

# Synthesis and Characterization of New Quaternary Li-Argyrodites

S.T. Kong<sup>1</sup>, H.J. Deiseroth<sup>1</sup>, C. Reiner<sup>1</sup>, H. Eckert<sup>2</sup> and J. Vannahme<sup>2</sup>

<sup>1</sup>Department of Inorganic Chemistry, University of Siegen, 57068 Siegen/Germany

<sup>2</sup>Department of Physical Chemistry, University of Münster, 48149 Münster/Germany

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## Introduction

The family of Argyrodites is named after the mineral  $\text{Ag}_8\text{GeS}_6$  and characterized by a broad spectrum of substitution possibilities for all three elements. (e.g.  $\text{Ag}_8\text{AlSe}_6$ ,  $\text{Hg}_8\text{SiS}_6$ ,  $\text{Cu}_8\text{PS}_2\text{Cl}_2$ , etc). The structure of these compounds is based on a tetrahedrally close-packed arrangement of the chalcogen/halogen atoms, topologically related to the cubic Laves phase (e.g.  $\text{MgCu}_2$ ) [1]. The A atoms, almost exclusively Ag or Cu, occupy a part of the tetrahedral holes in a more or less disordered manner, resulting in a significant ionic conductivity for some of these compounds. Surprisingly, up to now, only one Li-argyrodite was known. Brice described the synthesis of a "poudre noire" containing  $\text{Li}_6\text{PS}_5$  together with  $\text{Li}_6\text{P}_2\text{S}_9$  [2].

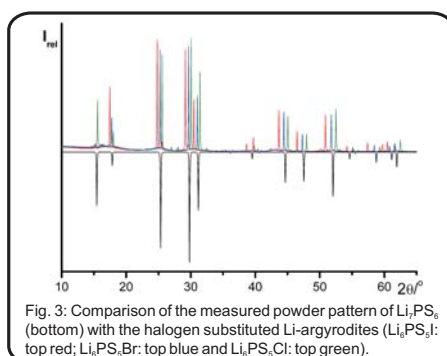
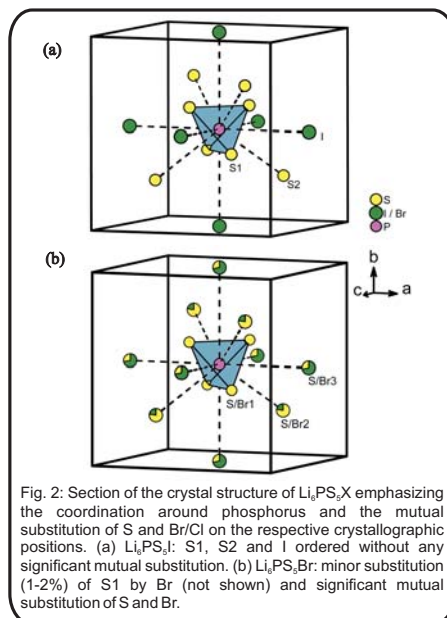
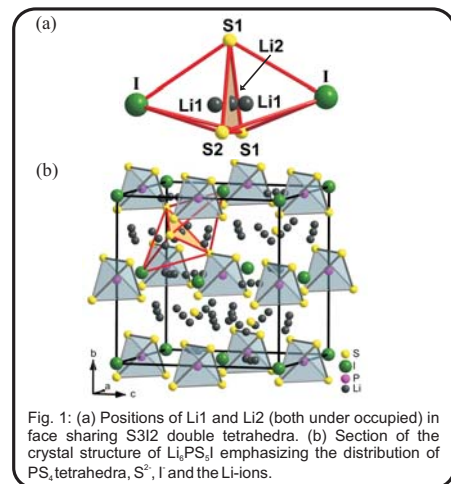
In the course of our investigation on Li-argyrodites, we obtained  $\text{Li}_6\text{PS}_5$  (white,  $F43m$ ,  $a = 993.2(1)$  pm) and the quaternary title compounds  $\text{Li}_6\text{PS}_5\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ). A first measurement of the ionic conductivity of  $\text{Li}_6\text{PS}_5\text{I}$  resulted in a specific conductivity of  $6 \times 10^{-5}$  S  $\text{cm}^{-1}$  at room temperature which represents one of the highest known conductivities of Li ionic conductors.

In the meantime, we could prove the existence of the As-containing quaternary Li-argyrodites  $\text{Li}_6\text{AsS}_5\text{X}$  ( $\text{X} = \text{Br}, \text{I}$ ).

## Single crystal structure analysis

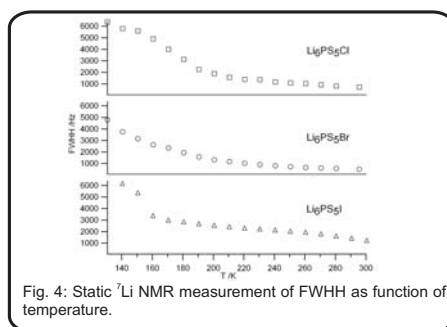
Single crystals of  $\text{Li}_6\text{PS}_5\text{X}$  were measured at room temperature on a Stoe IPDS diffractometer.

The compounds crystallize in space group  $F43m$  ( $Z = 4$ ;  $\text{Li}_6\text{PS}_5\text{I}$ :  $a = 1014.4(8)$  pm,  $\text{Li}_6\text{PS}_5\text{Br}$ :  $998.8(2)$  pm,  $\text{Li}_6\text{PS}_5\text{Cl}$ :  $985.8(5)$  pm) (see Fig. 3). Additionally low temperature single crystal measurements were performed for  $\text{Li}_6\text{PS}_5\text{I}$ . No phase transition could be observed down to 100 K. For  $\text{Li}_6\text{PS}_5\text{Br}$  and  $\text{Li}_6\text{PS}_5\text{I}$  two underoccupied Li positions could be refined while for  $\text{Li}_6\text{PS}_5\text{Cl}$  only the refinement of Li1 was possible. The Li atoms follow a specific distribution pattern which is known from Ag- and Cu- argyrodites: Li1 is located above and below the common face of a  $(\text{Ch}/\text{X})_2$ -double tetrahedron, Li2 occupies the center of the common face (Fig. 1a). In  $\text{Li}_6\text{PS}_5\text{I}$ , the iodine atoms are completely ordered on one of the three crystallographically independent anion positions (Fig. 1b). In contrast to that, the bromine atoms are distributed on two positions with different fractions (S2/Br: 84%/16%, S3/Br: 40%/60%). S1 which is connected to phosphorus remains nearly unsubstituted in both compounds (Fig. 2). Due to the small X-ray contrast of Cl and S, the occupation distribution of the anions at different positions could not be refined.

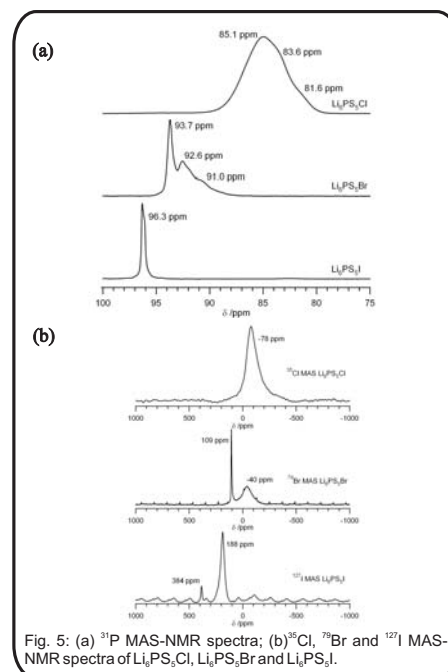


## Solid state NMR analysis

The three Li-argyrodites were additionally investigated by solid state NMR.  $^7\text{Li}$ ,  $^{31}\text{P}$ ,  $^{35}\text{Cl}$ ,  $^{79}\text{Br}$  and  $^{127}\text{I}$  NMR studies were carried out on a Bruker DSSX 400 NMR spectrometer at different operating frequencies. The  $^7\text{Li}$  static NMR spectra for all three argyrodites show single sharp lines which indicate a high mobility of the Li ion. The line narrowing effect ("motional narrowing") is observed already at particularly low temperatures for  $\text{Li}_6\text{PS}_5\text{Br}$  in comparison to  $\text{Li}_6\text{PS}_5\text{I}$  and  $\text{Li}_6\text{PS}_5\text{Cl}$  at around 200 K. This is a possible indication that the  $\text{Li}_6\text{PS}_5\text{Br}$  shows the highest Li ion mobility (see Fig. 4).



The  $^{31}\text{P}$  MAS-NMR spectrum of  $\text{Li}_6\text{PS}_5\text{I}$  is very sharp and well-defined, that of  $\text{Li}_6\text{PS}_5\text{Cl}$  is extremely broad, indicating a number of poorly resolved contributions. Most interestingly, the  $^{31}\text{P}$  MAS-NMR spectrum of  $\text{Li}_6\text{PS}_5\text{Br}$  seems to show both, a sharp and a broadened component, the latter again consisting of several contributions (see Fig. 4a). An analogous behaviour is observed for the halide resonances (Fig. 4b). Both results indicate that the iodide phase appears to be fully ordered, the chloride phase fully disordered, while the sample of  $\text{Li}_6\text{PS}_5\text{Br}$  consists of both, ordered and disordered crystallites or domains. The NMR measurements confirmed the results of the single crystal investigations for  $\text{Li}_6\text{PS}_5\text{I}$  and  $\text{Li}_6\text{PS}_5\text{Br}$  (Fig. 2), which accordingly complete the results for  $\text{Li}_6\text{PS}_5\text{Cl}$ .



## Experimental

$\text{Li}_6\text{PS}_5\text{X}$  was prepared by the reaction of stoichiometric amounts of  $\text{Li}_2\text{S}$  (prepared from  $\text{LiOH}$  and  $\text{H}_2\text{S}(\text{g})$  at 573 K [3]),  $\text{P}_4\text{S}_{10}$  and  $\text{LiX}$  in an evacuated, carbon coated and sealed quartz ampoule (120h at a temperature of 823 K). After the reaction, the ampoule was slowly cooled down to room temperature. The experimental operations were carried out in an argon-filled glove-box.

The products consist of colorless transparent, air sensitive microcrystals and traces of yellow air sensitive unreacted educts ( $\text{Li}_2\text{S}$  and/or  $\text{LiX}$ ).

## Acknowledgement

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## Literature

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