	$Li_{6.25}PSe_{5.25}I_{0.75}$	Ch3

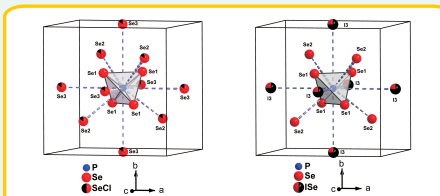


Figure 3: Sections of the structures of $Li_{6.69}PSe_{5.69}Cl_{0.31}$ (left) and $Li_{6.25}PSe_{5.25}I_{0.75}$ (right) emphasizing the distribution of selenium and halide on the 3 crystallographically independent positions.

^{31}P NMR studies were carried out for the phosphorous compounds (Figure 4). These signals give information about the **statistical distributions of neighborhoods**. The NMR measurements confirmed the results of the single crystal investigations.

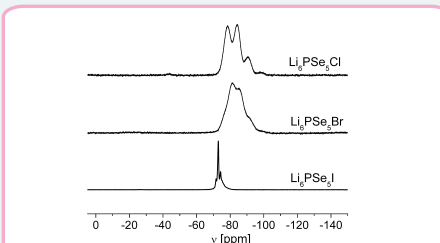


Figure 4: ^{31}P MAS-NMR spectra of the phosphorous compounds.

Literature

[1] Winkler, C.: Chem. Ber. 19 (1886) 210-211.
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 [4] Deiseroth, H. J., Kong, S. T., Eckert, H., Vannahme, J., Reiner, C., Zaiß, T., Schlosser, M.: Angew. Chem. Int. Ed. 47 (2008) 755-758.

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