

# **Li<sub>6</sub>PO<sub>5</sub>Br and Li<sub>6</sub>PO<sub>5</sub>Cl: The first Lithium-Oxide-Arnyrodites**

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*Dedicated to Professor Rüdiger Kniep on the Occasion of His 65. Birthday*

**Keywords:** Lithium; X-ray diffraction; Conducting materials; Arnyrodites; Oxides

**Abstract.** The title compounds Li<sub>6</sub>PO<sub>5</sub>Br ( $F\bar{4}3m$ ,  $a = 8.297(1)$  Å,  $Z = 4$ ) and Li<sub>6</sub>PO<sub>5</sub>Cl ( $F\bar{4}3m$ ,  $a = 8.2234(9)$  Å,  $Z = 4$ ) represent the first oxodic arnyrodites in general and the first lithiumoxoarnyrodites in particular. The overall crystal structure corresponds to the cubic high temperature (HT) modification of all known cubic arnyrodites, however, with a seemingly small but important difference concerning the lithium positions. In all other HT arnyrodites with similar lithium content the 24 lithium atoms per unit cell are disordered over a 48 fold position in close vicinity to a 24 fold one causing a high mobility of the Li<sup>+</sup>. In the title compounds, however, they occupy the 24 fold one in a strictly ordered manner thus establishing a planar triangular first sphere coor-

dination environment. This detail is of great importance for the amount of the specific lithium ionic conductivity and for the possible phase transition to an LT (low temperature) modification accompanied by an ordering of the disordered lithium atoms. Apparently the latter transition is suppressed in the title compounds because the Li<sup>+</sup> are already frozen out in the cubic (HT = LT) form. The initially open question how this structural peculiarity influences the ionic conductivity (strengthening or weakening in comparison to oxygen free arnyrodites?) is answered by a series of impedance measurements. The specific lithium ionic conductivity of the title compounds in the range 313 K <  $T$  < 518 K is significantly lower than in oxygen free arnyrodites.

## Introduction

The rare mineral Ag<sub>8</sub>GeS<sub>6</sub> [1] is representative for a growing group of solids named “arnyrodites”. Many if not all of them appear in a high temperature (HT) and a low temperature (LT) modification. In these compounds, which are available by suitable solid state synthesis methods, the highly mobile Ag<sup>+</sup> can be replaced by Cu<sup>+</sup> and other not necessarily monovalent cations [2]. A substitution of germanium by group 13 or 15 elements (e.g. Ga or P) or a substitution of *one* chalcogen atom per formula unit by a halide atom results in a different number of the mobile cations (e.g.  $\gamma$ -Cu<sub>7</sub>PSe<sub>6</sub> [3] or Ag<sub>9</sub>GaSe<sub>6</sub> [4]). With Li<sub>7</sub>PCh<sub>6</sub>, Li<sub>7-δ</sub>PCh<sub>6-δ</sub>X<sub>δ</sub> (Ch: S, Se; X: Cl, Br, I;  $\delta \leq 1$ ) and Li<sub>6</sub>AsCh<sub>5</sub>I (Ch: S, Se) we recently published the first arnyrodites in which Ag(Cu) is completely replaced by lithium [5–7]. The high mobility of lithium in these compounds extends over a broad temperature range and was proven by MAS-NMR spectroscopy [8, 9] and conductivity measurements. The title compounds presented in this paper are the first *oxygen based* arnyrodites. This unusual arnyrodite variant was not known up to now neither as mineral nor as synthetic solid. With respect

to potential practical applications of lithium arnyrodites as solid electrolytes in rechargeable batteries [10, 11] the possibility to replace the more or less toxic chalcogen atoms by oxygen is highly interesting. The crystal structure of the title compounds has been refined on the basis of X-ray single crystal and powder data. In this paper we report the essential aspects of the crystal structure of these new compounds and compare them with other arnyrodites without repeating overviews that have been published recently [5, 6, 8]. Furthermore, we try to rationalize the structural properties on the background of the generally accepted *Frank-Kasper* model of “tetrahedral close packing” and finally we present values for the specific lithium ionic conductivity in the temperature range between 313 and 518 K based on impedance measurements.

## Results and Discussion

A summary of relevant X-ray single crystal data and interatomic distances for Li<sub>6</sub>PO<sub>5</sub>Br and Li<sub>6</sub>PO<sub>5</sub>Cl measured at  $T = 293$  K for both compounds and at 573 K for the bromide compound is given in Table 1, Table 2 and Table 3. The unit cell of the cubic title compounds that emphasizes the isolated PO<sub>4</sub><sup>3-</sup> groups and one characteristic coordination polyhedron of Li<sup>+</sup> is shown in Figure 1. Although the new compounds crystallize in space group  $F\bar{4}3m$  like all other high temperature phases of arnyrodites, they show a significant structural difference to the latter ones concerning the crystallographic positions of the 24 lithium atoms per unit cell (see below).

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**Table 1.** Summary of data collection and refinement details for cubic Li<sub>6</sub>PO<sub>5</sub>Br (293 K and 573 K) and Li<sub>6</sub>PO<sub>5</sub>Cl.

Sum formula	Li <sub>6</sub> PO <sub>5</sub> Br	Li <sub>6</sub> PO <sub>5</sub> Br	Li <sub>6</sub> PO <sub>5</sub> Cl
Temperature /K	<i>T</i> = 293	<i>T</i> = 573	<i>T</i> = 293
Formula weight /g·mol <sup>-1</sup>	232.52	232.52	188.07
Space group	<i>F</i> 43 <i>m</i>	<i>F</i> 43 <i>m</i>	<i>F</i> 43 <i>m</i>
Formula units per unit cell	<i>Z</i> = 4	<i>Z</i> = 4	<i>Z</i> = 4
Color	Colorless	Colorless	Colorless
Crystal dimension /mm	0.14 × 0.12 × 0.08	0.14 × 0.12 × 0.08	0.10 × 0.07 × 0.04
Lattice constants /Å	<i>a</i> = 8.2971(10)	<i>a</i> = 8.334(1)	<i>a</i> = 8.2234(9)
Volume /Å <sup>3</sup>	<i>V</i> = 571.2(1)	<i>V</i> = 578.7(1)	<i>V</i> = 556.1(1)
Density (calcd.) /g·cm <sup>-3</sup>	<i>ρ</i> = 2.70	<i>ρ</i> = 2.669	<i>ρ</i> = 2.246
Absorption coefficient /mm <sup>-1</sup>	<i>μ</i> = 7.41	<i>μ</i> = 7.317	<i>μ</i> = 0.909
<i>F</i> (000)	432	432	360
Diffractometer	STOE-IPDS (Graphite monochromator)	STOE-IPDS (Graphite monochromator)	STOE-IPDS (Graphite monochromator)
Wavelength /Å	0.71073 (Mo- <i>K<sub>a</sub></i> )	0.71073 (Mo- <i>K<sub>a</sub></i> )	0.71073 (Mo- <i>K<sub>a</sub></i> )
Measured <i>θ</i> range /°	4.25–30.33	4.24–30.30	4.29–30.26
Index ranges	−11 ≤ <i>h</i> ≤ 11, −11 ≤ <i>k</i> ≤ 10, −11 ≤ <i>l</i> ≤ 10	−11 ≤ <i>h</i> ≤ 11, −11 ≤ <i>k</i> ≤ 11, −11 ≤ <i>l</i> ≤ 11	−11 ≤ <i>h</i> ≤ 11, −11 ≤ <i>k</i> ≤ 11, −11 ≤ <i>l</i> ≤ 9
Measured reflections	1230	2201	1328
Independent reflections	116	120	114
Completeness to <i>θ</i> /%	100	100	100
<i>R</i> <sub>int</sub>	0.0571	0.0674	0.062
Data/Restraints/Parameter	116 / 0 / 12	120 / 0 / 12	114 / 0 / 12
<i>R</i> values ( <i>I</i> ≥ 2σ( <i>I</i> ))	<i>R</i> <sub>1</sub> = 0.0149	<i>R</i> <sub>1</sub> = 0.0167	<i>R</i> <sub>1</sub> = 0.0256
	<i>wR</i> <sub>2</sub> = 0.0362	<i>wR</i> <sub>2</sub> = 0.0377	<i>wR</i> <sub>2</sub> = 0.051
<i>R</i> values (all data)	<i>R</i> <sub>1</sub> = 0.0157	<i>R</i> <sub>1</sub> = 0.0170	<i>R</i> <sub>1</sub> = 0.0308
	<i>wR</i> <sub>2</sub> = 0.0364	<i>wR</i> <sub>2</sub> = 0.0378	<i>wR</i> <sub>2</sub> = 0.0521
GooF	1.183	1.203	1.078
Difference Fourier residuals /e·Å <sup>-3</sup>	<i>ρ</i> <sub>max.</sub> = 0.333	<i>ρ</i> <sub>max.</sub> = 0.336	<i>ρ</i> <sub>max.</sub> = 0.228
	<i>ρ</i> <sub>min.</sub> = −0.420	<i>ρ</i> <sub>min.</sub> = −0.354	<i>ρ</i> <sub>min.</sub> = −0.240

$$R = \sum |F_o| - |F_c| / \sum |F_o|; wR = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$$

**Table 2.** Atomic coordinates, equivalent isotropic displacement parameters *U*<sub>eq</sub> /Å<sup>2</sup> for Li<sub>6</sub>PO<sub>5</sub>Br (293 K and 573 K (**bold**)) and Li<sub>6</sub>PO<sub>5</sub>Cl (*italic*). All atom positions are within the threefold standard deviations fully occupied and for the final refinement fixed to 1.

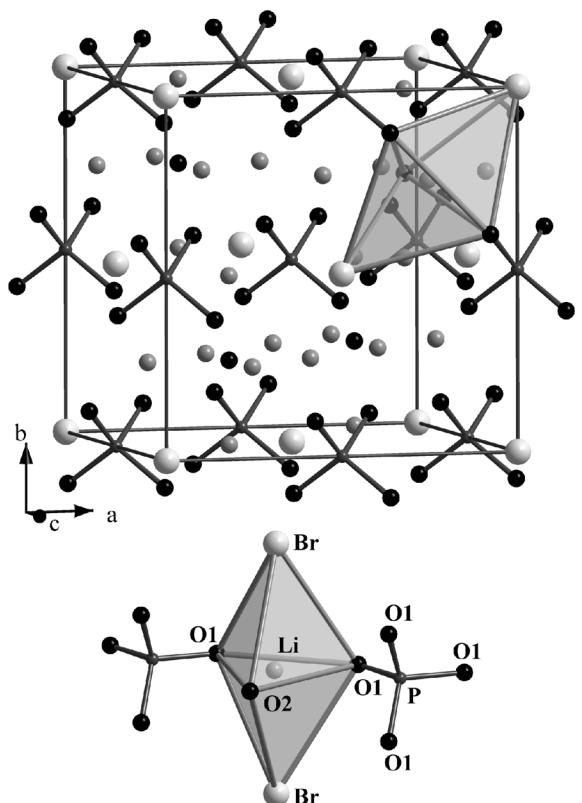
Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
P	4 <i>b</i>	1/2	x	x	0.0046(3)
		1/2	x	x	<b>0.0090(3)</b>
		1/2	x	x	0.0059(5)
O1	16 <i>e</i>	0.6073(2)	x	x	0.0062(5)
		<b>0.6070(1)</b>	x	x	<b>0.0137(5)</b>
		0.6083(2)	x	x	0.0094(6)
O2	4 <i>c</i>	3/4	x	x	0.0061(8)
		3/4	x	x	<b>0.0141(8)</b>
		3/4	x	x	0.0074(9)
X	4 <i>a</i>	0	x	x	0.0103(2)
		<b>0</b>	x	x	<b>0.0214(3)</b>
		0	x	x	0.0167(6)
Li	24 <i>g</i>	1/4	0.0183(8)	3/4	0.016(1)
		1/4	<b>0.0177(7)</b>	3/4	<b>0.028(1)</b>
		1/4	0.0154(7)	3/4	0.0265(1)

From a general view the title compounds can be rationalized as normal valence oxide halide phosphates (Li<sup>+</sup>)<sub>6</sub>(PO<sub>4</sub>)<sup>3</sup>O<sup>2-</sup>*X*<sup>-</sup> (*X* = Cl, Br). As already discussed for other lithium arnyrodites like Li<sub>7</sub>PS<sub>6</sub> [8] and Li<sub>6</sub>PS<sub>5</sub>I [6] the simple ionic description gives no deeper insight into the crystal chemical background of arnyrodites and their chemical and physical properties. In-

**Table 3.** Comparison of selected distances /Å for Li<sub>6</sub>PO<sub>5</sub>Br (293 K and 573 K) and Li<sub>6</sub>PO<sub>5</sub>Cl.

	Li <sub>6</sub> PO <sub>5</sub> Br	Li <sub>6</sub> PO <sub>5</sub> Br	Li <sub>6</sub> PO <sub>5</sub> Cl
Li—	273 K	573 K	273 K
	O1 (2 × )	1.972(3)	1.980(3)
	O2	1.922(6)	1.936(6)
P—	<i>X</i> (2 × )	2.9374(5)	2.9500(5)
	O1 (4 × )	1.543(2)	1.544(2)
			1.543(3)

stead a rationalization based on the *Frank-Kasper* model [12] of tetrahedral close packing is more fruitful. Such a description implies (similar to all other non-oxygen arnyrodites) that the oxygen–halogen partial structure is topologically equivalent to the structure of Mg and Cu in the cubic Laves phase MgCu<sub>2</sub> [13]. Thus it constitutes a cubic structure matrix consisting of a three-dimensional arrangement of distorted tetrahedra formed by oxygen and halogen atoms. These tetrahedra are intimately connected by common corners edges and faces. In this framework the phosphorus atoms occupy tetrahedral holes in a regular way forming isolated PO<sub>4</sub><sup>3-</sup> groups. One oxygen atom and one halogen atom per formula unit are not directly coordinated to phosphorus. In all lithium arnyrodites investigated up to now the spatial distribution of the Li<sup>+</sup> changes reversibly from an extended dynamical disorder over a fraction of the tetrahedral holes at higher temperatures (HT phase) to a static order



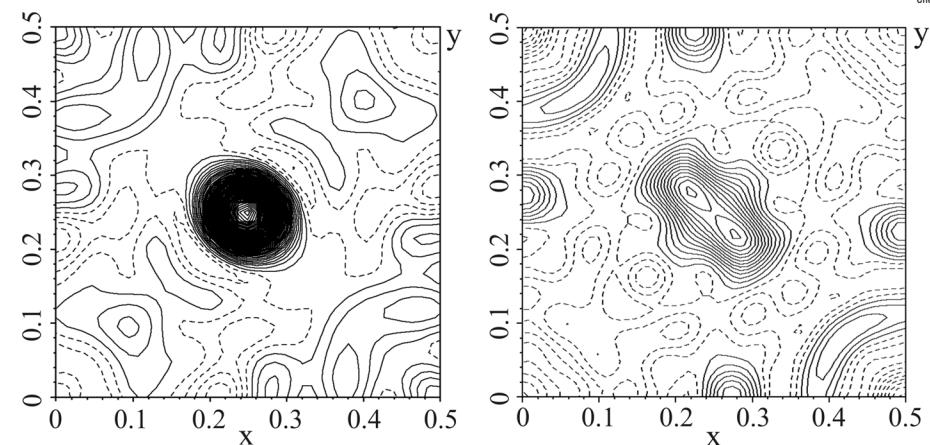
**Figure 1.** above: Representative section of the crystal structure of  $\text{Li}_6\text{PO}_5\text{Br}$  showing the arrangement of  $\text{Li}^+$ ,  $\text{O}^{2-}$  and  $(\text{PO}_4)^{3-}$  groups with the face sharing double tetrahedron around  $\text{Li}^+$  emphasized. Below: Double tetrahedron (trigonal bipyramidal) around  $\text{Li}^+$  in 24g/48h with two  $\text{Br}^-$ , one single  $\text{O}^{2-}$  ( $\text{O}_2$ ) and two  $\text{O}^{2-}$  ( $\text{O}_1$ ) of neighbored  $\text{PO}_4^{3-}$ -groups.

at lower temperatures (LT phase, order-disorder transition). Surprisingly the title compounds are the first lithium argyrodite examples where the  $\text{Li}^+$  are ordered in the whole accessible temperature range ( $173 \text{ K} < T < 873 \text{ K}$ ). They occupy well defined positions in the tetrahedral framework of single  $\text{O}^{2-}$ ,  $\text{Br}^-$  (or  $\text{Cl}^-$ ) atoms and  $\text{PO}_4^{3-}$  groups (Figure 1) and consequently no HT/LT phase transition is observed. The particular lithium position 24g, which is important for a deeper understanding of the crystal structure, defines a trigonal bipyramidal 3+2 coordination (face shared double tetrahedra) for the lithium atoms. In the bromide compound three  $\text{O}^{2-}$  are at distances of 1.97 Å ( $\text{O}_1$ , 2 ×) and 1.92 Å ( $\text{O}_2$ ) and two  $\text{Br}^-$  at a distance of 2.94 Å. The  $\text{Li}-\text{O}$  distances are slightly smaller and the  $\text{Li}-\text{Br}$  distance slightly longer than those found in the Li-bromide-oxides  $\text{Li}_2\text{OBr}$  [octahedral coordination of Li, 2 × O (2.02 Å) and 4 × Br (2.85 Å, [14])] and  $\text{Li}_7\text{O}_2\text{Br}_3$  [octahedral coordination of Li, 1 × O (2.01 Å) and 5 × Br (2.85 Å) or 2 × O (2.02 Å) and 4 × Br 2.85 Å, [14]]].

The single crystal measurement for the bromide carried out at 573 K shows no significant structural differences in comparison to the RT measurement except a normal thermal expansion for all structural data. For the chloride compound the smaller lattice constants also induce smaller  $\text{Li}-\text{O}$  distances (Table 3). The P–O distances are similar in both compounds.

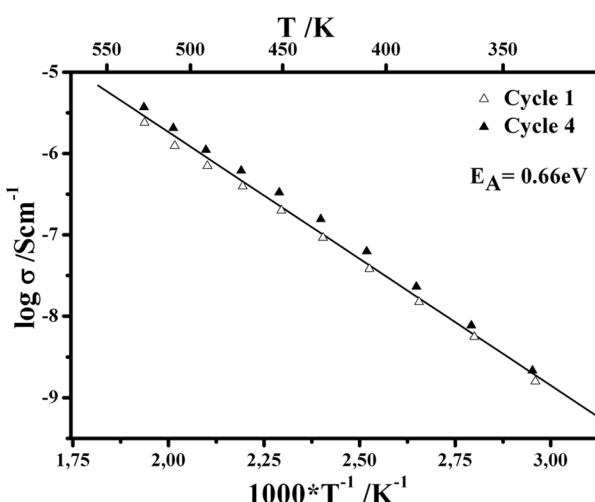
As stated above there is no indication for disorder in the accessible temperature range  $173 \text{ K} < T < 873 \text{ K}$ . Thus a HT/LT transition as in all other argyrodites is missing. In order to make this seemingly unusual behavior of the title compounds more plausible one has to be aware of the different lithium content of halide free and halide containing argyrodites with group 15 elements, e.g. the difference between  $\text{Li}_7\text{PO}_6$  (hypothetic, corresponding to  $\text{Li}_7\text{PS}_6$  [8]) and  $\text{Li}_6\text{PO}_5\text{X}$  (title compounds). This is important because *all* known argyrodites regardless of the number of lithium atoms per formula unit crystallize in the *same* HT structure type, based on space group  $F\bar{4}3m$  with  $Z = 4$  with 28 (" $\text{Li}_7\text{PO}_6$ ") or 24 disordered lithium atoms ( $\text{Li}_6\text{PO}_5\text{X}$ ) per unit cell. The latter is favored because in all such structures the delocalized electron density corresponding to the disordered lithium atoms is smeared over an extended space around the Wyckoff position 24g (Figure 1). Alternatively it can be described by a nearby split position (48h) [6]. In any case, 24 marks the upper limit for the number of lithium atoms in or near the crystallographic position 24g, which is in particular favored by crystal chemical arguments [6]. Thus, the four "excess" lithium atoms in argyrodites of the type  $\text{Li}_6\text{PCh}_5\text{X}$  ( $\text{Ch}$ : O, S, Se, X: Cl, Br, I) have to occupy less suitable positions in the structure. There is some experimental experience (e.g. preferred crystallization, fast formation of single phase samples) that the composition type  $\text{Li}_6\text{PCh}_5\text{X}$  ( $\text{Ch}$ : O, S, Se, X: Cl, Br, I) is easier accessible than alternative ones with more or less lithium per formula unit. An additional difference between argyrodites with HT/LT transition (e.g.  $\text{Li}_6\text{PS}_5\text{I}$ ) and those ones without HT/LT transition (title compounds) is the specific crystal chemical situation around the 24g position. For  $\text{Li}_6\text{PS}_5\text{I}$  (and other argyrodites of this composition type) the distance between lithium in 24g and I (corresponding to Br in Figure 1) is unusually long (~3.6 Å, [6], expected for  $r(\text{Li}^+) + r(\text{I}^-)$  ( $\text{CN} = 6$ ) according to [15]: ~2.95 Å). Because there is no closer cationic neighbor for  $\text{I}^-$ , it seems "undercoordinated". This unfavorable situation is relaxed upon the HT/LT transition, because only 12 of 24 lithium atoms in LT- $\text{Li}_6\text{PS}_5\text{I}$  are frozen out on the "ideal" trigonal 24g position (with too long  $d(\text{Li}-\text{I})$ ). The remaining twelve  $\text{Li}^+$  ions occupy tetrahedral positions away from the trigonal plane with significantly shorter  $d(\text{Li}-\text{I})$  (3.02 Å) [6]. Such an "asymmetric" ordering is observed for the phase transitions of all other known silver- and copper argyrodites based on the optimal composition with 6 M atoms. Because the  $\text{Li}-\text{Cl}$ - or  $\text{Li}-\text{Br}$  distances (2.91 Å and 2.93 Å) in the title compounds with all  $\text{Li}^+$  ions in 24g correspond to expected values no order-disorder transition is required and consequently not observed. A comparison between a section of the electron density around the  $\text{Li}^+$  ion in 24g/48h Wyckoff position for HT- $\text{Li}_6\text{PS}_5\text{I}$  and  $\text{Li}_6\text{PO}_5\text{Br}$  (Figure 2) confirms the difference in the spatial distribution of disordered and ordered lithium atoms.

Concerning the lithium ionic conductivity of oxide based argyrodites in comparison to those ones based on S/Se, one has to be aware that the lattice constants of the latter ones (cubic, HT) amount to about 10 Å whereas the lattice constants of the oxide argyrodites amount to ~8 Å only. This implies a denser packing of the O/X atoms (oxygen/halogen: 2.5 Å <  $d(\text{O}-\text{O}/\text{X})$

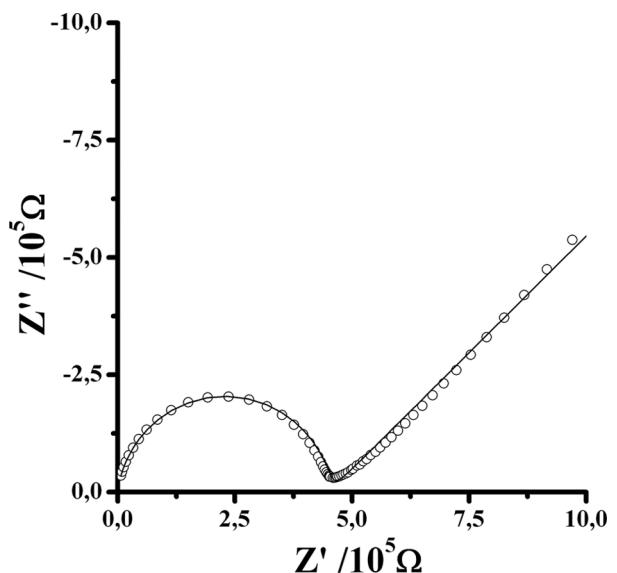


**Figure 2.** A comparison between difference density calculations (based on  $F_o - F_c$  without Li) around lithium in Wyckoff position 24g/48h. left: Li<sub>6</sub>PO<sub>5</sub>Br ( $T = 573$  K) single atom position for Li (24g), similar results for  $T = 293$  K are not shown; right: HT-Li<sub>6</sub>PS<sub>3</sub>I (293 K, *strong disorder*) split position for Li (48h).

< 3 Å) that define the tetrahedral close packing in comparison to the respective S/Se-atoms ( $3.3$  Å <  $d(S-S)$  <  $4.1$  Å). Due to the more narrow diffusion channels one would expect a lower mobility of Li<sup>+</sup> in the oxide argeyrodite. Figure 3 shows the total conductivity based on a series of temperature dependent impedance measurements for samples of Li<sub>6</sub>PO<sub>5</sub>Cl between 313 K and 518 K. Using titanium electrodes the appearance of a Warburg response in the low frequency region (Figure 4) for the ionically blocking cell arrangement indicates that Li<sub>6</sub>PO<sub>5</sub>Cl is predominantly an ionic conductor. The capacity derived from the peak frequency of the high frequency semi-circle is about 5 to 10 pF and indicate clearly bulk processes (corresponding dielectric constants are about 15–35). As expected the conductivity is low and increases from  $\sim 10^{-9}$  S·cm<sup>-1</sup> at ambient temperature to  $\sim 10^{-6}$  S·cm<sup>-1</sup> at 518 K. This is less by 2–3 orders of magnitude than for S/Se argeyrodites [16]. The activation energy of 0.66 eV of Li<sub>6</sub>PO<sub>5</sub>Cl is also significantly higher than S/Se argeyrodites (~ 0.33 eV).



**Figure 3.** Arrhenius plots for the total bulk conductivity of Li<sub>6</sub>PO<sub>5</sub>Cl obtained for the first and the fourth cooling cycle.



**Figure 4.** Typical impedance plot for Li<sub>6</sub>PO<sub>5</sub>Cl at 516 K ( $p(O_2) \approx 10^{-4}$  bar, Warburg response not shown completely for clarity).

## Experimental Section

### Synthesis

Li<sub>6</sub>PO<sub>5</sub>Cl and Li<sub>6</sub>PO<sub>5</sub>Br were synthesized starting from stoichiometric amounts of Li<sub>3</sub>PO<sub>4</sub> (99+ %, Chempur), Li<sub>2</sub>O (99.5 %, Alfa-Aesar) and LiCl (99.99 %, Chempur) or LiBr (99.99 %, Alfa-Aesar). The starting materials were homogenized, pressed to pellets and transferred into a gold crucible, which was placed in a quartz ampoule. A reaction in carbon coated quartz glass ampoules results in less homogeneous products. All experiments were carried out in an argon-filled glovebox ( $O_2 < 1$  ppm,  $H_2O < 1$  ppm) and the starting materials and hardware (mortar, pressing tool, ampoules etc.) were carefully dried at  $T \sim 593$  K–720 K (ampoules). The evacuated quartz glass ampoules were annealed for 120 h at 723 K. After the reaction, the ampoules were slowly cooled to room temperature. The colorless and hygroscopic products were handled in a glovebox. The absence of OH in the samples was checked by Raman spectroscopy. This is indispensable because OH-

bands were observed for the initial samples due to the unwanted presence of small quantities of Li<sub>2</sub>OHBr [17] and related compounds which are easily formed with traces of water.

### Powder X-ray Analysis

X-ray powder patterns were measured with a Siemens D5000 diffractometer with Cu-K<sub>α</sub> radiation (Ge monochromator). The hygroscopic samples were grounded and measured between two Mylar foils (diameter of 0.01 mm) sealed with grease. Li<sub>3</sub>PO<sub>4</sub> was detected as minor crystalline impurities. For high-temperature investigations the powdered samples were measured in quartz capillaries.

### Crystal Structure Determination

For single crystal measurements the respective crystal was transferred into a glass capillary which was sealed under inert conditions. The glass capillary was mounted on a STOE IPDS I imaging plate diffraction system. The data were collected in the f-scan mode using graphite monochromatized Mo-K<sub>α</sub> radiation (graphite monochromator) at room temperature. Data analysis and evaluation was carried out with the STOE IPDS program package [18]. For the structure solution (direct methods) and refinement the programs SHELXS-97 and SHELXL-97 [19] were used. A summary of crystal and experimental data as well as structure refinement details for both compounds are given in Table 1 and Table 2. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata(at)fiz-karlsruhe.de) on quoting the depository numbers CSD-421479 (Li<sub>6</sub>PO<sub>5</sub>Cl), CSD-421480 (Li<sub>6</sub>PO<sub>5</sub>Br,  $T = 293$  K) and CSD-421481 (Li<sub>6</sub>PO<sub>5</sub>Br 573 K).

### Impedance Measurements

Polycrystalline pellets of the argyrodites were prepared in a glove box ( $O_2 \leq 0.1$  ppm,  $H_2O \leq 0.3$  ppm) by applying a monoaxial pressure of 1.24 kbar onto carefully grinded samples using a stainless steel pressing tool (typical sample thickness: 1 mm, typical diameter 6 mm).

Impedance measurements were carried out in an argon atmosphere in an air tight quartz tube with a High Resolution Dielectric Analyzer (Novocontrol) in the frequency range of  $10^6$  Hz– $10^{-1}$  Hz. A symmetric cell Ti/Li<sub>6</sub>PO<sub>5</sub>X/Ti with titanium foil as ionically blocking electrodes was used, and measurements were performed in the temperature range 313–518 K with steps of 20 K for the heating and cooling cycle. The impedance spectra were evaluated using the software ZVIEW [20].

The corresponding equivalent circuit consists of a resistor and a constant phase element connected in parallel, followed by a Warburg element in series.

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