New Hexavalent Iron Compound, $K_2Sr(FeO_4)_2$

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A new compound containing iron in its hexavalent state (Fe^{6+}) was found, which was identified as $K_2Sr(FeO_4)_2$. The crystal structure was rhombohedral ($a=7.80$Å $\alpha=42.2°$) and isomorphous with $K_2Sr(CrO_4)_2$ as determined by X-ray diffraction technique. It was antiferromagnetic at low temperature and the Nèel temperature was estimated to be near 3K from Mössbauer-effect measurement. The isomer shift was -0.91 mm/s (vs Fe metal) at room temperature and the magnetic hyperfine field was about 87kOe at 2K, these values being characteristic of a ferrate ion (FeO_4^{2-}).

KEY WORDS: $K_2Sr(FeO_4)_2$/ Ferrate ion (FeO_4^{2-})/ Crystal structure/ Mössbauer-effect/

1. INTRODUCTION

Iron is ionized to Fe^{2+} or Fe^{3+} in most compounds, but there are some containing more highly charged iron like Fe^{4+}, Fe^{5+} and Fe^{6+}. To our knowledge, only five compounds containing Fe^{6+} have been found, that is, K_2FeO_4[1], Cs_2FeO_4[2], Rb_2FeO_4[2], $BaFeO_4$[3] and $SrFeO_4$[3] in all of which ferrate ions (FeO_4^{2-}) are formed. However, we succeeded in preparing a new type of hexavalent iron compound, $K_2Sr(FeO_4)_2$ which also contains FeO_4^{2-}.

Hexavalent iron compounds or, to be accurate, compounds containing ferrate ions (FeO_4^{2-}), have some intriguing properties. First of all, water soluble compounds containing alkali metals are all oxidizing agents, more powerful than MnO_4^- [4,5]. They are relatively stable in base but decompose quickly in acid generating hydroxide ions and molecular oxygen. Secondly, a FeO_4^{2-} ion is strongly covalent owing to its high iron charge, but detailes of the bonding character have not been reported.

This paper reports a part of our systematic study concerning preparation and characterization of oxides containing highly charged transition metals.

2. SAMPLE PREPARATION

K_2FeO_4 was prepared from $Fe(NO_3)_2 \cdot 9H_2O$ in accordance with the procedure of Thompson et al.[1] as a starting material for preparation of $K_2Sr(FeO_4)_2$. The steps following are:

1) 3 g of $Sr(CH_3COO)_2 \cdot 1/2H_2O$ was dissolved in 15 ml of distilled water. An aqueous solution saturated with $Sr(OH)_2$ (15 ml) was added to the above solution, and the mixture was cooled to near 0°C.

2) 8 g of KCl was dissolved in 10 ml of 0.5% KOH solution, and the solution was cooled to near 0°C.

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3) 2.5 g of K_2FeO_4 was dissolved in the KOH solution prepared in 2). After a filtration using a 11G3 glass filter for removing contaminants containing Fe^{3+}, the filtrate was collected in a flask, to which the Sr^{2+} solution prepared in 1) was added slowly with vigorous stirring. The temperature was kept near 0°C.

After stirring for five minutes, the precipitate was filtered out as quickly as possible using a 11G3 glass filter.

4) The precipitate was washed with 200 ml of cooled absolute ether and then dried in a vacuum desiccator.

In this preparation, special care was taken to avoid contact with CO_2 and the temperature was always kept near 0°C.

The sample thus obtained was examined by powder X-ray diffraction using Cu-Kα radiation (Rigaku RU-200 equipped with a diffracted beam monochrometer using a pyrolytic graphite crystal) and also by Mössbauer-effect measurements using a conventional spectrometer and a $^{57}Co/Rh$ source.

By X-ray diffraction technique, a small amount of KCl was found to be involved in the sample as a contaminant. Such contaminants as containing Fe^{4+} or Fe^{3+} were not detected by the Mössbauer-effect.

We also tried to prepare $K_2Ba(FeO_4)_2$ and $K_2Ca(FeO_4)_2$ in a similar way, but our attempts ended in failure. In the case of Ba, the precipitate was identified as BaFeO$_4$, and in the case of Ca, no precipitate was obtained.

3. RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction pattern of $K_2Sr(FeO_4)_2$, which is very similar to that of $K_2Sr(CrO_4)_2$[6]. The rhombohedral unit cell has parameters a=7.80Å, α=42.2° as obtained from a least-squares fitting of the peak positions. The cell is
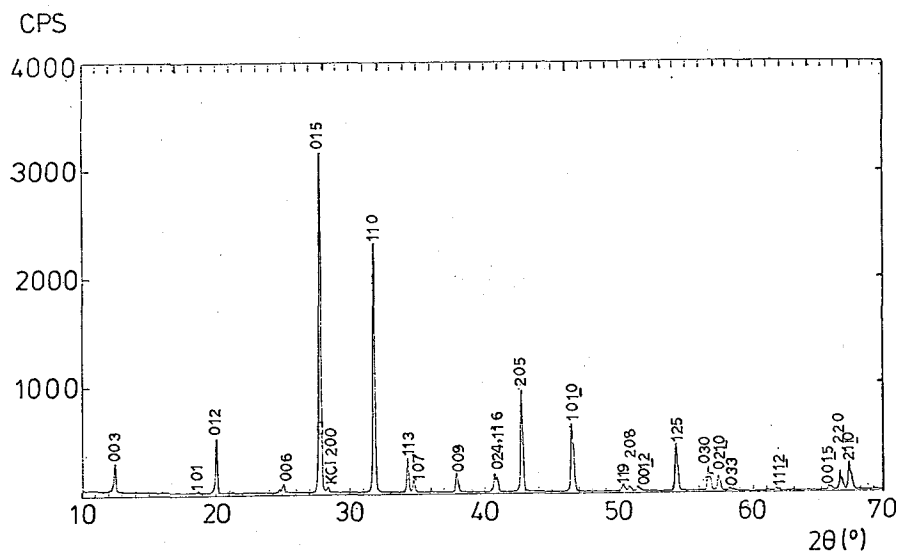

Fig. 1. X-ray diffraction pattern of $K_2Sr(FeO_4)_2$.

unimolecular, and the extinction rule observed is consistent with a space group $R\bar{3}m$. The corresponding trimolecular hexagonal cell has dimensions of $a_h=5.62A$, $c_h=21.32\text{\AA}$. The indexation in Fig. 1 is made on the hexagonal cell. A small peak assigned to KCl (200) can be seen near $2\theta \simeq 28°$. In $K_2Sr(FeO_4)_2$, each Sr atom is surrounded by six oxygen atoms, and the K ions have ten oxygen neighbors. The ferrate ion has its usual tetrahedral shape[7].

Fig. 2 shows the Mössbauer spectrum of this compound at room temperature. There appears a paramagnetic singlet with an isomer shift of -0.91 mm/s (vs Fe metal). This negative large value is characteristic of a ferrate ion as also seen in K_2FeO_4 and others[8].

Fig. 3 and Fig. 4 show the Mössbauer spectra of this compound at 4.8K and 2K, respectively. At 4.8K the absorption spectrum remainds a singlet, while at
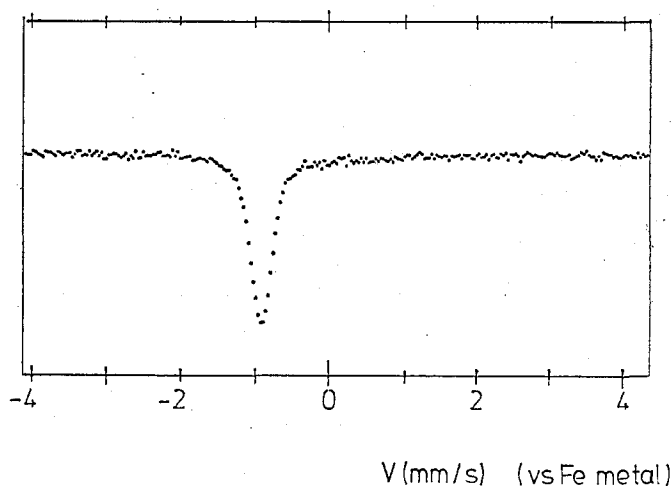
V (mm/s) (vs Fe metal)

Fig. 2. Mössbauer spectrum of $K_2Sr(FeO_4)_2$ at room temperature

V (mm/s) (vs Fe metal)
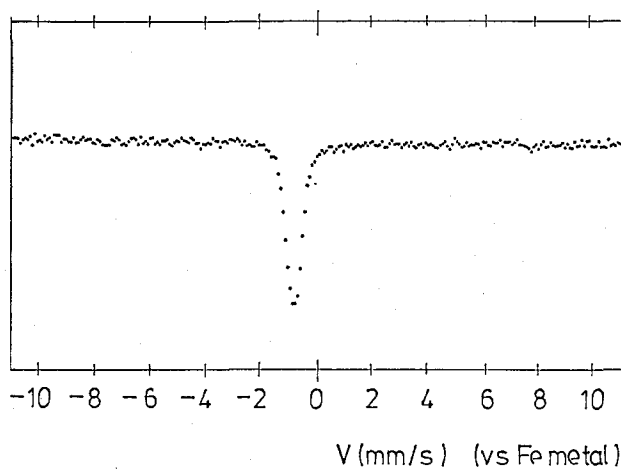
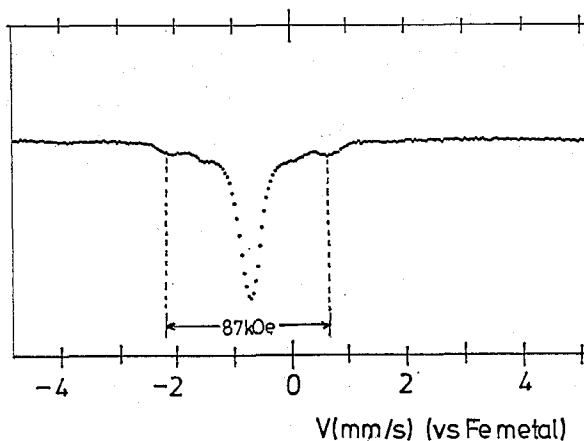Fig. 3. Mössbauer spectrum of $K_2Sr(FeO_4)_2$ at 4.8K.

Fig. 4. Mössbauer spectrum of $K_2Sr(FeO_4)_2$ at 2K

2K, a magnetic splitting, though not fully developed, can be seen. $K_2Sr(FeO_4)_2$ has been supposed to be antiferromagnetic at low temperature from the magnetic susceptibility measured by the Faraday method down to 4K. The Mössbauer data shows that the Nèel temperature should be around 3K. The magnetic hyperfine field estimated from the spectrum at 2K is about 87kOe. The field would increase to 130~140kOe at lower temperatures as found in other Fe^{6+} compounds. A theoretical analysis of the strongly covalent bonding in a $FeO_4{}^{2-}$ ion using discrete variational (DV)-Xα cluster model by Adachi et al.[9] well explains the strongly negative isomer shift and the small hyperfine field as will be published elsewhere.

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