

## MS23-04 | THE 1D MODULATED STRUCTURE OF THE MIXED-VALENT CHAIN SULFIDO FERRATE $K_{7.09}[FeS_2]_4$

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The series of alkaline (A) sulfido ferrates  $A_{1+x}[Fe^{III}_{1-x}Fe^{II}_xS_2]$  starts ( $x=0$ ) with the longest-known pure ferrates(III)  $A[FeS_2]$ , which contain linear chains of edge-sharing  $[FeS_4]$  tetrahedra [1]. The recently prepared pure ferrate(II),  $Na_2[FeS_2]$  ( $x=0$ , [2]), which likewise contains linear tetrahedra chains, completes the series. In-between ( $0.33 < x < 0.75$ ), several mixed-valent ferrates with always buckled chains of edge-sharing tetrahedra are reported: This encompasses the long-known salts  $A_3[FeQ_2]_2$  with an equiatomic  $Fe^{II}/Fe^{III}$  ratio ( $x=0.5$ , [1]) and the complex monoclinic structures of  $Rb_4[FeS_2]_3$  ( $x=0.33$ ) and  $K_7[FeS_2]_4$  ( $x=0.75$ ) [3]. Herein we present the 1D modulated structure of  $K_{7.09}[Fe^{II,III}S_2]_4$  (space group  $C222(00\gamma)00s$ ,  $a=1363.87(5)$ ,  $b=2487.23(13)$ ,  $c=583.47(3)$  pm,  $q=0,0,0.444$ ,  $R1=0.0767$ ,  $x=0.773$ ), in which the position modulation of the  $[FeS_2]$  chain (i.e. its undulation) and the surrounding  $K^+$  cations is associated with an occupation modulation of two of the five cation sites. In the case of the new rubidium ferrate  $Rb_7[FeS_2]_5$  ( $x=0.4$ ) and its isotopic mixed Rb/Cs-analog, the shape of the tetrahedra chain is again commensurable resulting in a monoclinic structure with a large  $a$  lattice parameter. In all mixed-valent chain compounds, the buckling of the chains is evidently controlled by the local coordination of the changing number of alkali cations with different sizes, but not by an Fe charge ordering.

[1] P. Stüble, C. Röhr, Z. Anorg. Allg. Chem., 643, 1462 (2017) and references therein.

[2] P. Stüble, S. Peschke, D. Johrendt, C. Röhr, J. Solid State Chem., 258, 416 (2018).

[3] M. Schwarz, M. Haas, C. Röhr, Z. Anorg. Allg. Chem., 639, 360 (2013).