Journal of Thermal Analysis, Vol. 36 (1990) 645-656

THERMAL STABILITY AND REACTIVITY IN OXYGEN OF POTASSIUM FERRITES WITH SPINEL STRUCTURE

*B. Gillot, M. Laarj, B. Maachi** and *A. Rousset**

LABORATOIRE DE RECHERCHES SUR LA RÉACTIVITÉ DES SOLIDES. U. A. 23 CNRS.
UNIVERSITÉ DE BOURGOGNE, FACULTÉ DES SCIENCES MIRANDE, B. B. 138, F-21004
DIJON, FRANCE
* LABORATOIRE DE CHIMIE DES MATÉRIAUX INORGANIQUES, LOE-CNRS,
UNIVERSITÉ PAUL SABATIER, 29, RUE JEANNE MARVIG, B. P. 4347, F-31055 TOULOUSE
CEDEX, FRANCE

(Received September 13, 1989)

The potassium content really incorporated in the spinel lattice of the magnetite determined by thermogravimetric analysis in vacuum or in oxygen was about 2.45 wt%. In spite of this low content, the potassium strongly stabilises the defect spinel structure resulted by the potassium-substituted magnetite oxidation and increases the transformation temperature of the defect phases into α-Fe_2O_3 or $KFe_{11}O_{17}$.

In present study on the reactivity in oxygen of finely divided ferrites with spinel structure [1, 2] we present the results of studies on the thermal stability and the behaviour in oxygen of potassium doped magnetites with large specific areas enabling finely divided substituted magnetites and non-stoichiometric ferrites with β-alumina-like structure to be formed. These metastable phases are deemed to have novel interesting physicochemical properties as catalysts for example in the dehydrogenation of ethyl-benzene to styrene due to the redox properties of spinel and defect spinel compounds [3, 4].

In the past, most of the dehydrogenation catalysts based on Fe-K-O and Fe-M-K-O systems (M = Cr, Al) have been obtained by mechanical mixing of α-Fe_2O_3 with potassium salts at calcination temperatures above 1000° [5] and under these conditions, it is difficult to achieve a homogeneous distribution of the doping element, potassium, and to obtain mixed oxides with a

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

small crystallite size to allow the oxidation in metastable phases of the same spinel structure.

Experimental

Samples

The technique of preparation and the characterizations (thermal analysis, X-ray diffraction, specific area, chemical analysis, morphology) of submicron potassium substituted magnetites, have already been described alsewhere [6]. These phases were prepared via decomposition of mixed oxalate precursors $[(NH_4)_{1-y}K_y]_3\ (Fe(C_2O_4)_3\ 3H_2O$ in air at 300° followed by thermal treatment in 70% H_2-30% H_2O gas mixture at low temperature (< 450°).

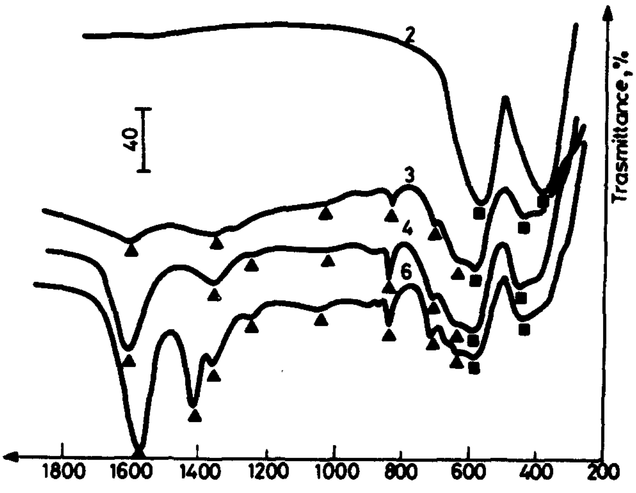

Fig. 1 IR spectra of iron-potassium oxides resulting from decomposition of oxalate precursors for different initial content of potassium. 2, 1.44 wt%; 3, 3.46 wt%; 4, 5.41 wt%; 6, 9.75 wt%. ■: spinel phase; ▲ :potassium hydrogen carbonate phase

XRD analysis indicated only the presence of a spinel phase for a potassium content below 4 wt% and for samples containing more than 4 wt% of potassium, the phase $KHCO_3$ (or K_2CO_3-3/2H_2O) has also been detected.

However, a better identification of samples resulting from the pyrolysis of the oxalates with a slightly crystalline structure has been performed by IR spectroscopy (Perkin Elmer 983 IR spectrometer) from a mixture of 1 mg of sample dispersed in 200 mg of CsI. In the IR spectra (Fig. 1), great differences are evident between sample 2 with 1.44 wt% of potassium which exhibits only a couple of bands at 580 and 380 cm^{-1} typical of a spinel phase [7] and samples 3, 4 and 6. For these three samples, the two bands at 595 and 410 cm^{-1} attributed to the spinel phase are accompanied by most of the absorption bands at 1618, 1405, 1367, 1001, 998, 830, 698 and 655 cm^{-1} attributed to $KHCO_3$ [8].

Table 1 Sample characteristics

Sample number	0	1	2	3	4	5	6
Initial % (in mass) of potassium	0	0.55	1.44	3.46	5.41	7.84	9.75
IR data	Sp	Sp	Sp	Sp+ $KHCO_3$	Sp+ $KHCO_3$	Sp+ $KHCO_3$	Sp+ $KHCO_3$
Cristallite size, nm	88	48	55	80	70	45	"
Lattice parameter, nm	0.8387	0.8394	0.8401	0.8402	0.8402	"	"

The measured lattice parameter of spinel phase which slightly increased as the potassium content increased (Table 1) indicates that the incorporation of K^+ ions in magnetite is very low (2 at 3 wt%). Crystallite size determination by electron microscopy and from specific surface areas shows that the samples consist of almost spherical grains and that the crystallite size depends on the potassium content (Table 1).

It is clear that with increase of the potassium content from 0 to 1.5 wt%, the crystallite size decreases and then increases to a maximum for about 4 wt% of potassium. The decrease in crystallite size coincides with the incorporation of potassium ions in the spinel lattice because is was well known that the substitution often leads to a decrease in particle size [9]. For samples containing more than 1.5 wt% of potassium, the increase in crystallite size may be explained by the fact that potassium ions cannot be accommodated in the iron oxide and are progressively rejected outside the structure which facilitates the sintering of the crystallites. Above 4 wt% of potassium, the presence of a large amount of potassium hydrogencarbonate suppresses the sintering process.

Based on a first-short analysis of the results thus obtained with the hypothesis of a partial substitution of Fe^{2+} ions by K^+ ions following the scheme $2Fe^{2+} \rightarrow Fe^{3+} + K^+$, a general cation distribution can be proposed for the spinel, $(Fe^{3+}_{2+x} Fe^{2+}_{1-2x} K^+_x) O^{2-}_4$ with the formation of $KHCO_3$ at high potassium content.

Measurements

The behaviour in vacuum or in oxygen of the samples was studied in a Seteram MTB-10 8 microbalance under isothermal conditions or the temperature was increased at a rate of 2.5° min^{-1}. The phases present at various stages of the reaction were determined by X-ray diffraction and IR spectroscopy from samples rapidly cooled in the TG apparatus. The oxidation temperature of the spinel phases and the transformation temperature of the defect spinel phases have been determined DTA and from a characteristic IR peak of γ-Fe_2O_3 (720 cm^{-1}) or α-F_2O_3 (470 cm^{-1}) [10].

Results and discussion

Thermogravimetric analysis in vacuum

Figure 2 shows the mass loss, Δm, when the samples were heated in vacuum (10^{-3}Pa) at a constant rate from 20 to 900°· It may be seen that samples with a potassium content lower than around 2 wt% show no mass loss (samples 1 and 2) whereas samples containing more potassium (samples 3, 4, 5 and 6) exhibit total mass losses approximatively proportional to those corresponding to the decomposition of potassium carbonate and depending on the temperature as indicated in Table 2. For samples 3, 4, 5 and 6 three major thermal effects are observed (Fig. 2):

a) An initial mass loss in the range 20-200° which can be attributed to a decomposition of potassium hydrogen carbonate to give the solid carbonate, water vapour and carbon dioxide [11] according to the reaction:

$$2KHCO_3 \rightarrow K_2CO_3 + H_2O + CO_2 \qquad (1)$$

b) Nearly constant mass between 200-350° (Table 2)

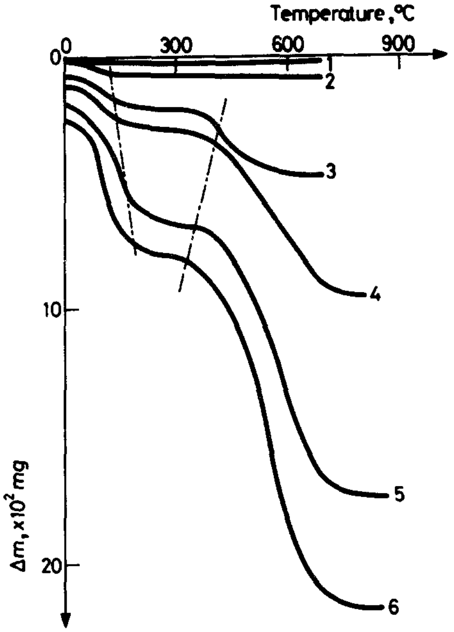

Fig. 2 TG curves recorded in vacuum for potassium-doped magnetite with different potassium content. 1, 0.55 wt%; 2, 1.44 wt%; 3, 3.46 wt%; 4, 5.41 wt%; 5, 7.84 wt%; 6, 9.75 wt%

c) Sharp mass loss in the temperature region of 360-750° (Table 2) as a result of the total decomposition of potassium carbonate according to the successive reactions:

$$K_2CO_3 \rightarrow K_2O + CO_2 \quad (2)$$

$$K_2O \rightarrow 2K + 1/2\,O_2 \quad (3)$$

Table 2 Determination from TG analysis of percentage of mass loss in vacuum for different ranges of temperature

Sample No	1	2	3	4	5	6
Temperature range, 20-200°C	0.11	0.76	1.66	2.40	6	6.80
Temperature range, 200-350°C	0	0	0.38	0.34	0.65	0.64
Temperature range, 360-750°C	0	0	2.50	6.01	9.85	12.92
Global mass loss	0.11	0.76	0.454	8.73	16.50	20.36

From this mass loss (Table 2, line 4) the percentage of potassium rejected outside the spinel structure can be calculated (Table 3, line 3) and compared with the initial percentage (Table 3, line 2). Based on the difference of mass loss given by the 2nd and 3rd lines, the potassium content really incorporated in the spinel lattice can be calculated (Table 3, line 4). It is 2.45 wt% which corresponds to an extent of substitution for the spinel of 0.145.

Table 3 Determination from TG analysis of percentage of potassium substituted in the spinel lattice of $Fe_{3-x}K_xO_4$ in vacuum and in oxygen

Sample No	0	1	2	3	4	5	6
K initial % (in mass)	0	0.55	1.44	3.46	5.41	7.84	9.75
K %(in mass) over the range 360-750°C	0	0	0	1.41	3.40	5.57	7.30
K %(in mass) in the spinel lattice	0	0.55	1.44	2.05	2.01	2.27	2.45
x extent of substitution in $Fe_{3-x}K_xO_4$	0	0.033	0.086	0.124	0.120	0.135	0.145
Mass gain due to the oxidation of Fe^{2+} ions	3.40	3.15	2.80	2.53	2.45	2.43	2.43
x extent of substitution in $Fe_{3-x}K_xO_4$	0	0.035	0.091	0.125	0.140	0.140	0.143

Reactivity in oxygen below 450° with maintained spinel structure

- Non-isothermal oxidation

Before oxidation, the samples are degassed at 460° in order to eliminate the water vapour and carbon dioxide (reaction 1) without changing the oxidation degree of Fe^{2+} ions initially present. This oxidation may be due at higher temperatures to the oxygen liberated during reaction 2 [12]. The results of the spinel oxidation are illustrated in Fig. 3 and for comparison, a sample of pure magnetite ($x = 0$) was also oxidized. In order to determine by a second method the extent of substitution x, it would be of interest to evaluate the effect of the potassium content on the oxidized amount, compared to pure magnetite. The results are given in Table 3 (line 6), where, in spite of a small uncertainty concerning the number of Fe^{2+} ions unoxidized really during the degassing at 460°, the x values calculated from the mass gain for the region plateau (Fig. 3, point A) agree reasonably well with the values obtained previously in vacuum (compare lines 5 and 7, Table 3). The

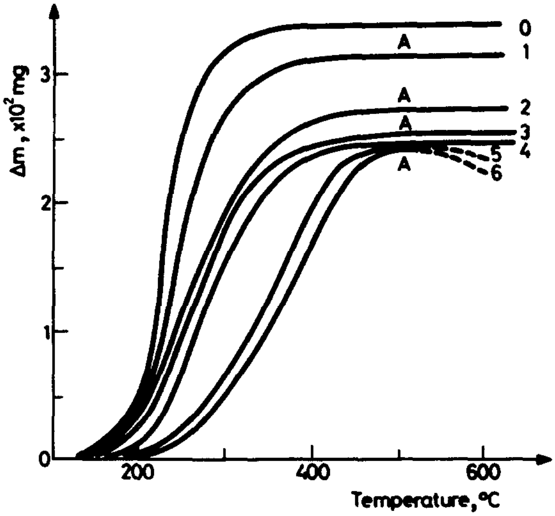

Fig. 3 TG curves recorded in air for potassium-doped magnetite with different potassium content. 0, pure magnetite; 1, 0.55 wt%; 2, 1.44 wt%; 3, 3.46 wt%; 4, 5.41 wt%; 5, 7.84 wt%; 6, 9.75 wt%

X-ray diffractogram of the oxidized spinel phase can be ascribed to γ-Fe_2O_3 with a lattice parameter of 0.834 nm.

From these results it appears that the amount of potassium really incorporated in the spinel lattice of the magnetite was limited to 2.45 wt% because the K^+ ionic radius (0.138 nm with 6-coordination [13]) is far too large to allow a total substitution of Fe^{2+} ions by K^+ ions. For such substitution the reaction of low-temperature oxidation may be written as

$$2\,(Fe^{3+}_{2+x}\,Fe^{2+}_{1-2x}\,K^{+}_{x})\,O_4^{2-} + (1-2x)/2\,O_2 \rightarrow$$

$$\rightarrow (9-2x)/4\,Fe^{3+}\left[Fe^{3+}_{(5-t)/3}\,K^{+}_{t}\right]O_4^{2-}$$

with $t = 8x/(9\text{-}2x)$ and $0 < t < 0.5$.

These phases are derived from γ-Fe_2O_3 through substitution of Fe^{3+} ions and vacancies by K^+ ions according to the scheme: $Fe^{3+} + ¤ \rightarrow 3\,K^+$ resulting to cation-deficient spinels of type

$$Fe^{3+}_{(8-t/3}\,¤_{(1-2t)/3}\,K^{+}_{t}\,)\,O_4^{2-}$$

¤ : vacancies

- Isothermal oxidation

Figure 4 shows the isothermal mass change for the oxidation of sample 2

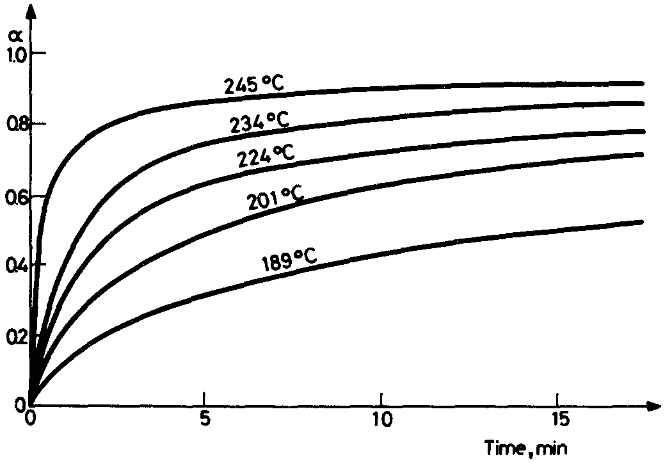

Fig. 4 Oxidation kinetic curves $\alpha = f(t)$ for sample with 1.44 wt% of potassium

at various temperatures. Whatever the potassium content, the kinetics of this oxidation can be interpreted by a diffusion controlled process of vacancies generated at the solid-gas interface [14]. The experimental curves can be described by the expression:

$$\log(1-\alpha) = \log 6/\pi^2 - kt = f(t) \tag{4}$$

with $k = \pi^2 \hat{D}/r^2$, where $\hat{D}$ is the chemical diffusion coefficient and r the mean grain radius.

A linear regression analysis of the log k *vs.* $1/T$ plots yields the activation energy E for each composition. Figure 5 shows the variation of E and the change in mean oxidation temperature T_M as a function of the potassium content. The oxidation temperature of undoped magnetite is known to depend on its crystallite size: the smaller the size, the lower is the oxidation temperature [15]. It has also been shown that the oxidation temperature (and the activation energy) of doped magnetite increased with the dopant content [16]. Taking into account the parameters, Fig. 5 indicates that the presence of potassium has increased the activation energy and the oxidation temperature of these spinel phases, especially for low substitution extents. Lichtner et al. [17] mentioned that the oxidation temperature of potas-

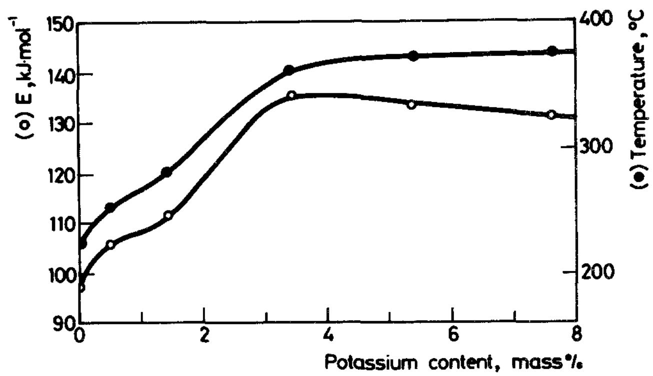

Fig. 5 Variation of the activation energy (*E*) and oxidation temperature (*T*) of the spinel with the potassium content

sium/doped magnetites could be considered as unaltered by the presence of potassium.

Oxidation above 450° with transformation of the spinel structure

The structural changes occurring when metastable defect spinel phases undergo thermal treatment above 450° in air, followed by XRD, DTA and IR spectroscopy lead to either corundum phase or β-alumina-like phase or a mixture of both, depending on the potassium content. In the case of samples with a potassium content lower than 2 wt%, the IR spectrum (Fig. 6) of the defect phases (curve a), which can be identified to be γ-Fe_2O_3 up to 710° with an ordering of vacancies and cations on octahedral sites [18], progressively reveals the absorption bands of α-Fe_2O_3 (curve b) [10] for higher temperatures. These observations are consistent with the results of DTA which show an exothermic peak around 725°. For compositions between 2 and 6 wt% of potassium and at temperatures above 720°, the IR spectrum exhibits also, beside α-Fe_2O_3, new absorption bands at 713, 627, 573, 528, 437, 312, 289 and 239 cm^{-1}. These new absorption bands can be attributed to potassium ferrite $KFe_{11}O_{17}$ resulting from a reaction between K_2O and Fe_2O_3 as the Fe_2O_3-K_2O system presents several iron potassium oxides [19]. For samples 5 and 6 containing more than 6 wt% of potassium, only the potassium ferrite has been detected in the temperature range 700-900° (Fig. 7, curve a) and in many cases by XRD analysis as well. At temperatures above 900° and for long annealing time the IR spectrum closely resembles that of α-Fe_2O_3 (Fig. 7, curve b). This could be caused by evaporation of

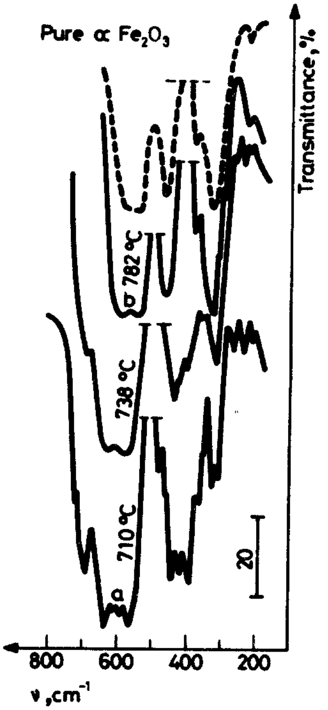

Fig. 6 Variation with temperature of the IR spectrum of the defect spinel phase with 1.44 wt% of potassium. The spectrum of $\alpha - Fe_2O_3$ is given for comparison

potassium, thus resulting in decomposition of potassium ferrite and its transformation to α-Fe_2O_3. The transformation temperature of metastable defect spinel phases to α-Fe_2O_3 resulting or not from $KFe_{11}O_{17}$ decomposition is shown in Fig. 8. It may be seen that potassium has altered to a large degree the transformation temperature. It is interesting to note the strong increase in temperature during the insertion of a very small amount of potassium (0.55 wt%).

Therefore it may be suggested that the re-staking and shifting of the oxygen atomic planes as well as the cooperative migration of iron(III) ions required for the transformation [20] are locked by the presence of potassium which may account for the increase in transformation temperature.

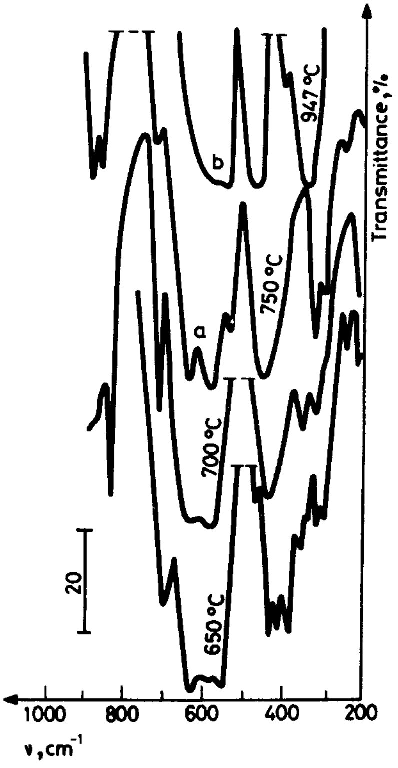

Fig. 7 Variation with temperature of the IR spectrum of the defect spinel phase with 9.75 wt% of potassium. Curve (a) represents the spectrum of pure $KFe_{11}O_{17}$

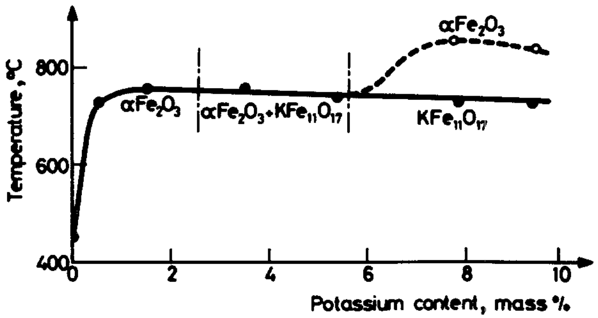

Fig. 8 Variation of the transformation temperature of the defect spinel phases and nature of the phases formed with the potassium content

Conclusion

From the study of the thermal stability of $Fe_{3-x}K_xO_4$ +$KHCO_3$ phase mixture and of oxidized portion of Fe^{2+} ions, we conclude that the percentage of potassium determined by either of these two methods and really incorporated in the spinel lattice of the magnetite was 2.45 wt. The insertion of small amounts of potassium (as low as 0.55 wt%) probably in the distorted sites of the outer layers of the spinel, strongly increased the oxidation temperature of magnetite in defect spinel phases and the transformation temperature. However, the nature of the phases formed above 700°, α-Fe_2O_3 and $KFe_{11}O_{17}$ depends on the potassium content.

References

1 B. Gillot, M. El Guendouzi, P. Tailhades and A. Rousset, React. Solids, 1 (1986) 139.
2 B. Gillot, F. Jemmali, L. Clerc and A. Rousset, React. Solids, 2 (1986) 95.
3 W. D. Mross, Catal. Rev. Sci. Eng., 25 (1983) 591.
4 A. Rousset, B. Maachi, B. Gillot and M. Gougeon, Brevet Fr, no. 87.17575.
5 F. H. Lee, Catal. Rev. 28 (1973) 285.
6. M. Gougeon, B. Maachi, A. C. Vajpei and A. Rousset, Solid State Ionic, 32/33 (1989) 1025.
7 B. Gillot, F. Bouton and J. F. Ferriot, J. Solid State Chem., 21 (1977) 375.
8 K. Nakamoto, Y. A. Sarma and H. Ogoshi, J. Chem. Phys., 43 (1965) 1177.
9 B. Gillot, J. Tyranowicz, Mater. Res. Bull., 10 (1975) 775.
10 B. Gillot, F. Jemmali and A. Rousset, J. Solid State Chem., 50 (1983) 138.
11 H. Tanaka, J. Thermal Anal., 32 (1987) 521.
12 M. Laarj, Thesis, Dijon (1987).
13 R. Shannon, Acta Crystallogr., Sect. A, 32 (1976) 751.
14 B. Gillot, D. Delafosse and P. Barret, Mater. Res. Bull., 8 (1973) 1431.
15 B. Gillot, A. Rousset and G. Dupré, J. Solid State Chem., 25 (1978) 263.
16 B. Gillot, A. Rousset and F. Chassagneux, J. Solid State Chem., 76 (1988) 355.
17 E. Lichtner and G. Szalek, Z. Anorg. Allg. Chem., 360 (1968) 151.
18 B. Gillot, Mat. Chem. Phys., 10 (1984) 375.
19 T. Takahashi, K. Kuwabara and Y. Kase, Denki Kagaka oyoki Kogyo Butsuri Kagaku, 43 (1973) 273.
20 S. Kachi, K. Mumiyama and S. Shimizu, J. Phys. Soc. Japan, 18 (1963) 106.

Zussamenfassung — Der tatsächlich in das Spinellgitter von Magnetit eingebaute Kaliumgehalt beträgt 2.45 Gewichtsprozente. Dies wurde durch TG-Analyse in Vakuum bzw. Sauerstoff ermittelt. Trotz dieses geringen Gehaltes wird das defekte Spinell des durch Oxydation erhaltenen kaliumsubstituierten Magnetits durch Kalium stark stabilisiert, was ein Ansteigen der Temperatur für die Umwandlung der defekten Phase in αFe_2O_3 oder $KFe_{11}O_{17}$ nach sich zieht.