Li_2TeS_3 and Li_2TeSe_3: Preparation, Crystal Structure and Impedance Spectroscopic Characterization

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Dedicated to Professor Rüdiger Kniep on the Occasion of his 60th Birthday

Abstract. Li_2TeS_3 and Li_2TeSe_3 were synthesized by the reaction of stoichiometric amounts of Li, Te and Q (Q = S, Se) in the ratio 2 : 1 : 3. Both products are extremely air and moisture sensitive. The crystal structures were determined by single crystal X-ray diffraction at room temperature. Red Li_2TeS_3 and metallic black Li_2TeSe_3 crystallize isotypically in the monoclinic space group $P2_1/c$ (no. 14) with four formula units per unit cell and the lattice parameters: Li_2TeS_3: a = 5.437(1) Å, b = 11.564(1) Å, c = 7.907(1) Å, β = 91.57(1)°, V = 496.96(1) Å^3; Li_2TeSe_3: a = 5.658(1) Å, b = 12.032(1) Å, c = 8.278(1) Å, β = 92.690(1)°, V = 562.93(1) Å^3 (data at 20 °C). The atomic arrangements persist of isolated trigonal pyramidal $[TeQ_3]^{2-}$ anions which are arranged in layers. Li is coordinated by six Q atoms from four (Li1) or five (Li2) different thiotellurate or selenidotellurate units, respectively. Impedance spectroscopic measurements in the temperature range 90 − 200 °C show that Li_2TeS_3 is a semiconductor with an activation energy of 0.71 eV. Li_2TeSe_3 is a mixed conductor with an activation energy of 0.68 eV.

Keywords: Lithium; Thiotellurates; Selenidotellurates; Impedance spectroscopy; Crystal structure

Introduction

Lots of efforts have been made in the past to design new ion-conducting materials. Especially proton, lithium, silver and copper ion conductors are of great interest. Using copper(I) or silver halides as solid solvent revealed a number of solid state compounds with partly good ionic conducting properties [1]. These compounds can be regarded as consisting of a copper(I) or silver halide part on the one hand and of a copper or silver chalcogenometalate on the other hand, see for example [2, 3]. We recently started to transfer the findings concerning the mixed halide thiometalate ion conductors of copper and silver to homologous lithium compounds. A first example for a resulting lithium ion conducting material is $(LiI)_2Li_3SbS_3$ [4] which is closely related to $(CuI)_2Cu_3SbS_3$ [3]. Trying to synthesize $(LiI)_3Li_2TeS_3$ and $(LiI)_3Li_2TeSe_3$ in analogy to $(CuI)_3Cu_2TeS_3$ [14] we always obtained Li_2TeS_3 and Li_2TeSe_3 embedded in a LiI flux. These compounds are two new representatives of a larger group of thiotellurates and selenidotellurates. Thiotellurate(IV) ions are observed in several solid state compounds, e. g. in K_2TeS_3 [5], $BaTeS_3$ [6], $(NH_4)_2TeS_3$ [7], $BaTeS_3 \cdot 2\,H_2O$ [7, 8], $K_3(SH)TeS_3$ [9], Ag_2TeS_3 [10], $Cs_2Mn(TeS_3)_2$ [11], and $RbCuTeS_3$ [12]. $[TeS_3]^{2-}$-units can also be found in composite copper chalcogenide halides, e. g. $(CuCl)Cu_2TeS_3$ [13] and $(CuI)_3Cu_2TeS_3$ [14]. A tetraphenylphosphonium salt with $[TeS_3]^{2-}$-anions is also known [15]. First hints for the existence of a compound with the formula "$Li_2TeS_3 \cdot 2\,Li_2S$" are given in [16]. In 1902 "$Na_2TeS_3 \cdot 2\,Na_2S$" was reported [17]. However, details about the synthesis or the structures of "$M_2TeS_3 \cdot 2\,M_2S$" (M = Li, Na) are very ambiguous. Knowledge about the homologous selenidotellurates is small to date. Only a few compounds are known, i. e., Na_2TeSe_3 and K_2TeSe_3 [18] or (2, 2, 2-crypt-K)$_2TeSe_3 \cdot$en [19]. All these materials have $[TeQ_3]^{2-}$-units in common. These complex anions can be regarded as isolated from each other in the compounds under discussion.

Herein we report about the synthesis and the structural and impedance spectroscopic characterization of Li_2TeS_3 and Li_2TeSe_3 [20].

Results

Structure determination

Crystallographic data of the structure determination are summarized in Table 1. Atomic coordinates and isotropic displacement parameters are collected in Table 2. Table 3 lists the anisotropic displacement parameters, and Table 4 shows selected interatomic distances and angles.

Structure description and discussion

Li_2TeS_3 and Li_2TeSe_3 are isotypic and crystallize in the monoclinic system. The sulphide and selenide ions, respectively, are cubic close packed and form an arrangement of octahedral voids, see Figure 1. Lithium and tellurium atoms are distributed in the octahedral voids in an ordered way.

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Table 1 Crystallographic data for the structure analysis of Li_2TeS_3 and Li_2TeSe_3.

Compound	Li_2TeS_3	Li_2TeSe_3
Formula weight (g mol^{-1})	237.66	378.36
Crystal size (mm^3) and colour	0.07 x 0.08 x 0.12, dark red	0.05 x 0.03 x 0.15, metallic black
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
Lattice constants (Å) from single crystal	a = 5.437(1)	a = 5.658(1)
	b = 11.559(1)	b = 12.032(2)
	c = 7.907(1)	c = 8.278(1)
	β = 91.57(1)°	β = 92.69(1)°
Cell volume, Z	496.74(12) Å^3, 4	562.92(15) Å^3, 4
ρ_{calc} (g cm^{-3})	3.178	4.464
Diffractometer	STOE IPDS, MoKα, λ = 0.71073 Å, oriented graphite monochromator	STOE IPDS, MoKα, λ = 0.71073 Å, oriented graphite monochromator
φ-range (°), $\Delta\varphi$ (°)	0.0 ≤ φ ≤ 300.0, 1.2	0.0 ≤ φ ≤ 189.0, 1.4
Absorption correction	numerical, crystal description with 16 faces, shape optimized with X-SHAPE [24]	numerical, crystal description with 15 faces, shape optimized with X-SHAPE [24]
No. of measured images	250	135
Irradiation time/image (min)	8	5
Temperature (°C)	20	20
2θ-range (°)	6.1 ≤ 2θ ≤ 60.4	6.0 ≤ 2θ ≤ 55.9
hkl-range	$-7 \le h \le 7$	$-6 \le h \le 7$
	$-16 \le k \le 16$	$-15 \le k \le 15$
	$-11 \le l \le 11$	$-10 \le l \le 10$
No. of reflections, R_{int}	8420, 0.0202	4988, 0.0560
No. of independent reflections	1366	1254
No. of parameters	55	55
Program	SHELX 97 [26]	SHELX 97 [26]
Final $R/wR2$ ($I > 2\sigma_I$)	0.0187, 0.0501	0.0334, 0.0773
Final $R/wR2$ (all reflections)	0.0203, 0.0504	0.0453, 0.0839
GooF	1.160	0.875
Largest difference peak $\Delta\rho_{max}$	1.110	1.247
and hole $\Delta\rho_{min}$ (e Å^{-3})	−0.720	−1.748

Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), Fax: 0049 7247 808 666, E-mail: crysdata@fiz-karlsruhe.de, on quoting the depository numbers CSD-415121 (Li_2TeS_3) or CSD-415120 (Li_2TeSe_3), the name of the authors, and the reference of the publication.

Table 2 Atomic coordinates and equivalent isotropic displacement parameters U_{eq} for Li_2TeS_3 and Li_2TeSe_3.

Li_2TeS_3

Atom	x	y	z	U_{eq}[a)]
Li1	0.238(1)	0.9149(5)	0.3681(9)	0.038(1)
Li2	0.739(1)	0.7711(5)	0.1431(7)	0.034(1)
Te1	0.7173(1)	0.0871(1)	0.1839(1)	0.015(1)
S1	0.7704(1)	0.2426(1)	0.3784(1)	0.020(1)
S2	0.7448(1)	0.9270(1)	0.3681(1)	0.021(1)
S3	0.2859(1)	0.0983(1)	0.1384(1)	0.019(1)

Li_2TeSe_3

Atom	x	y	z	U_{eq}[a)]
Li1	0.238(4)	0.914(2)	0.367(2)	0.045(4)
Li2	0.732(3)	0.772(1)	0.146(2)	0.041(3)
Te1	0.7102(1)	0.0875(1)	0.1891(1)	0.022(1)
Se1	0.7700(2)	0.2467(1)	0.3850(1)	0.028(1)
Se2	0.7444(2)	0.9241(1)	0.3746(1)	0.029(1)
Se3	0.2694(1)	0.0972(1)	0.1340(1)	0.027(1)

[a)] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3 Anisotropic displacement parameters U_{ij} for Li_2TeS_3 and Li_2TeSe_3.

Li_2TeS_3

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Li1	0.033(4)	0.042(3)	0.039(3)	0.003(2)	−0.001(2)	0(2)
Li2	0.038(3)	0.029(2)	0.036(2)	0.001(2)	0.001(2)	0(2)
Te1	0.014(1)	0.015(1)	0.015(1)	−0.001(1)	0(1)	0(1)
S1	0.023(1)	0.018(1)	0.019(1)	−0.004(1)	0(1)	−0.001(1)
S2	0.025(1)	0.018(1)	0.020(1)	0.003(1)	0(1)	0.001(1)
S3	0.014(1)	0.023(1)	0.022(1)	−0.001(1)	0(1)	0(1)

Li_2TeSe_3

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Li1	0.040(1)	0.060(1)	0.034(7)	0.008(7)	−0.004(7)	0.001(9)
Li2	0.040(1)	0.059(9)	0.028(5)	0.003(6)	0.004(5)	0.004(7)
Te1	0.019(1)	0.025(1)	0.023(1)	0(1)	0.002(1)	0(1)
Se1	0.029(1)	0.027(1)	0.026(1)	−0.004(1)	0.002(1)	−0.001(1)
Se2	0.032(1)	0.028(1)	0.027(1)	0.004(1)	0.002(1)	0.001(1)
Se3	0.020(1)	0.033(1)	0.028(1)	0(1)	0.001(1)	0.001(1)

Having the composition in mind it becomes immediately clear that the structure must be an ordered variant of the rocksalt structure type. However, the coordination spheres of the cations are more or less distorted. Whereas the lithium atom is six-coordinate, see Figure 2, the coordination sphere of the tellurium atom has to be regarded as 3+3. Therefore we find isolated $[TeQ_3]^{2-}$ anions (Q = S, Se), see Figure 3, which are typical for Te^{4+}. These $[TeQ_3]^{2-}$ units are comparable with the isosteric $[TeO_3]^{2-}$ or $[SO_3]^{2-}$ anions, i. e., Te has a trigonal pyramidal (ψ-tetrahedral) environment of Q atoms. The short distances d(Te-S) in the $[TeS_3]^{2-}$ ions are 2.357(1), 2.367(1), and 2.378(1) Å, respectively. For d(Te-Se) in $[TeSe_3]^{2-}$ 2.498(1), 2.517(1), and 2.523(1) Å are found. The S-Te-S bond angles range from 99.15(2) to 100.52(2)°, and the Se-Te-Se bond angles from

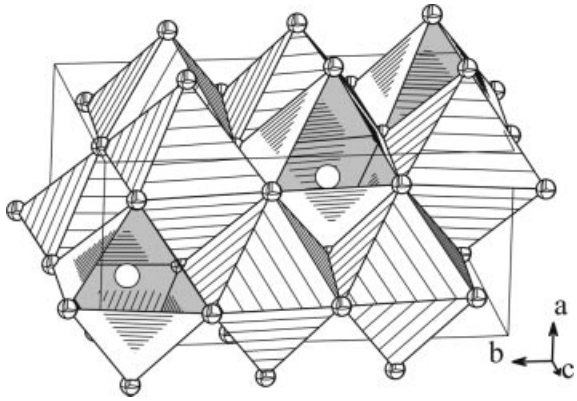

Figure 1 Section of the crystal structure of Li_2TeQ_3 showing the octahedral voids formed by the chalcogenide ions. Two thirds of the octahedral voids are occupied by Li, and one third is occupied by Te (open octahedra). Q atoms are cubic closed packed.

100.55(3) to 101.44(3)°. Three further sulphur or selenium atoms are observed in the coordination sphere of the Te atom. These Q neighbours show distances of more than 3.0 Å (Li_2TeS_3: 3.125(1), 3.136(1), 3.329(1) Å; Li_2TeSe_3: 3.220(2), 3.241(1), 3.484(1) Å). The difference between the short bonds Te-Q and the so-called non bonding distances Te-Q gives an idea about the distortion of the corresponding TeQ_6 octahedra. Te is located off centre and shifted towards one face of the octahedra.

In the crystal structures of the title compounds the $[TeQ_3]^{2-}$ anions are located in layers parallel to the *ab*-plane (see Figure 3). Lithium is localized between the $[TeQ_3]^{2-}$-units. The alkali metal ions have six Q neighbours arranged as distorted octahedra. The Q atoms belong to four different $[TeQ_3]^{2-}$-units in case of Li1 and to five different complex anions in case of Li2, see Figure 2a and b. The distances *d*(Li-S) in Li_2TeS_3 range from 2.684(7) to 2.809(6) Å for Li1 and from 2.523(6) to 3.159(6) Å for Li2, cf. Table 4. Comparable distances for six-coordinate Li in rhombohedral $LiSbS_2$ [21] are about 2.56 to 2.81 Å. The Li-Se contacts in Li_2TeSe_3 are in the range from 2.80(2) to 2.94(2) Å for Li1 and from 2.63(2) to 3.26(1) Å for Li2. Searching for further examples for Li with a sixfold coordination by Se in an ordered structure to the best of our knowledge reveals only one example in the literature. This example is the perselenoborate $Li_2B_2Se_5$ [22] with distances *d*(Li-Se) in the range from 2.54 to 3.38 Å. Usually Li prefers a coordination number of four by Se.

Figure 4 gives a view over the complete crystal structure of Li_2TeQ_3. It becomes obvious that the TeQ_3 units are separated from each other, i.e., there are no Te-Q-Te fragments to be observed.

At a very first glance K_2TeS_3 [5] seems to be closely related to Li_2TeQ_3 since the lattice constants of the lithium compound and the potassium compound show similar ratios and the monoclinic angle is close to 90° for all of them. However, the unit cells cannot be transformed into each other. A closer inspection of the structure of K_2TeS_3 shows

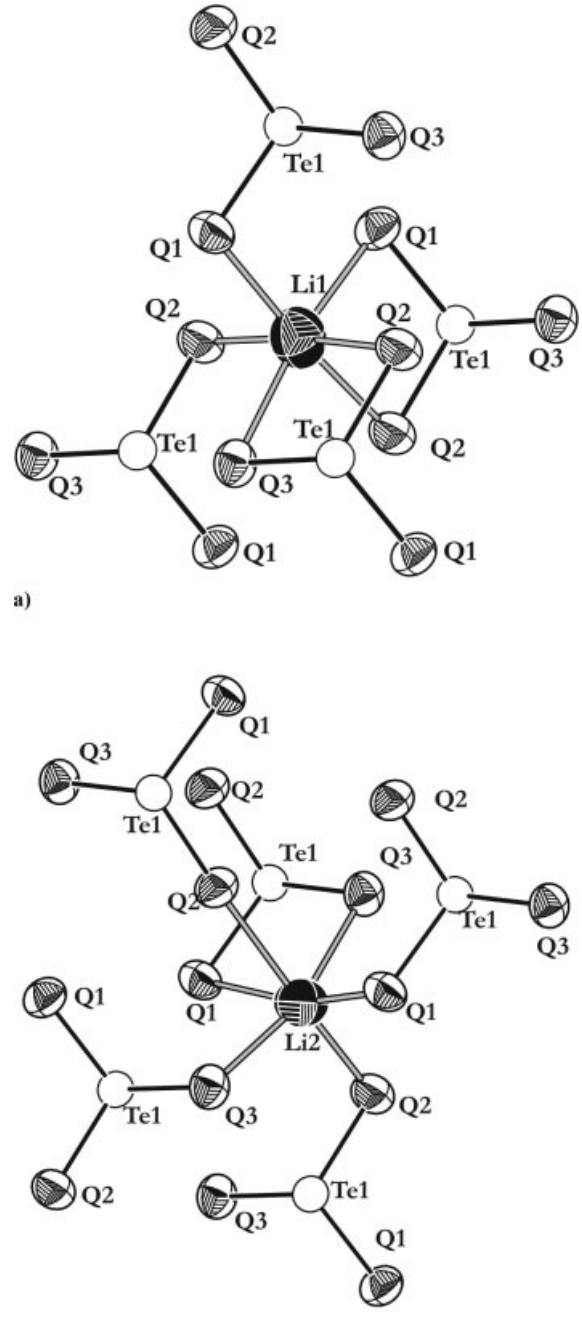

Figure 2 Section of the crystal structure of Li_2TeQ_3 showing the connectivity for a) Li1 and b) Li2 in a distorted $[LiQ_6]$ octahedron. The Q atoms belong to four different $[TeQ_3]^{2-}$-units in case of Li1 and to five different $[TeQ_3]^{2-}$-units in case of Li2. Ellipsoids are drawn at the 95 % level.

that the arrangement of the $[TeS_3]^{2-}$-units and the connectivity towards the KS_6 octahedra differ significantly from the findings for Li_2TeQ_3. A more detailed discussion of these and other $M^I_2TeQ_3$ compounds with M^I = alkaline metal and Q = S, Se will be given in a forthcoming publication on Na_2TeQ_3 [27].

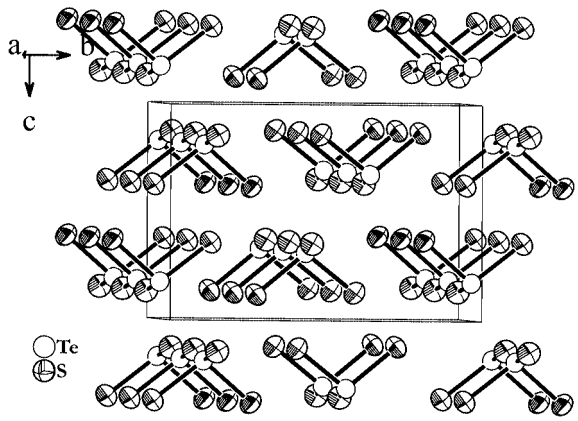

Figure 3 Section of the crystal structure of Li_2TeQ_3 showing the arrangement of the $[TeQ_3]^{2-}$-anions. They are located in layers parallel to the *ab*-plane.

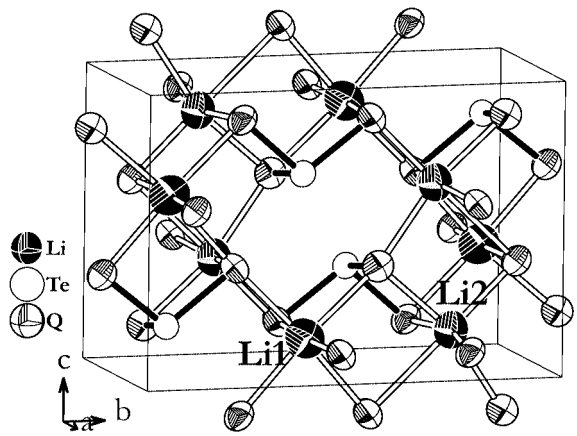

Figure 4 The crystal structure of Li_2TeQ_3 viewed along the *a* axis. Ellipsoids are drawn at the 95 % level.

Table 4 Selected interatomic distances (in Å), and angles (in degrees) for Li_2TeQ_3 (Q = S, Se) at room temperature. Compare Figure 2 for the labelling scheme.

	Li_2TeS_3	Li_2TeSe_3
Li1-Q1	2.709(6)	2.83(2)
Li1-Q1	2.786(6)	2.91(2)
Li1-Q2	2.760(7)	2.87(2)
Li1-Q2	2.773(6)	2.89(2)
Li1-Q2	2.684(7)	2.80(2)
Li1-Q3	2.809(6)	2.94(2)
Li2-Q1	2.696(6)	2.86(2)
Li2-Q1	2.791(6)	2.86(2)
Li2-Q2	2.532(6)	2.63(2)
Li2-Q2	3.159(6)	3.26(1)
Li2-Q3	2.647(6)	2.79(2)
Li2-Q3	2.690(6)	2.79(2)
Te1-Q1	2.378(1)	2.523(1)
Te1-Q2	2.357(1)	2.498(1)
Te1-Q3	2.367(1)	2.517(1)
Q2-Te1-Q3	100.52(2)	101.25(3)
Q2-Te1-Q1	100.90(2)	101.44(3)
Q3-Te1-Q1	99.15(2)	100.55(3)

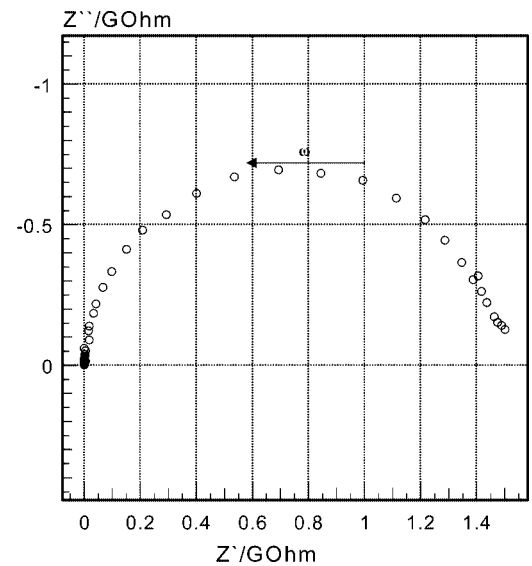

Figure 5 Impedance spectrum of Li_2TeS_3 at 200 °C. From the missing spike in the impedance plot it can be concluded that Li_2TeS_3 is predominantly an electronic conductor.

Conductivity Measurements

The finely grounded powders of the title compounds were pressed into pellets for temperature dependent conductivity measurements. They were contacted to gold electrodes and then loaded into a home made measuring cell. The samples were kept under a stream of purified Ar gas in order to prevent hydrolysis. The use of blocking electrodes allows recording impedance spectra that show significant hints either for ionic or for electronic conductivity. Figures 5 and 6 display typical impedance plots of the title compounds. The impedance spectrum of Li_2TeS_3 (Figure 5) shows only a semicircle whereas the spectrum of Li_2TeSe_3 (Figure 6) consists of a semicircle in the high frequency region and an inclined spike at low frequencies. A low frequency spike is typical for ionic conductors in combination with blocking electrodes. Therefore we conclude from the spectra that the conductance of Li_2TeS_3 is predominantly electronic whereas Li_2TeSe_3 turns out to be a mixed conductor with a significant ionic concutivity. Figure 7 illustrates the temperature dependence of the specific conductivities of Li_2TeS_3 and Li_2TeSe_3. A pure linear dependence of log σ vs 1/T is observed for Li_2TeS_3 and Li_2TeSe_3. The activation energies are 0.71 eV for Li_2TeS_3 and 0.68 eV for Li_2TeSe_3. The specific conductivities are about two to three orders of magnitude higher for the selenide as compared to the sulphide. Selected conductivity data are 2.5 x 10^{-8} Scm^{-1} (Li_2TeS_3 at 200 °C) and 4.5 x 10^{-6} Scm^{-1} (Li_2TeSe_3 at 200 °C). The different conductivity behaviour of the title compounds might be due to the increased polarizability of selenium in comparison to sulphur. However, the mobility of the Li^+

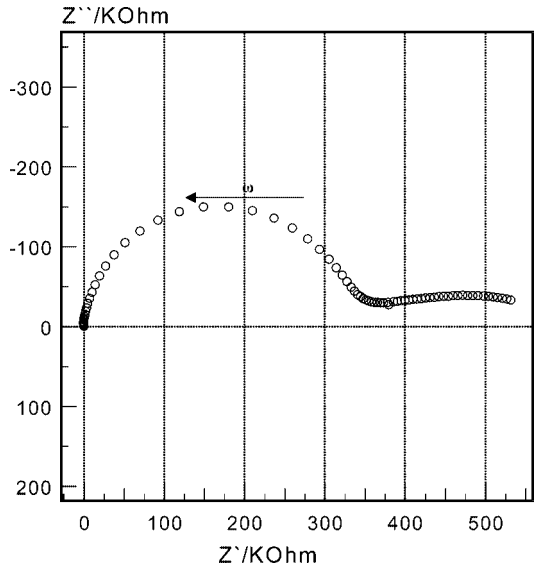

Figure 6 Impedance plot of Li_2TeSe_3 at 200 °C. We obtain the typical semicircle in the high frequency region and an inclined spike in the low frequency region. It can be concluded that the compound is a mixed conductor.

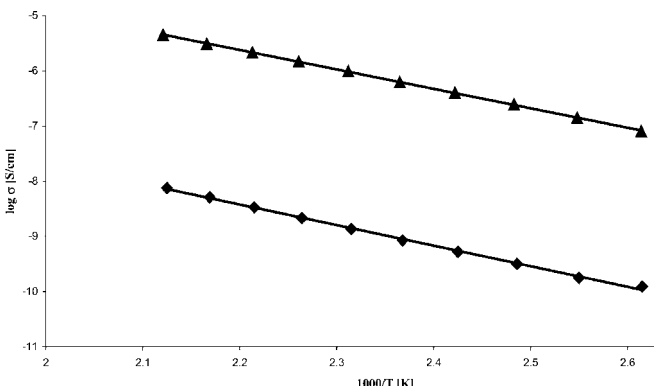

Figure 7 Arrhenius type representation of the specific conductivities of the title compounds (heating cycle). Li_2TeS_3 shows semiconducting properties and Li_2TeSe_3 seems to be a mixed conductor. ▲ = Li_2TeSe_3, E_a = 66 kJ/mol (0.68 eV); ◆ = Li_2TeS_3, E_a = 69 kJ/mol (0.71 eV).

ion in octahedral coordination is usually much smaller than for the Li^+ ion in tetrahedral coordination [23]. Therefore, one could expect only small ionic conductivities from regarding the crystal structures even if the displacement parameters of Li^+ are much bigger than those for the heavier elements.

Experimental Part

Li_2TeS_3 and Li_2TeSe_3 were synthesized from stoichiometric amounts of the elements. Li (Merck), Te (99.999 % Alfa Aesar), S (99.9995 %, Alfa Aesar), and Se (99.999 %, Alfa Aesar), respectively, in a ratio of 2 : 1 : 3 were filled into small graphite crucibles. The crucibles were closed and then put into evacuated silica ampoules. All manipulations were performed in a glove box under an atmosphere of argon. In each case the starting materials were slowly heated up to 200 °C, and then faster to 460 °C for 48 hours. Then they were cooled down to room temperature within 72 hours. Red crystals of Li_2TeS_3 and metallic black crystals of Li_2TeSe_3, both suitable for a single crystal X-ray structure determination, could be separated from the pure reaction products. X-ray powder diffraction showed the purity of the samples. The polycrystalline samples contained only some traces of graphite but no other phases Li-Te-Q were observed. Both compounds are extremely air and moisture sensitive. For the structure determination at room temperature single crystals were placed in a glass capillary, sealed under argon, and then mounted on an IPDS (Stoe) single crystal diffractometer providing monochromatic Mo $K\alpha$ radiation (λ = 0.71073 Å). Crystallographic data are collected in Table 1. Absorption was corrected numerically after an optimization of the description of the crystal shape with the X-SHAPE [24] routine.

Differential thermal analysis measurements were performed on a SETARAM TG-DTA 92-16 in evacuated silica tubes. Li_2TeS_3 decomposes peritectically at 433 °C (onset temperature). Li_2TeSe_3 melts at 428 °C (onset temperature) without decomposition.

Impedance spectroscopic investigations were performed in the frequency range from 100 mHz to 4 MHz, using an IM6 impedance analyzer from Zahner Elektrik. The temperature was varied between 90 °C and 200 °C (heating and cooling mode). Pressed pills (8 mm in diameter and about 1.2 mm thick) of finely grounded crystalline samples of the title compounds were contacted between gold electrodes and platinum wires. During the measurements the pellets were kept continuously under an atmosphere of purified argon. Further details of the experimental setup are given in ref. [25].

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References

[1] A. Pfitzner, *Chem. Eur. J.* **2000**, *6*, 1891.
[2] T. Nilges, S. Reiser, J. H. Hong, E. Gaudin, A. Pfitzner, *Phys. Chem. Chem. Phys.* **2002**, *4*, 5888.
[3] A. Pfitzner, *Chem. Eur. J.* **1997**, *3*, 2032.
[4] A. Pfitzner, C. Preitschaft, F. Rau, *Z. Anorg. Allg. Chem.* **2004**, *630*, 75.
[5] C. Rumpf, C. Näther, W. Bensch, *Acta Crystallogr.* **1999**, *C55*, 1046.
[6] P. J.-C. Jumas, M. Ribes, M. Maurin, E. Philippot, *Acta Crystallogr.* **1976**, *B32*, 444.
[7] H. Gerl, B. Eisenmann, P. Roth, H. Schäfer, *Z. Anorg. Allg. Chem.* **1974**, *407*, 135, and references therein.
[8] G. Dittmar, H. Schäfer, *Z. Anorg. Allg. Chem.* **1978**, *439*, 212.
[9] H. Gerl, H. Schäfer, *Z. Naturforsch.* **1972**, *27b*, 1421.
[10] F. Pertlik, *Monatsh. Chem.* **1997**, *128*, 157.
[11] X. Zhang, M. Kanatzidis, *Inorg. Chem.* **1994**, *33*, 1238.
[12] X. Zhang, M. Kanatzidis, *J. Am. Chem. Soc.* **1994**, *116*, 1890.
[13] A. Pfitzner, *Inorg. Chem.* **1998**, *37*, 5164.
[14] A. Pfitzner, S. Zimmerer, *Angew. Chem.* **1997**, *109*, 1031; *Angew. Chem. Int. Ed. Eng.* **1997**, *36*, 982.

[15] W. Bubenheim, G. Frenzen, U. Müller, *Z. Anorg. Allg. Chem.* **1994**, *620*, 1046.
[16] F. A. Jaeger, J. B. Menke, *Z. Anorg. Allg. Chem.* **1912**, *75*, 251.
[17] A. Gutbier, F. Flury, *Z. Anorg. Allg. Chem.* **1902**, *32*, 276.
[18] R. Zagler, B. Eisenmann, *Z. Anorg. Allg. Chem.* **1988**, *183*, 193.
[19] M. Björgvinsson, J. F. Sawyer, G. J. Schrobilgen, *Inorg. Chem.* **1991**, *30*, 4238.
[20] C. Preitschaft, A. Pfitzner, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1753.
[21] J. Olivier-Fourcade, M. Maurin, E. Philippot, *Rev. Chim. Min.* **1983**, *20*, 196.
[22] A. Lindemann, J. Kuchinke, C. Koester, A. Hammerschmidt, M. Doech, T. Pruss, B. Krebs, *Phosphorus, Sulfur, Silicon, Rel. Elem.* **2001**, *168–169*, 493.
[23] H. D. Lutz, P. Kuske, A. Pfitzner, *Ber. Bunsen-Ges. Phys. Chem.* **1989**, *93*, 1340.
[24] X-SHAPE, STOE, Darmstadt **1996**.
[25] E. Freudenthaler, A. Pfitzner, *Solid State Ionics* **1997**, *101–103*, 1053.
[26] G. M. Sheldrick, SHELX 97 Programs for the solution and refinement of crystal structures, University of Göttingen, Germany, **1997**.
[27] A. Pfitzner, C. Preitschaft, in preparation.

