

Cesium – Iron – Oxygen

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Introduction

Basic oxides such as Cs_2O are known to stabilize the highest oxidation states (IV and VI) of iron. There is a growing interest to the ferrate (VI) compounds due to their potential as powerful oxidizing agents [2001Ded]. It has also been suggested that dry extraterrestrial environments promote the formation of higher oxidation states of iron. Investigations on ferrates (IV and VI) of Cs has been carried out by Mössbauer spectroscopy [1994Kop, 1995Ran, 1999Kul, 2001Ded], which is one of the most appropriate approach to characterize iron containing materials. The Cs–Fe–O system could be important to oxide fuel and cladding interactions in the LMFBR (Liquid Metal Fast Breeding Reactor) systems [1981Lin]. The latest experimental works carried out on the Cs–Fe–O system are summarized in Table 1.

Binary Systems

Cs and Fe present no mutual solubility in the solid and in the liquid state [Mas2]. The Fe–O system is accepted from thermodynamic assessment of [1991Sun]. This diagram is in a very good agreement with evaluation of [Mas2] mainly based on the fundamental work of [1945Dar, 1946Dar]. The Cs–O system has never been thermodynamically assessed. There data on phase equilibria in the Cs–O system are scarce and contradictory. The latest phase diagram is from [1979Kni], where it was claimed that phase diagram data between Cs_7O and Cs_3O were not correct. According to [1979Kni] Cs_4O melts incongruently at 53°C that is higher than 10.5°C given by [Mas2]. According to [Mas2] Cs_3O has homogeneity range, while [1979Kni] show this phase as stoichiometric. The Cs_2O_3 phase [V-C2] was not found in [1979Kni]. Probably this phase is metastable. The accepted Cs–O phase diagram from [1979Kni] is presented in the evaluation of the Cs–Mo–O system in the present volume. Crystallographic data are from [V-C2].

Solid Phases

Crystallographic data of all unary phases and binary and ternary oxides are listed in Table 2. The mixed oxides of Cs and Fe lie mainly on the joint Cs_2O – Fe_2O_3 . All these phases are easily synthesized by solid-state reaction between Fe_2O_3 and a cesium salt such as Cs_2CO_3 or CsNO_3 . The compound $\text{CsFe}_{11}\text{O}_{17}$ whose structure is the “magnetoplumbite” type is decomposed above 800°C by heating under N_2 , air or O_2 [1987Ito]. It is also easily reduced and gives $\text{Fe}_3\text{O}_4 + \text{CsFeO}_2$.

The mixed oxide Cs_2FeO_4 in which iron is in the oxidation state VI can be synthesized via the oxidation of $\text{Fe}(\text{OH})_3$ in concentrated alkaline media by Cl_2 or using the interaction between solid Fe_2O_3 and CsO_2 in dry oxygen flow at high temperatures [1995Kul]. It may also be obtained by reacting a mixture ($\text{Fe} + \text{CsO}_2$) with the ratio $\text{Cs}/\text{Fe} = 4$, at 200°C during 10 hours under an oxygen atmosphere [1999Kul]. Cs_2FeO_4 decomposes above $500 - 600^\circ\text{C}$ with the formation of $\text{CsFeO}_{2.5}$ in which iron is in the state of oxidation IV [1992Kop]. Mössbauer studies [1995Kul] detected iron IV in Cs_2FeO_4 , which is explained by the result of electron capture decay of ^{57}Co in the solid matrix of Cs_2FeO_4 . A slight non stoichiometry has been proposed for $\text{CsFeO}_{2.5}$ which is sometimes labelled $\text{Cs}_x\text{FeO}_{2+0.5x}$ (with $x \sim 1$). However, Mössbauer investigation and magnetic measurements carried out by [1994Kop] failed to detect iron with an oxidation state different from IV. Further lattice of $\text{CsFeO}_{2.5}$ is indexed in a P cubic structure perovskite like. A superstructure may be observed, which is due to the ordering of the oxygen vacancies. By taking into account the superstructure, $\text{CsFeO}_{2.5}$ may be indexed in a F cubic structure with a parameter twice. The ferrate CsFeO_2 in which iron is in the oxidation state III may be obtained by decomposition of the mixed oxalate $\text{Cs}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 2\text{H}_2\text{O}$ in a shorter time and a lower temperature (700°C) than by the conventional ceramic method [1995Ran].

The compound $\text{Cs}_8\text{Fe}_2\text{O}_7$ in which Fe has a mean oxidation state of 2.33 is obtained by reacting Fe_2O_3 with metallic Cs under Ar at 500°C [2004Fri]. It is probable that the phases $\text{Cs}_8\text{Fe}_2\text{O}_7$ and $\alpha\text{Cs}_5\text{FeO}_4$ with the same structure $P2_1/c$ and whose compositions are very close belong to the same solid solution $P2_1/c$.

Isothermal Section

The Cs-Fe-O diagram in the solid state given in Fig. 1 is taken from the informations given in [1981Lin] related to ferrates in which iron is in a state of oxidation lower than 3. First, they pointed out the fact that no reference to the compounds Cs_4FeO_3 and Cs_2FeO_2 could be found. Nevertheless, they assumed the existence of these compounds and evaluated their properties. In the Fig. 1, the compound Cs_4FeO_3 has been identified with $\text{Cs}_4\text{FeO}_{3.5}$ (or $\text{Cs}_8\text{Fe}_2\text{O}_7$) and the compound Cs_2FeO_2 (or $\text{Cs}_6\text{Fe}_3\text{O}_6$) have been identified with $\text{Cs}_5\text{Fe}_3\text{O}_6$, both compounds being described by [2004Fri]. The main characteristics of the diagram is the existence of the triangle Cs-Fe- $\text{Cs}_5\text{Fe}_3\text{O}_6$, which means that the mixture Cs+Fe oxidize more easily than pure Cs, that is under oxygen pressures lower than the oxygen pressure at Cs- Cs_2O equilibrium. This diagram may be used in the temperature range between 600 and 1000°C; below 570°C, FeO is never stable and the tie lines between FeO and CsFeO_2 have to be deleted. The ferrate (VI) Cs_2FeO_4 stable in highly basic medium [2004Lic] loses its oxygen by heating and thus, is not shown in Fig. 1.

Thermodynamics

The thermodynamic properties of some cesium ferrates given in Table 3 are mainly taken from the evaluation of [1981Lin]. However, as seen above, the compounds Cs_4FeO_3 and Cs_2FeO_2 whose existence was assumed by these authors were identified respectively with the compounds $\text{Cs}_8\text{Fe}_2\text{O}_7$ and $\text{Cs}_5\text{Fe}_3\text{O}_6$ described by [2004Fri]. The entropies were estimated by the same authors with the hypothesis that the entropy of formation of ferrates from pure oxides equals zero, which is fairly unrealistic. The entropies given in Table 2 are thus corrected by using a more probable value of 3 J per mole of metal observed with analogous chromium compounds. [1981Lin] propose a tentative Ellingham (p_{O_2} - T) diagram comparing the stability domains of iron oxides, $\text{Cs}_5\text{Fe}_3\text{O}_6$ and CsFeO_2 . However, this diagram is very unlikely, because the authors assumed that FeO does not exists below 200°C, while this temperature is commonly accepted to be 570°C.

Notes on Materials Properties and Applications

The ferrite $\text{CsFe}_{11}\text{O}_{17}$ is an excellent ionic conductor. However its conductivity, electronic and ionic, measured between 300 and 600°C by [1987Ito] is lower than that of analogous compounds $\text{RbFe}_{11}\text{O}_{17}$ and $\text{KFe}_{11}\text{O}_{17}$ because of the higher ionic radius of the Cs^+ ion. The ferrate VI Cs_2FeO_4 present a high solid state stability, is hardly soluble in concentrated KOH and may be used as an alkali cathode able to sustain current densities similar to that of conventional MnO_2 cathodes [2004Lic].

Miscellaneous

Mössbauer spectra are given for Cs_2FeO_4 [1999Kul], CsFeO_2 [1995Ran] and $\text{CsFeO}_{2.5}$ [1994Kop]. $\text{CsFeO}_{2.5}$ presents a simple symmetrical line with an isomer shift $\delta = 0.15 \text{ mm}\cdot\text{s}^{-1}$ corresponding to Fe^{IV} in an octahedra oxygen environment. The ferrate (VI) presents also a simple line with an isomer shift $\delta = -0.59 \text{ mm}\cdot\text{s}^{-1}$ corresponding to Fe^{VI} in an octahedral environment and an antiferromagnetic transition at 2.8 K.

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Table 1: Recent Investigations of the Cs–Fe–O System

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1986Mor]	X-Ray diffraction analysis	20°C, CsFe ₁₁ O ₁₇
[1987Ito]	Ionic conductivity measurements	300 - 600°C, CsFe ₁₁ O ₁₇
[1992Kop]	Thermal analysis, X-Ray determination	20 - 600°C, Cs ₂ FeO ₄ –CsFeO _{2.5}
[1994Kop]	Thermal analysis, Mössbauer	20 - 600°C, Cs ₂ FeO ₄ –CsFeO _{2.5}
[1995Kul]	Synthesis, Mössbauer	–196°C, +20°C, Cs ₂ FeO ₄
[1995Ran]	Synthesis, Mössbauer	20 - 700°C, CsFeO ₂
[1999Kul]	Synthesis, Mössbauer	200°C, Cs ₂ FeO ₄
[2001Ded]	Mössbauer, Magnetic measurements	2 - 6 K, 20°C, Cs ₂ FeO ₄
[2004Fri]	Synthesis, X-Ray diffraction analysis	500°C, Cs ₈ Fe ₂ O ₇ , Cs ₅ Fe ₃ O ₆ , CsFeO ₂
[2004Lic]	Electrochemistry, IR measurement	20°C, Cs ₂ FeO ₄
[2005Fri]	X-Ray diffraction analysis	20°C, Cs ₅ FeO ₄ , Cs ₇ Fe ₂ O ₈

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Cs) < 28.39	<i>cI2</i> <i>Im</i> $\bar{3}m$ W	<i>a</i> = 614.1	at 25°C [Mas2]
(α Fe) 1538 - 1394, 912	<i>cI2</i> <i>Im</i> $\bar{3}m$ W	<i>a</i> = 286.65	at 25°C [Mas2]
(γ Fe) 1394 - 912	<i>cF4</i> <i>Fm</i> $\bar{3}m$ Cu	<i>a</i> = 364.67	at 25°C [Mas2]
Cs ₇ O < 3	<i>hP24</i> <i>P6m2</i> Cs ₇ O	<i>a</i> = 1639.3 <i>c</i> = 919.3	at 0°C [Mas2, V-C2]
Cs ₄ O < 53	<i>oP*</i> <i>Pna2</i> ₁	<i>a</i> = 1682.3 <i>b</i> = 2052.5 <i>c</i> = 1237.2	[1979Kni, V-C2]
Cs ₇ O ₂ < –10.5	<i>mP56</i> <i>P2</i> ₁ / <i>c</i> Cs ₁₁ O ₃	<i>a</i> = 1761.0 <i>b</i> = 921.8 <i>c</i> = 2404.7 β = 100.14°	[1979Kni, V-C2] labelled Cs ₁₁ O ₃ in [Mas2],
Cs ₃ O < 164	-	-	23 to 25 at.% O [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Cs ₂ O < 495	<i>hR9</i> <i>R$\bar{3}m$</i> WN ₂	<i>a</i> = 425.6 <i>c</i> = 1899.2	[1979Kni, 2005Gem]
CsO < 590	<i>oI8</i> <i>Immm</i> CsO	<i>a</i> = 432.2 <i>b</i> = 751.7 <i>c</i> = 643.0	[1979Kni, V-C2]
Cs ₂ O ₃ < 502	<i>cI28</i> <i>I$\bar{4}3d$</i> Th ₃ P ₄	<i>a</i> = 988	[Mas2, V-C2]. Not given in [1979Kni]. Probably metastable
α CsO ₂ (r) < 200	<i>tI6</i> <i>I4/mmm</i> CaC ₂	<i>a</i> = 446.2 <i>c</i> = 732.6	[Mas2, V-C2]
β CsO ₂ (h) 450 - 200	<i>cF8</i> <i>Fm$\bar{3}m$</i> NaCl	<i>a</i> = 662	[Mas2, V-C2]
CsO ₃ < 70	<i>mP16</i> <i>P2₁/c</i> RbO ₃	<i>a</i> = 670.9 <i>b</i> = 624.4 <i>c</i> = 899.7	[1979Kni, V-C2]
Fe _{1-x} O (wüstite) 1422 - 569	<i>cF8</i> <i>Fm$\bar{3}m$</i> NaCl	<i>a</i> = 431.0 <i>a</i> = 429.3	0.05 < <i>x</i> < 0.12 [1991Sun] <i>x</i> = 0.05 <i>x</i> = 0.12
Fe ₃ O ₄ (r) < 580	<i>oP56</i> <i>Pbcm</i> Fe ₃ O ₄ (r)	<i>a</i> = 1186.8 <i>b</i> = 1185.1 <i>c</i> = 1675.2	[V-C2]
Fe ₃ O ₄ (h) (magnetite) 1597 - 580	<i>cF56</i> <i>Fd$\bar{3}m$</i> MgAl ₂ O ₄	<i>a</i> = 839.6 <i>a</i> = 854.5	at 25°C at 1000°C [V-C2]
α Fe ₂ O ₃ (hematite) < 1451	<i>hR30</i> <i>R$\bar{3}c$</i> Al ₂ O ₃	<i>a</i> = 503.42 <i>c</i> = 1374.83	at 600°C [Mas2, V-C2]
β Fe ₂ O ₃	<i>cI80</i> <i>Ia$\bar{3}$</i> Mn ₂ O ₃	<i>a</i> = 939.3	metastable phase [V-C2]
γ Fe ₂ O ₃ (maghemite)	<i>tP60</i> <i>P4₁2₁2</i> Mn ₅ Si ₂ (?)	<i>a</i> = 833.96 <i>c</i> = 832.21	metastable phase [V-C2]
* CsFe ₁₁ O ₁₇	<i>hP64</i> <i>P6₃/mmc</i> NaAl ₁₁ O ₁₇ (β alumina)	<i>a</i> = 592.3 <i>c</i> = 2415.8	[1986Mor]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* CsFeO _{2.5}	<i>cP</i> 36 <i>Pm</i> $\bar{3}m$ CaTiO ₃ (perovskite)	<i>a</i> = 419.9	[1992Kop, 1994Kop]
* CsFeO ₂	<i>cF</i> 32 <i>Fd</i> $\bar{3}m$ β cristobalite	<i>a</i> = 839.2	[2004Fri]
* Cs ₅ Fe ₃ O ₆	<i>oP</i> 56 <i>P</i> ₂₁ <i>2</i> ₁ <i>2</i> ₁ Cs ₅ Fe ₃ O ₆	<i>a</i> = 867.1 <i>b</i> = 872.9 <i>c</i> = 1670.1	at – 22°C [2004Fri]
* Cs ₂ FeO ₄	<i>oP</i> 28 <i>Pnma</i> β K ₂ SO ₄	<i>a</i> = 843.43 <i>b</i> = 629.23 <i>c</i> = 1112.74	[1992Kop] Complete conversion of K ₂ FeO ₄ by CsOH [2004Lic]
* Cs ₇ Fe ₂ O ₈	<i>mP</i> 68 <i>P</i> ₂₁ / <i>c</i> Rb ₇ Fe ₂ O ₈	<i>a</i> = 666.0 <i>b</i> = 1097.4 <i>c</i> = 2156.6 β = 92.83°	at 22°C [2005Fri]
* Cs ₈ Fe ₂ O ₇	<i>mP</i> 68 <i>P</i> ₂₁ / <i>c</i> Cs ₈ Fe ₂ O ₇	<i>a</i> = 722.32 <i>b</i> = 1789.0 <i>c</i> = 733.9 β = 118.98°	at – 28°C [2004Fri]
* α Cs ₅ FeO ₄ (r)	<i>mP</i> 40 <i>P</i> ₂₁ / <i>c</i> α Cs ₅ FeO ₄	<i>a</i> = 1133.9 <i>b</i> = 1269.5 <i>c</i> = 725.05 β = 99.07°	at 22°C [2005Fri]
* β Cs ₅ FeO ₄ (l)	<i>mP</i> 40 <i>P</i> ₂₁ / <i>c</i> β Cs ₅ FeO ₄	<i>a</i> = 880.78 <i>b</i> = 1067.4 <i>c</i> = 1115.7 β = 97.35°	at – 25°C [2005Fri]

Table 3: Thermodynamic Properties of Single Phases

Phase	Temperature Range [°C]	Property, per mole of atoms [J, mol, K]	Comments
1/17 (Cs ₈ Fe ₂ O ₇)	25	<i>S</i> [°] = 47.2 ± 1 $\Delta_f H^\circ = -138\,500 \pm 500$	see text [1981Lin]
1/14 (Cs ₅ Fe ₃ O ₆)	25	<i>S</i> [°] = 44.4 ± 1 $\Delta_f H^\circ = -148\,500 \pm 500$	see text [1981Lin]
1/4 (CsFeO ₂)	25	<i>S</i> [°] = 32.3 ± 1 $\Delta_f H^\circ = -175\,000 \pm 500$	see text [1981Lin]

Fig. 1: Cs-Fe-O.
The equilibria in the
solid state

