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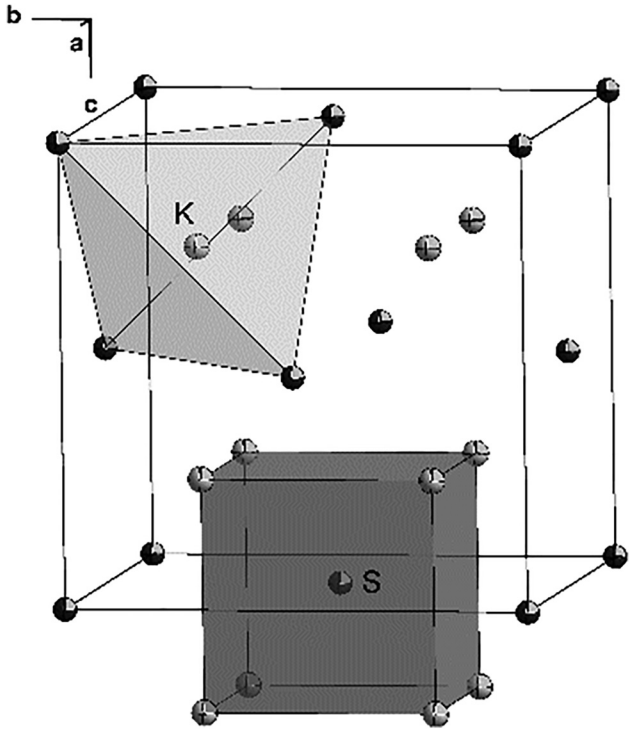
The crystal structure of dipotassium sulfide, K_2S



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Abstract

K_2S, cubic, $Fm\overline{3}m$ (no. 225), a = 7.3642(5) Å, V = 399.37(8) Å^3, Z = 4, R_{int} = 0.0348, $R_{gt}(F)$ = 0.0137 $wR_{ref}(F^2)$ = 0.0379, GooF = 1.037, T = 100(1) K.

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1 Source of material

Single crystals of K_2S were obtained by means of solvothermal treatment of a phase of the nominal composition "K_4CeS_3". Elemental cerium (99 %, OnyxMet) was used as received, K_2S and K_2S_2 were synthesized in liquid ammonia according to the literature procedure,[4] with slight modifications: potassium (98 %, Acros Organics, 20.0 g, 511.5 mmol, 2 eq.) was dissolved in approx. 300 ml of liquid ammonia first, then sulfur (99 %, abcr GmbH, 8.2 g, 255.7 mmol, 1 eq.) was slowly added under vigorous stirring. The product was dried in vacuo at 573 K for 48 h. All manipulations were performed under strict exclusion of air and moisture using standard Schlenk techniques or an argon filled glovebox.

In an attempt to obtain novel ternary potassium sulfidocerates, K_2S (2.12 g, 19.2 mmol, 1 eq.), K_2S_2 (2.74 g, 19.2 mmol, 1 eq.) and Ce (2.70 g, 19.2 mmol, 1 eq.) are fused inside a silica glass ampoule using an oxygen methane hand torch. The reaction product is extracted manually and finely ground. 0.09 g of the resulting solid of the nominal composition "K_4CeS_3" is suspended in 2 ml of 2,6–dimethylpyridine and transferred in a 5 mL glass vial and sealed. The reaction mixture is heated to 423.15 K for 48 h and allowed to cool to room temperature within 12 h. Visual inspection of the resulting reaction mixture is carried out under a light microscope and yields transparent light-yellow plates of K_2S as determined by crystallographic refinement, alongside various Ce-containing species. Collection and handling of the data for the single crystal measurement is illustrated in Table 1.

Table 1: Data collection and handling.

Crystal:	Clear yellow plate
Size:	0.42 × 0.36 × 0.27 mm^3
Wavelength:	Mo $K\alpha$ radiation (λ = 0.71073 Å)
μ:	2.64 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω scans
θ_{max}, completeness:	29.9°, >98 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	1563, 49, 0.035
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 49
$N(param)_{refined}$:	3
Programs:	Bruker,[1] Olex2,[2] SHELX[3]

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2 Comment

The series of A_2S (A = alkali metal) exhibits a renewed interest due to potential applications in alkali metal ion batteries.[5,6] As an example, K_2S depicts a high theoretical gravimetric energy density which may be used in next-generation potassium-sulfur batteries, where the low redox-voltage of potassium plays a crucial rule in the reversible redox process of K_2S_3–K_2S.[7]

Despite this renewing interest in binary chalcogenides, all reported structural data of the series of A_2S are based on powder diffraction data, ranging back to 1925 when Claassen et al. reported Li_2S to crystallize in the anti-fluorite structure type.[8] The K_2S structure presented herein represents the first single crystal structure determination within the A_2S family.

The refinement results are in a good agreement with the literature data obtained through powder diffraction by Zintl *et al.*[9] and West.[10] The obtained cell parameters in the $Fm\bar{3}m$ modification at 100(1) K of a = 7.3642(5) Å and V = 399.37(8) Å^3 are comparable to those obtained from powder diffraction analysis at room temperature a = 7.370 Å and V = 400.32 Å^3.[10] The slight difference could be attributed to the thermal expansion. The asymmetric unit contains one K^+ cation and one S^{2-} anion with a K–S distance of 3.1888(2) Å, compared to literature reports in the range of 3.1826 Å to 3.2069 Å.[10]

We note in passing that an orthorhombic modification of K_2S was reported based on powder diffraction data by Vegas *et al.* where they remarked a phase transition upon compression at about 6 GPa into a distorted Ni_2In-structure type adopting *Pmma* space group.[11]

Other members of the A_2Ch_x family (Ch = Chalcogen) were recently obtained in crystalline form through solvothermal treatment, such as K_2Se_2, K_2Se_2[12] and K_2Te_x with x = 1, 2, and 3.[13] It is therefore expected, that further single crystalline representatives of A_2Ch can be obtained, either through recrystallization or *in situ* formation.

A recrystallization of pure K_2S under otherwise unchanged conditions does not yield single crystalline material. This indicates that the crystallization was achieved *via* the formal decomposition during the solvothermal treatment. The ternary compound "K_4CeS_3" does not yield any reflexes in the PXRD, indicating amorphous or glassy constitution. The influence of a (slow) decomposition to yield small-enough concentrations of K_2S for crystallization versus a potential templating effect of side products will be investigated in future studies.

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References

1. BRUKER. SAINT, APEX2 and SADABS; Bruker AXS Inc.: Madison, Wisconsin, USA, 2009.
2. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.* **2009**, *42*, 339–341.
3. Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3–8.
4. Klemm, W.; Sodomann, H.; Langmesser, P. Beiträge zur Kenntnis der Alkalimetallchalkogenide. *Z. Anorg. Allg. Chem.* **1939**, *241*, 281–304.
5. Lai, N.-C.; Cong, G.; Lu, Y.-C. A High-Energy Potassium-Sulfur Battery Enabled by Facile and Effective Imidazole-Solvated Copper Satalysts. *J. Mater. Chem. A* **2019**, *7*, 20584–20589.
6. Zhao, X.; Lu, Y.; Qian, Z.; Wang, R.; Guo, Z. Potassium-Sulfur Batteries: Status and Perspectives. *EcoMat* **2020**, *2*, e12038.
7. Ye, C.; Shan, J.; Chao, D.; Liang, P.; Jiao, Y.; Hao, J.; Gu, Q.; Davey, K.; Wang, H.; Qiao, S.-Z. Catalytic Oxidation of K_2S via Atomic Co and Pyridinic N Synergy in Potassium–Sulfur Batteries. *J. Am. Chem. Soc.* **2021**, *143*, 16902–16907.
8. Claassen, A. The Crystal Structure of the Anhydrous Alkali Monosulphides. *I. Recl. Trav. Chim. Pays–Bas* **1925**, *44*, 790–794.
9. Zintl, E.; Harder, A.; Dauth, B. Gitterstruktur der Oxyde, Sulfide, Selenide und Telluride des Lithiums, Natriums und Kaliums. *Z. Elektr. Angew. Phys.* **1934**, *40*, 588–593.
10. West, C. D. The Crystal Structures of Some Alkali Hydrosulfides and Monosulfides. *Z. Kristallogr. Cryst. Mater.* **1934**, *88*, 97–115.
11. Vegas, A.; Grzechnik, A.; Hanfland, M.; Mühle, C.; Jansen, M. Antifluorite to Ni_2 In-type Phase Transition in K_2S at High Pressures. *Solid State Sci.* **2002**, *4*, 1077–1081.
12. Thiele, G.; Vondung, L.; Dehnen, S. β–K_2Se_2 and K_2Se_4: Missing Links in the Binary System K–Se. *Z. Kristallogr. Cryst. Mater.* **2016**, *231*, 257–260.
13. Albrecht, R.; Ruck, M. Chalcogenides by Reduction of their Dioxides in Ultra–Alkaline Media. *Angew. Chem. Int. Ed.* **2021**, *60*, 22570–22577.