Fehlende Glieder bekannter Reihen:
Die Oxoferrate(III) \( \text{Rb}_8[\text{Fe}_2\text{O}_7] \), \( \text{Rb}_6[\text{Fe}_2\text{O}_6] \) und \( \text{K}_4[\text{Fe}_2\text{O}_5] \)

Missing Links in Known Series: The Oxoferrates(III) \( \text{Rb}_8[\text{Fe}_2\text{O}_7] \), \( \text{Rb}_6[\text{Fe}_2\text{O}_6] \), and \( \text{K}_4[\text{Fe}_2\text{O}_5] \)

Gero Frisch und Caroline Röhr

Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstraße 21, D-79104 Freiburg

Sonderdruckanforderungen an Prof. Dr.-Ing. C. Röhr.
E-mail: caroline@ruby.chemie.uni-freiburg.de

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The title compounds were synthesized at temperatures between 775 and 1175 K from (mostly stoichiometric) mixtures of \( \text{Fe}_2\text{O}_3 \), elemental rubidium or potassium (A) and their hyperoxides \( \text{AO}_2 \). The structures have been determined by single crystal X-ray diffraction. The alkaline rich ferrate(III) \( \text{Rb}_8[\text{Fe}_2\text{O}_7] \) (Cs\( _8\)[Fe\( _2\)O\( _7\)] structure type, space group \( P2_1/c \), \( a = 696.7, b = 1722.1, c = 692.0 \) pm, \( \beta = 119.40^\circ \), \( Z = 2, R1 = 0.0496 \)) exhibits diferrate anions \( [\text{Fe}_2\text{O}_7]^8^- \) composed of two vertex-sharing \( [\text{Fe}^{\text{III}}\text{O}_4] \) tetrahedra with a linear \( \text{Fe-O-Fe} \) bridge and nearly ideal \( 3m \) symmetry. This is in marked contrast to the Na homologue, where the diferrate anions are decidedly angular. In the series \( \text{A}_3[\text{FeO}_3] \), the anions in the compounds of the light alkaline cations are chains \( \text{O}_2\text{FeO}_2\text{FeO}_2 \) composed of two edge sharing \( [\text{FeO}_4] \) tetrahedra. The new potassium ferrate of the series \( \text{A}_4[\text{Fe}_2\text{O}_5] \), \( \text{K}_4[\text{Fe}_2\text{O}_5] \) (space group \( P2_1/c \), \( a = 645.91(14), b = 593.69(13), c = 1003.0(2) \) pm, \( \beta = 103.124(4)^\circ, Z = 4, R1 = 0.0355 \)), constitutes a new structure type, but its structure is still closely related to the Na compound, which crystallizes in the isomorphous subgroup \( P2_1/n \) with a doubled \( a \) axis. Both compounds are phylloferrates with layers \( \text{O}_2\text{FeO}_2\text{FeO}_2 \) consisting of six-membered rings of \( [\text{FeO}_4] \) tetrahedra. In contrast, \( \text{Rb}_4[\text{Fe}_2\text{O}_5] \) contains chains of vertex and edge sharing tetrahedra, so that in both series, \( \text{A}_3[\text{FeO}_3] \) and \( \text{A}_4[\text{Fe}_2\text{O}_5] \), the linkedness of the ferrate tetrahedra increases with the ionic radii of the A counterions.

**Key words:** Ferrates, Rubidium, Potassium