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The new phase $Ba_{0.167}Fe_{0.083}WO_{3+0.29}$ — a product of the thermal degradation of the heteropoly KEGGIN compound $Ba_2H[\alpha\text{-}FeO_4W_{12}O_{36}] \cdot 26H_2O$

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Abstract

The thermal degradation of the polyoxometallate $Ba_2H[\alpha\text{-}FeO_4W_{12}O_{36}] \cdot 26H_2O$ was investigated by means of X-ray heating patterns, thermal analysis (TG, DTG, DTA, DSC) and spectroscopic methods (IR, ESR, Mössbauer).

The formation of the new hexagonal phase $Ba_{0.167}Fe_{0.083}WO_{3+0.29}$ ($a = 7.320$, $c = 7.389$ Å) can be observed. The phase is stable at room temperature. Its structure is related to hexagonal tungsten bronzes but differs from them due to the presence of oxygen in addition to barium and iron along the hexagonal channels. The high positive charge of the cations leads to the maximum contraction of the cell parameter c.

Keywords: Bronze; Degradation; DSC; DTA; DTG; ESRS; IRS; KEGGIN; Moessbauer; Polyoxometallate; TG; XRPD

1. Introduction

In the last few years, polyoxometallates have often been used as catalysts in technical processes [1,2]. For this reason, investigations of the thermal degradation of these compounds, often called heteropoly compounds, are of great interest with respect to catalytically effective phases. Because of their wide variety in terms of

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material and structure, these compounds are possible starting materials for oxidic functional ceramics. In addition, the combination of different elements in an atomic area is the basis for the synthesis of phases which are either difficult or impossible to produce in other ways.

Many elements of the periodic table can act as the so-called "hetero"-element E in polyoxometallate structures. They have a tetrahedral, octahedral, quadratic-antiprismatic or an icosahedral coordination with oxygen, whereas the structure-building "poly"-elements Z (Z is Mo, W, V, Nb, Ta) have a six-fold coordination with oxygen [3].

The heteropoly compound dibarium-α-dodecatungstoferrate(III)-26-hydrate, $Ba_2H[\alpha\text{-}FeO_4W_{12}O_{36}] \cdot 26H_2O$ ($Ba\text{–}FeW_{12}$), contains the heteropoly anion $[\alpha\text{-}FeO_4W_{12}O_{36}]^{5-}$ which has been characterized by X-ray structure analysis [4] as an α-KEGGIN structure. In this well-known structure type of the 1:12 polyoxometallates, which can be described by the general formula $[\alpha\text{-}E^eO_4Z_{12}O_{36}]^{(8-e)-}$ (e is the oxidation number of the heteroelement), a four-fold coordinated iron(III) ion is located in the central cavity of the anion structure.

A systematic investigation of the thermal degradation of $Ba\text{–}FeW_{12}$ should provide information on the change in the coordination number of the Fe(III). Under the particular conditions of a given structure and stoichiometry of the heteropoly compound, the expected compositions of the new oxide phases have been investigated.

2. Experimental

The compound $Ba_2H[\alpha\text{-}FeO_4W_{12}O_{36}] \cdot 26H_2O$ was prepared from an aqueous solution of the free acid $H_5[\alpha\text{-}FeO_4W_{12}O_{36}] \cdot 6H_2O$, as described elsewhere [4]. The chemical composition of the prepared compound was determined photometrically by means of ICP (ICP Emission Spectral Photometer Plasma 2000, Perkin-Elmer). An IR and UV–VIS spectroscopic characterization of the product was also made.

The thermal analysis was carried out in an atmosphere of dynamic air by means of a NETZSCH STA 429 thermoanalyser at a heating rate of 5 K min^{-1} in the range 25–900°C. The DSC investigations were made with a Setaram DSC 92 thermoanalyser at a heating rate of 3 K min^{-1} in the range 25–500°C. X-ray powder patterns of the solid samples were obtained with a HZG-4 diffractometer using Cu Kα radiation. The high-temperature X-ray investigations were carried out with an Enraf Nonius Guinier-Lenné camera. IR spectra of the samples were obtained from KBr tablets using a Nicolet 510 FTIR spectrometer in the range 4000–400 cm^{-1}. For the ESR spectroscopic investigations, a Varian EA X/Q band spectrometer was used.

3. Thermoanalytical investigations

Freshly prepared crystals of the compound $Ba\text{–}FeW_{12}$ were used as the starting material. The results of the TG/DTG/DTA analyses confirmed that the number of

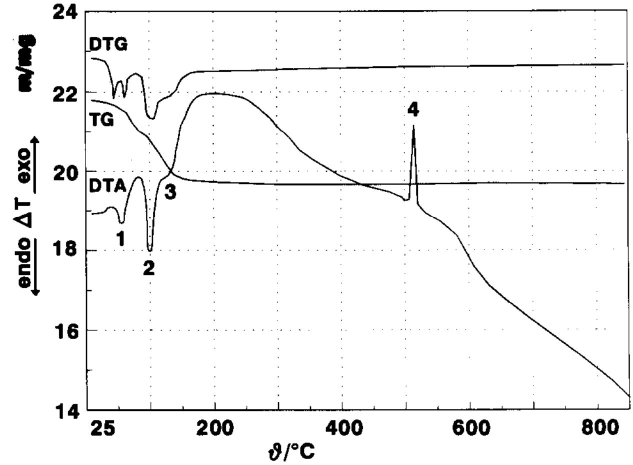


Fig. 1. Characteristic TG, DTG and DTA curves of $Ba_2H[\alpha\text{-}FeO_4W_{12}O_{36}] \cdot 26H_2O$.

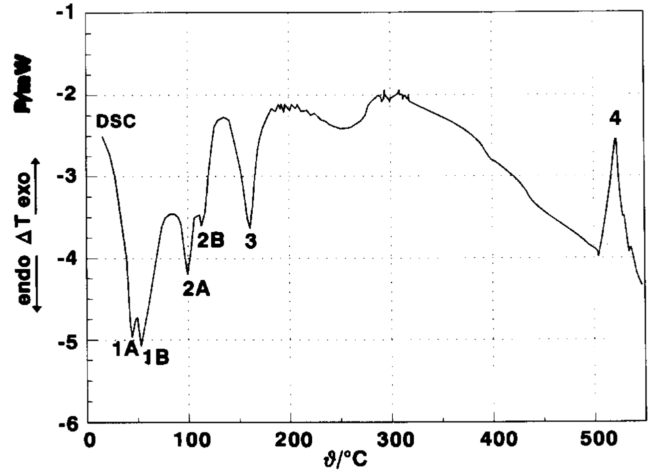


Fig. 2. Characteristic DSC curve of $Ba_2H[\alpha\text{-}FeO_4W_{12}O_{36}] \cdot 26H_2O$.

molecules of hydrate water per unit formula is 26. This, however, is decreased by weathering at room temperature to a value of 23 mol. Characteristic TG, DTG and DTA curves are shown in Fig. 1.

The endothermic effects (Figs. 1 and 2, and Table 1) correspond with the gradual loss of water. In the DSC investigations (Fig. 2), they were found to be in the temperature range 33–168°C (endo 1–3). A weight loss of 9.77% (TG) can be registered up to a temperature of 129°C. This corresponds with the loss of 19 mol of water, i.e. at 129°C only 4 mol of crystal water remain from the starting compound. The loss of the first 19 mol of crystal water requires 685 kJ mol^{-1}, corresponding to 23 kJ per mol of hydrate water. The loss of the last 4 mol of

Table 1
Summary of the observed thermal effects [a] for $Ba_2H[\alpha\text{-}FeO_4W_{12}O_{36}] \cdot 26H_2O$

Peak (see Fig. 1)			ϑ/°C
1	Endo	T_{on}	36
		$T_{on,ex}$	42
		T_{max}	56
2	Endo	T_{on}	73
		T_{max}	99
3	Endo	T_{sh}	118
4	Exo	T_{on}	517
		$T_{on,ex}$	522
		T_{max}	528
Peak (see Fig. 2)			ϑ/°C
1A	Endo	T_{on}	33
		T_{max}	45
1B	Endo	T_{max}	60
2A	Endo	T_{max}	100
2B	Endo	T_{max}	129
3	Endo	T_{on}	144
		T_{max}	168
4	Exo	T_{on}	507
		$T_{on,ex}$	512
		T_{max}	534
$\Delta_R H$	Σ Endo 1A–2B	658 kJ mol^{-1}	
$\Delta_R H$	Endo 3	219 kJ mol^{-1}	
$\Delta_R H$	Exo	−126 kJ mol^{-1}	

[a] The symbols used in this table conform to internationally recognized standards [5].

crystal water starts at 137°C and terminates at 144°C; 219 kJ mol^{-1} are needed, corresponding to 54 kJ per mol of hydrate water. The clearly greater consumption of energy for the loss of the last four water molecules is remarkable. The investigation by DSC techniques (Fig. 2) show a clear separation (endo 3) from the loss of the first 19 mol of crystal water (endo 1A–2B). After that, up to a temperature of 350°C, the compound $Ba_2H[\alpha\text{-}FeO_4W_{12}O_{36}]$ is devoid of hydrate water. Above 350°C, the loss of 0.5 mol of structural water takes place over a wide range of temperature. The ultimate loss of weight is complete at 415°C with the destruction of the KEGGIN anion.

In numerous investigations of free heteropoly acids, an exothermic peak can be observed immediately after the endothermic loss of the last molecules of water formed from the remaining protons and oxide ions of the anion. This exothermic peak is caused by the recrystallization of an oxidic lattice modified by the appropriate heteroatom [6,7].

The thermal degradation of polyoxometallates like $M^{I}_4[\alpha\text{-}SiO_4W_{12}O_{36}] \cdot nH_2O$ (M is Li, Na [8]; K [9]; Rb, Cs [10]; Tl [11]) and $K_8[\alpha\text{-}SiO_4W_{11}O_{35}] \cdot 13H_2O$ [12]

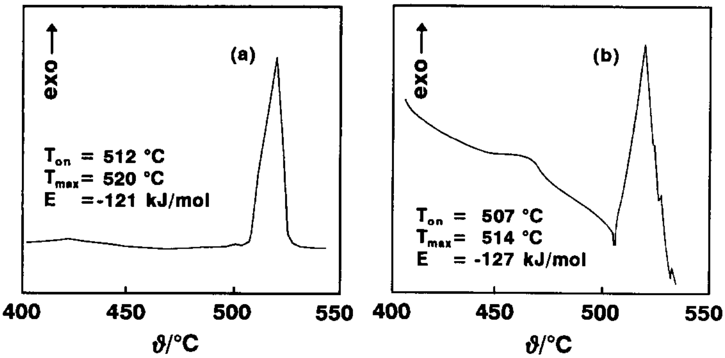


Fig. 3. Comparative DSC curves. (a) $Ba_3[\alpha\text{-}H_2O_4W_{12}O_{36}] \cdot 25H_2O$. (b) $Ba_2H[\alpha\text{-}FeO_4W_{12}O_{36}] \cdot 26H_2O$.

leads to different polytungstates $M^I{}_2W_nO_{3n+1}$ ($n = 3$, 4, 5, 6 and 8). The formation of hexatungstates has been observed only when M is Li, K, Rb, Cs and Tl.

In particular, the stoichiometry of the starting compound can be assumed to lead to the formation of a quasi-hexatungstate structure. The recrystallization of modified barium hexatungstate, $BaFe_{0.5}W_6O_{19.75}$ ($\rightarrow Ba_{0.167}Fe_{0.083}WO_{3+0.29}$; BaFeWO) starts at 505°C (DSC, Fig. 2, exo) from the products of the thermal degradation of the starting compound. An energy of -127 kJ mol^{-1} is released at this temperature. In Fig. 3 a comparison is made between the heat of formation of the tungstate under investigation and $Ba_{1.5}W_6O_{19.5}$ ($\rightarrow Ba_{0.25}WO_{3+0.25}$), the product of the thermal degradation of barium metatungstate-25-hydrate, $Ba_3[\alpha\text{-}H_2O_4W_{12}O_{36}] \cdot 25H_2O$, which reveals a large identical heat of recrystallization energy of -121 kJ mol^{-1}.

The phase $Ba_{0.167}Fe_{0.083}WO_{3+0.29}$ is destroyed above 720°C, and at 950°C tetragonal WO_3, $BaWO_4$ and $Fe^{III}{}_2(WO_4)_3$ are present as the final products of the thermal degradation of Ba–FeW_{12}. In addition, traces of $Fe^{II}WO_4$ (3%, related to the aggregate Fe) is produced as a result of the thermal reduction of WO_3 at a temperature of above 900°C.

4. X-ray and IR results

The starting compound crystallizes tetragonally as a 26-hydrate with the lattice parameters $a = 12.398(6)$ and $c = 18.721(6)$ Å, and with $Z = 2$ in the space group P4n2 [4].

At approximately 100°C, the decahydrate resulting from the starting compound is produced. Above 200°C and up to 350°C, the compound $Ba_2H[\alpha\text{-}FeO_4W_{12}O_{36}]$ with no hydrate water is present (in contrast to the free acid $H_5[\alpha\text{-}FeO_4\text{-}W_{12}O_{36}] \cdot 6H_2O$). This has been confirmed by IR spectroscopy (see Fig. 4). Above 350°C, an X-ray-amorphous phase is formed. The crystallization of BaFeWO starts at 507°C (see the DTA, TG and DSC investigations, Figs. 1 and 2) and terminates at approximately 630°C. The results of the IR spectroscopy (Fig. 4) confirm the on-going degradation. The plot of the degradation of a sample, heated at tempera-

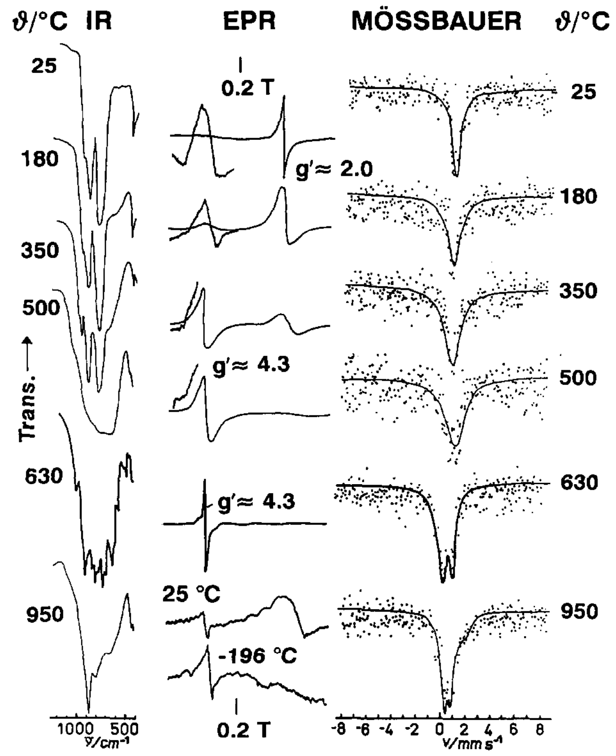


Fig. 4. IR, EPR and Mössbauer spectroscopic results for samples heated to different temperatures.

tures from 25 to 350°C, shows that the short-range order is preserved up to 350°C. However, within the temperature range from 350°C to approximately 500°C, it disappears completely. The IR spectrum of a sample heated to 630°C again reveals a definite structure. This indicates a new order and bears a marked resemblance to the IR spectrum of potassium hexatungstate, $K_2W_6O_{19}$.

The IR spectrum of a sample heated up to 950°C shows that the intermediate phase BaFeWO is destroyed again.

Because of the good reproducibility of the X-ray powder diffraction patterns, a set of data for the indexing of the phase BaFeWO could be obtained. All the reflection lines were measured and refined with the help of a FIT program [13] with reference to peak profile and half-width. The deviation in the scattering pattern is in the range 0.2%–0.03%. To verify whether or not all the reflection lines are related to a single phase, the half-width and a test for higher orders of reflection were used. Only two reflection lines with very low intensities ($I < 4\%$) could not be indexed. Obviously, they belong to an unknown minor phase. For indexing the powder pattern the program POWD [14,15] was used. The best solution found was a hexagonal unit cell with the lattice parameters $a = 7.320$ Å and $c = 7.389$ Å. All reflections observed could be indexed. The calculated lines are compared to the observed lines in Table 2. The volume of the unit cell is 342.9 Å^3. The pycnometric

Table 2
Data of the observed and calculated reflections for the hexagonal phase $Ba_{0.17}Fe_{0.08}WO_{3+0.29}$

Reflection no.	Indices			d_{obs} in Å	d_{calc} in Å	Δd in %	Half-width in deg	I/I_0 in %
	h	k	l					
1	1	0	0	6.2134	6.3393	−2.03	0.407	5
2	0	0	2	3.6570	3.6945	−1.02	0.232	49
3[a]	1	1	0	3.6388	3.6600	−0.58	–	3
4	2	0	0	3.1423	3.1697	−0.87	0.149	100
5	2	0	2	2.3904	2.4056	−0.64	0.165	36
6	1	1	3	2.0992	2.0434	2.66	0.479	2
7	0	0	4	1.8383	1.8472	−0.48	0.393	9
8	3	0	2	1.8220	1.8343	−0.68	0.170	26
9	2	2	2	1.6340	1.6399	−0.36	0.203	13
10	2	0	4	1.5904	1.5960	−0.35	0.278	11
11	4	0	0	1.5795	1.5848	−0.34	0.198	14
12	4	0	2	1.4523	1.4565	−0.29	0.212	3
13	3	2	1	1.4239	1.4270	−0.22	0.434	6
14	2	2	4	1.2973	1.3001	−0.22	0.360	4
15	5	0	2	1.2006	1.1992	0.12	0.350	3
16	4	2	0	1.1958	1.1980	−0.18	0.280	6
17	2	0	6	1.1457	1.1479	−0.19	0.563	2

[a] Indexed using the powder diffraction pattern of $(NH_4)_{0.25}WO_3$ [14].

determination of the powder density shows an average value of 6.85 g cm^{-3}. If we realistically assume $Z = 6$, D_x can be calculated as 7.67 g cm^{-3}.

Both the reflection line (100), with the value 6.21 Å, and the strongest line of 3.1423 Å (200) indicate a close structural correlation with the hexagonal tungsten bronzes.

Cubic, tetragonal and hexagonal tungsten bronzes are characterized by the empirical formula M_xWO_3. The particular connections of the WO_6 octahedra are different for each of these structural types, but uniform over all corners of the octahedra, which leads to the exact stoichiometry 1 W:3 O. The oxidation number of tungsten is always less than +6. For the hexagonal tungsten bronzes with M (for example, K, NH_4, Ca or Ba) in the hexagonal channels, x cannot be more than 0.33 for structural reasons [16]. The lattice parameter a varies only from 7.307 to 7.428 Å. The values of the parameter c, however, vary in accordance with the cation and the degree to which the hexagonal channels have been filled, within the limits of 7.426 ($Ba_{0.14}WO_3$ [17]) and 7.648 Å ($(NH_4)_{0.13}WO_3$ [18]). In the special case of hexagonal WO_3, characterized by empty channels and tungsten of oxidation number +6, this value amounts to 7.810 Å [19]. Polytungstates like $M^{I}_{x}WO_{3+x/2}$, e.g. $K_2W_6O_{19}$ ($\rightarrow K_{0.33}WO_{3+0.165}$), represent a second group of compounds with W^{VI}, which have long been regarded as structures of oxidized tungsten bronzes, the so-called "oxide-bronzes". Experimental evidence for the hypothesis that, in addition to the cations, O^{2-} anions are located in the hexagonal channels, has been demonstrated by recent neutron diffraction experiments and Rietveld analysis of hydrated and deuterated samples of $Na_xWO_{3+x/2} \cdot yH_2O$ ($x \approx 0.17$, $y \approx 0.23$) [20].

5. ESR spectroscopy

The change in the coordination number of the Fe^{3+} ions from four to six can be observed by means of ESR spectroscopy.

Whereas the starting compound contains only four-fold coordinated iron(III) ($g' \approx 2.0$), in a sample heated to 180°C, a second signal at $g' \approx 4.3$ can be observed, as well as a gradual broadening of the line at $g' \approx 2.0$. The degree of broadening of the signal at $g' \approx 2.0$ indicates an increase in the interactions between the Fe^{3+} ions. Above 350°C, no tetrahedrally coordinated iron(III) can be proved. The broadening line at $g' \approx 4.3$ points to a strongly orthorhombic distortion of the chemical environment of the Fe^{3+} ions, scattered about a relatively wide range. After recrystallization of the phase BaFeWO (630°C), only six-fold coordinated Fe(III) can be observed, which is to be found in a uniform chemical environment (a narrow and symmetrical line at $g' \approx 4.3$). Due to the strong increase in temperature to 950°C, the destruction of the phase formed can be observed from the ESR spectrum. The spectrum exhibits two broad lines at $g' \approx 2.2$ and $g' \approx 4.3$. While the signal at $g' \approx 4.3$ displays a small amount of orthorhombic Fe(III), the second broad line is caused by octahedrally coordinated Fe(III), which occupies (along with a small amount of Fe(II)) a lattice of a higher degree of symmetry. The formation of $BaWO_4$ as the one final product of thermal degradation suggests a structure, analogous to $CaWO_4$, in which Fe^{3+} ions may occupy sites within the lattice points.

6. Mössbauer spectroscopy

For the Mössbauer spectroscopic investigations of the thermal degradation of $Ba-FeW_{12}$, the starting compound was synthesized using ^{57}Fe. At 25°C, the starting compound already displays a relatively broad line ($\Gamma = 0.82\ mm\ s^{-1}$) with an isomeric shift of $\delta = 0.17\ mm\ s^{-1}$. The breadth of this line results from the structural disorder of the Fe^{3+} ions in the starting structure [4], and also from the self-absorption of γ-rays by the tungsten atoms.

In the temperature range of 25-350°C, the isomeric shift remains almost unchanged, whereas the width of the line increases continuously. Due to the transition from tetrahedral to octahedral coordination, the electron cloud around the Fe^{3+} ion increases, followed by a decrease in the s-electron density in the environment of the ^{57}Fe nucleus.

The ratio of the radius of the excited state and the ground state is negative in the case of iron ($\Delta R/R < 0$). This means that a decrease in s-electron density leads to an increase in the isomeric shift. The broadening of the line towards the sample, heated to 500°C, is caused by a partial distortion of the short-range order of Fe^{3+}

Table 3
Mössbauer spectroscopy results for the thermal degradation of $Ba_2H[\alpha\text{-}FeO_4W_{12}O_{36}] \cdot 26H_2O$

ϑ/°C	MS parameters/(mm s^{-1}) [a]	ϑ/°C	MS parameters/(mm s^{-1}) [a]	
25	$\delta = 0.17(2)$	630	$\delta = 0.34(2)$	
	$\Gamma = 0.82(6)$		$\Gamma = 0.81(0)$	
180	$\delta = 0.15(4)$		$\varepsilon = 0.82(4)$	
	$\Gamma = 1.30(1)$	950	$\delta = 0.38(2)$	0.95(8)
350	$\delta = 0.19(4)$		$\Gamma = 0.57(3)$	1.16(13)
	$\Gamma = 1.20(1)$		$\varepsilon = 0.56(7)$	0.80(0)
500	$\delta = 0.16(4)$			
	$\Gamma = 1.12(11)$			

[a] $\delta_{(\text{rel. } \alpha\text{-Fe})}$, isomeric shift; Γ, line width; ε, quadrupole splitting.

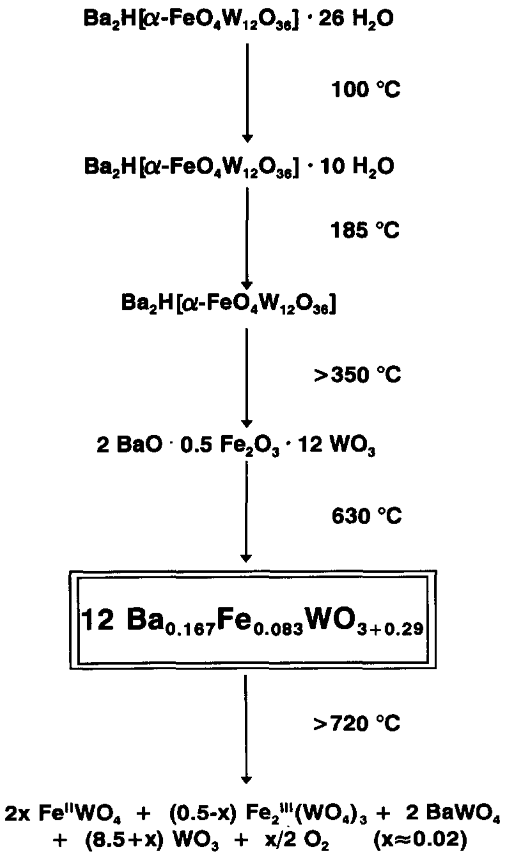
ions owing to a degradation of crystal and structural water. At 630°C, a clearly greater isomeric shift and a quadrupole splitting can be observed. The splitting results from an electric field gradient, caused by vacancies in the oxide lattice. The decreasing line width can be interpreted as the result of octahedrally coordinated Fe(III), whose distortion occurs over a relatively small range. For the final products of the thermal degradation at 950°C, two different Fe(III) positions can be deduced. The lines observed, the half-value widths (Γ) and the isomeric shifts (δ) for the current temperatures are summarized in Table 3.

It can be seen from the observation of the absorption line with an isomeric shift of 0.95 mm s^{-1} in the Mössbauer spectrum of a sample which was heated at 950°C, that traces of Fe(II) are present. While the bulk of the iron is trivalent in the form of $Fe_2(WO_4)_3$, some traces of Fe(II) are present as $FeWO_4$ with a $BaWO_4$ lattice. The formation of $FeWO_4$ is caused by the thermal decomposition of WO_3 above 900°C, when oxygen is released from the crystal. The liberated electrons are directly attracted by Fe^{3+} ions or, in a previous step, by W^{6+} ions. With the formation of $FeWO_4$ a thermodynamically stable compound is produced. This is corroborated by the fact the the mineral ferberite, $FeWO_4$, occurs in nature. Based on the results of the Mössbauer spectroscopic investigations, the two iron-containing compounds $Fe_2(WO_4)_3$ and $FeWO_4$ can be confirmed as the final products of the thermal degradation of Ba–FeW_{12}.

7. Summary

The polyoxometallate compound dibarium-α-dodecatungstoferrate(III)-26-hydrate, $Ba_2H[\alpha\text{-}FeO_4W_{12}O_{36}] \cdot 26H_2O$, contains the polyoxoanion $[\alpha\text{-}FeO_4W_{12}O_{36}]^{5-}$, which has been characterized by means of X-ray structure analysis as an α-KEGGIN structure. As a result of the thermal degradation of the starting compound Ba–FeW_{12}, the phase $Ba_{0.5}Fe_{0.083}WO_{3+0.29}$ has been investigated by means of thermal analysis (DTA, TG, DTG, DSC), X-ray diffraction methods, and IR, ESR and Mössbauer spectroscopy. The oxide bronze, formed at 630°C as a

pure phase, crystallizes hexagonally, within the structural type of a hexagonal tungsten bronze. The highly charged Ba^{2+} and Fe^{3+} cations bring about an extreme contraction of the lattice parameter *c* to a value of 7.389 Å. The stepwise thermal degradation of Ba–FeW_{12} in air leads at first to the compound $Ba_2H[\alpha\text{-}FeO_4W_{12}O_{36}]$, without hydrate water, which is stable up to 350°C. Above 350°C, 0.5 mol of structural water is released. This is linked with the decomposition of the KEGGIN anion. At 507°C, the recrystallization of the barium/iron hexatungstate, $Ba_{0.5}Fe_{0.5}W_6O_{19.75}$ ($Ba_{0.5}Fe_{0.083}WO_{3+0.29}$) begins. This is an exothermic process involving the release of $-127\ \mathrm{kJ\ mol^{-1}}$. The oxide bronze formed at 630°C as an individual phase, is stable at room temperature and decomposes further above 720°C. At 950°C, tetragonal WO_3, $BaWO_4$, $Fe_2(WO_4)_3$ and traces of $FeWO_4$ are present as the final products of the thermal decomposition. In conclusion, the thermal degradation of $Ba_2H[\alpha\text{-}FeO_4W_{12}O_{36}] \cdot 26H_2O$ is summarized in Scheme 1.



Scheme 1.

Acknowledgements

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