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THERMAL ANALYSIS OF APATITE STRUCTURE

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Abstract

Two types of thermal effects, caused by substitutions ($Ca^{2+}\leftrightarrow Na^{+}$, $PO_4^{3-}\leftrightarrow CO_3^{2-}$, SO_4^{2-}, $OH^{-}\leftrightarrow F^{-}$) in synthetic precipitated apatites as well as by sorption of Cd^{2+}, Zn^{2+}, and Cr^{3+} ions from the solutions were studied by TG/DTA, XRD and FTIR analysis. The temperatures of exothermic effect at 330–340°C and of decomposition of carbonate and sulfate apatites at 650–950°C were shown to depend on the substitutions in the apatite structure.

Keywords: apatite, Cd^{2+}, CO_3^{2-}, Cr^{3+}, F^{-}, Na^{+}, SO_4^{2-}, Zn^{2+}, substitutions, thermal analysis

Introduction

Apatite, a mineral with the formula $Ca_{10}(PO_4)_6X$ (X=F^-, OH^-, Cl^-), is an important raw material for phosphorous industry, a phosphorous migration controlling compound in soils and also a biomineral. The structure of apatite (Ap) is very tolerant of ionic substitutions and coupled substitutions frequently occur in apatites. The most widespread substitutions in the structure of natural and biological apatites are Na^+ and Mg^{2+} for Ca^{2+}, CO_3^{2-} for PO_4^{3-} and F^- for OH^- ions [1]. Natural and synthetic apatites have been found to be suitable materials for immobilization of toxic and radioactive metal ions in the environment [2–4].

The influence of F^-, CO_3^{2-}, Na^+ and Mg^{2+}substitutions in the apatite structure, including thermal effects caused by these substitutions, has been studied by numerous scientists, [1, 5–9]. The results obtained allow for the assumption that other cationic and anionic substitutions in the apatite structure can also be characterized by thermal analysis (TA).

The main aim of the study was to investigate the thermal effects caused by Zn^{2+}, Cd^{2+}, and Cr^{3+}sorption on apatite and SO_4^{2-}, F^-, CO_3^{2-}, and Na^+ substitutions in comparison with previously studied Na^+, Mg^{2+}, and CO_3^{2-} substitutions in apatite.

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Table 1 Chemical composition of apatites

Sample	Formula	Specific surface area/m^2 g^{-1}	Impurity mol CaF_2/mol Ap	Mol ratios M/Ca in apatites		
				Zn/Ca	Cd/Ca	Cr/Ca
	Hydroxy- and carbonateapatites					
HA-1	$Ca_{9.95}(PO_4)_{5.90}(CO_3)_{0.10}(OH)_2\cdot 2.01H_2O$	36.3	0	0.021	0.033	0.075
HA-2	$Ca_{9.89}(PO_4)_{5.77}(CO_3)_{0.23}(OH)_2\cdot 1.88H_2O$	85.4	0	0.055	0.069	0.090
A1-3	$Ca_{9.97}(PO_4)_{5.94}(CO_3)_{0.06}(OH)_2\cdot 1.77H_2O$	31.0	0	0.025	0.033	
A1N2	$Ca_{9.47}Na_{0.20}(PO_4)_{5.94}(CO_3)_{0.06}(OH)_{1.2}\cdot 1.58H_2O$	–	0		0.018	
D2-2	$Ca_{9.51}(PO_4)_{5.63}(CO_3)_{0.37}F_{0.35}(OH)_{1.04}\cdot 1.47H_2O$	55.0	0	0.038	0.044	0.081
F0C1	$Ca_{9.68}(PO_4)_{5.39}(CO_3)_{0.61}(OH)_2\cdot 1.91H_2O$	22.1	0			
F3C1	$Ca_{10}(PO_4)_{5.64}(CO_3F)_{0.36}F_{1.37}(OH)_{0.63}\cdot 1.52H_2O$	11.4	0.14			
F4C1	$Ca_{10}(PO_4)_{5.62}(CO_3F)_{0.39}F_{1.10}(OH)_{0.90}\cdot 1.41H_2O$	18.3	0.3			
F0C2	$Ca_{9.31}(PO_4)_{4.71}(CO_3)_{1.29}(OH)_2\cdot 1.52H_2O$	18.5	0			
F2C2	$Ca_{9.71}(PO_4)_{4.76}(CO_3)_{0.57}(CO_3F)_{0.67}F_{0.19}(OH)_{1.81}\cdot 1.83H_2O$	12.7	0			
F4C2	$Ca_{9.98}(PO_4)_{4.67}(CO_3)_{0.05}(CO_3F)_{1.28}F_{0.34}(OH)_{1.66}\cdot 1.86H_2O$	11.0	0			
	Sulfateapatites					
AS1	$Ca_{9.34}(PO_4)_{4.79}(SO_4)_{1.04}(CO_3)_{0.16}(OH)_{1.78}\cdot 1.96H_2O$	18.8	0			
AS3,5	$Ca_{9.61}(PO_4)_{5.22}(SO_4)_{0.67}(CO_3)_{0.11}(OH)_{1.01}F_{0.99}\cdot 1.95H_2O$	15.6	0.24			
AS4	$Ca_{9.35}(PO_4)_{4.72}(SO_4)_{1.08}(CO_3)_{0.21}(OH)_{0.69}F_{1.31}\cdot 1.30H_2O$	15.3	0.29			
AS1Na	$Ca_{9.63}Na_{0.16}(PO_4)_{5.42}(CO_3)_{0.05}(SO_4)_{0.52}(OH)_2\cdot 1.35H_2O$	–	0			
AS4Na	$Ca_{9.75}Na_{0.09}(PO_4)_{5.58}(CO_3)_{0.03}(SO_4)_{0.39}F_{1.83}(OH)_{0.17}\cdot 0.97H_2O$	–	0			

Experimental

Apatites with partial substitutions of Na^+, CO_3^{2-}, SO_4^{2-} and F^- were prepared by the precipitation method [8]. The apatites were identified as B-type carbonateapatites (CAp) or sulfateapatites (SAp), where CO_3^{2-} or/and SO_4^{2-} is substituted for PO_4^{3-}. The calculations of the molecular formula of apatite (Table 1) are based on the data of chemical analyses [8], assuming that the sum of P and C atoms equals six and considering the electroneutrality principle. The apatite samples used for binding Cd^{2+}, Zn^{2+}, and Cr^{3+} ions in aqueous solutions (pH=6) [4] were studied and compared with samples leached at pH=6.

The thermal analysis was carried out by a Setaram LabSys 2000 instrument at heating rate of 10°C min^{-1} in an air flow of 40 mL min^{-1} in Pt crucible, at sample mass ~30 and ~120 mg. The samples for IR and XRD analyses were calcined up to a selected temperature. The XRD analysis was carried out with a DRON-4 diffractometer ($2\Theta=8$–60°, step size 0.04°). IR spectra were obtained on an Interspectrum 2000 FTIR spectrometer in the range of 400–4000 cm^{-1}, using the KBr pellets (300 mg KBr/1 mg sample).

Results and discussion

Thermal analysis

In the course of calcination of precipitated Aps mainly three stages of mass loss can be differentiated (Fig. 1).

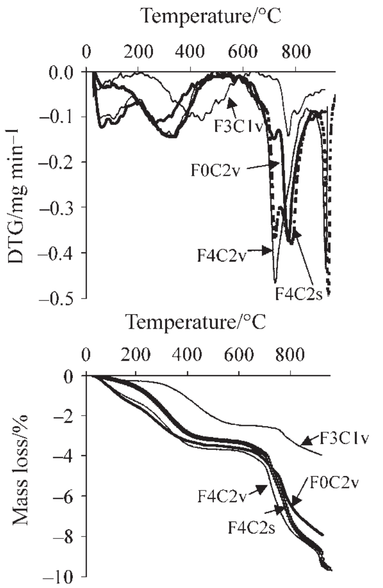

Fig. 1 DTG and TG curves of CAps F3C1, F0C2, and F4C2 on calcination in the air flow. Heating rate 10°C min^{-1}. Sample mass: s – ~120 mg, v – ~30 mg

1) The adsorption water (0.8–3%) is released at temperatures from 30 to 200°C [1].

2) The lattice water (1.3–3.8%) and some CO_2 (0.3–0.6%) [1, 9] evolves at 200–600°C. In the majority of cases for precipitated apatites and always for leached samples an exothermic effect appears at 330–340°C in the differential thermal analysis (DTA) curve (Fig. 2), indicating a reorganization in the structure. In the same temperature interval the speed of mass loss increases. The effect is a sum of two energetically opposite processes and the value of the thermal effect is not the real one, therefore not to be used for characterization of the reaction.

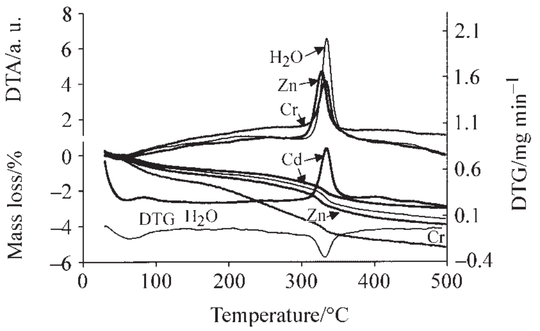

Fig. 2 TG, DTG and DTA curves of the leached sample HA–1 and of the samples used for sorption of Cd^{2+}, Zn^{2+}, and Cr^{3+} ions in a solution. Heating rate 10°C min^{-1} in the air flow. Sample mass ~30 mg

The temperature of the exothermic peak top changes depending on the composition of the sample (Table 2), but it is not directly related to the water content. An increase in the carbonate content in apatite from 0.8% (samples HA and A) to 5.5–6% (samples FC2) causes a shift of the peak top from 334–335 to 337°C.

For the apatites used for binding metal ions the exothermic effect is shifted to lower temperatures. The biggest change in the peak position (– 4.3 — – 7.4°C) appears for Zn^{2+} ions. When Cd^{2+} and Cr^{3+} are incorporated into apatite, the effect is smaller: the maximum shift for Cd was –2.6° and for Cr –1.9°, in spite of their bigger amounts bound compared with Zn^{2+} (Tables 1 and 2). Therefore, the shift of an exothermic peak position is related to the metal ion bound and its influence on apatite structure, the bond with water included.

In general fluorine has a very important role in the apatite structure and many characteristics depend on it [1], however, the temperature of the exothermic effect in CAps (FC1, FC2) does not depend on the fluorine content. This result supports the conclusion that most of the lattice water in Ap is related to carbonate ions [5].

3) CAp loses a major part of its carbonate in the temperature range from 600 to 1000°C in 1–3 steps depending on its composition (Table 2). As a result of an increase in the carbonate and fluorine content in Ap, the temperature of CO_2 evolvement decreases. The biggest mass loss in CAp with C/P≈0.1 (the samples C1) and C/P≈0.3 (the samples C2) occurs at 810–880 and at 700–800°C, respectively (Fig. 1). The different temperatures of decomposition were assigned to two different positions

Table 2 Data of thermal effects in apatite

A Samples used for metal ions binding

Sample	T/°C	ΔM/%	With Zn		With Cd		With Cr	
			T/°C	ΔM/%	T/°C	ΔM/%	T/°C	ΔM/%
HA-1*	334.4	–2.5	327.0	–2.6	334.0	–2.1	332.5	–3.6
HA-2*	335.7	–2.3	331.4	–1.9			334.5	–3.5
A1-3*	335.5	–2.1	329.5					
A1N2*	336.0	–2.5			332.0	–2.4		
D2-2*	335.6	–1.5	329.0	–1.3	333.0	–1.8	334.0	–2.7

B Thermal effects in carbonate and sulfate apatites

Sample	T/°C	ΔM/%	Temperature of the peak tops of endothermic effects/°C				T/°C
F0C1	336.3	–2.2			880	940	
F2C1	336.9	–2.1		770	810		
F4C1	336.1	–1.6	680	770			
F0C2	337.2	–2.0		776	813		
F2C2	337.6	–2.5		741	780		
F4C2	337.2	–2.8	717	780		920	
AS1	–	–3.0					
AS3,5	–	–2.3					826
AS4	340.3	–2.3				923	703
AS1Na	415.7	–1.9					
AS4Na	–	–1.3					704

* The leached samples
T – Temperature of a peak of exothermic effect
ΔM – Mass change according to exoeffect at 300–400°C

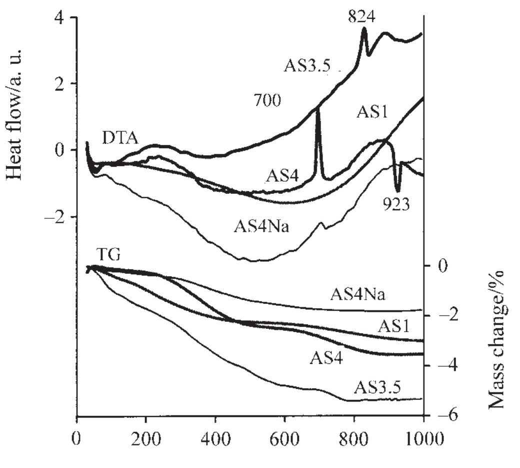

Fig. 3 DTA and TG curves of SAps AS1, AS3,5, AS4, and AS4Na. Heating rate 10°C min^{-1} in the air flow. Sample mass ~30 mg

of carbonate ions in the structure of fluorcarbonateapatite [6]. From the studied samples CO_2 evolves mainly in two steps, with an exception of sample F4C2, which decomposes in three steps. This allows to presume that there may be more than two positions for carbonate ions in fluorhydroxycarbonate apatite structure [1].

The mass of SAps decreases in correlation with the CO_3^{2-} ions content (0.2–1.0%) at 600–900°C. A sharp exothermic peak appears at 824°C (Fig. 3), if the content of F>0.7 mol/mol Ap and is shifted to lower temperatures with an increase in the fluorine content. The exo-effect is a result of $CaSO_4$ displacement reaction in the Ap structure [11]. The temperature of SAp decomposition is not influenced by Na substitution into the Ap structure. The endothermic effect at 920–940°C is a result of $CaSO_4$–CaF_2 fusion [11].

XRD analysis

The evolvement of lattice water on heating up to 500°C is accompanied by a slight decrease in the unit cell parameter *a* of hydroxyapatite (HAp) [1] and SAp, whereas for CAps it increases. At that temperature, a reduction in the regularity of crystals, expressed by an increase in the half-width of the peaks of XRD spectra, is observed (Fig. 4). This indicates an important role of water in the structure of precipitated Aps.

As a result of CO_3^{2-} and SO_4^{2-} displacement from Ap structure at temperatures above 600°C the unit cell parameter *a* achieves almost the value of pure HAp or FAp and the crystallinity improves again.

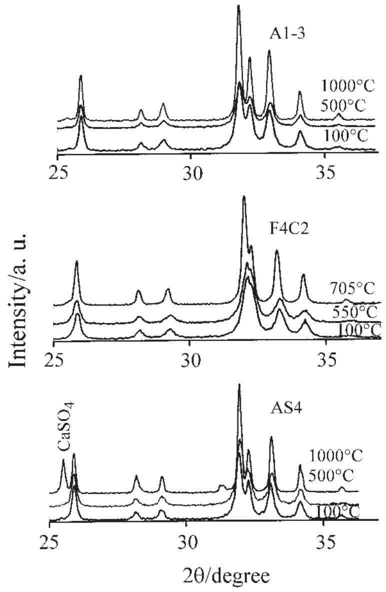

Fig. 4 XRD spectra of apatites A1-3, F4C2, and AS4 calcined at different temperatures

IR spectroscopy

In the IR spectra of CAps heated to 500°C, changes in the region of CO_3^{2-} ν_3 mode take place, more obvious for the samples with a high carbonate content. Several side-bands appear next to the main bands that locate at 1414–1428 and 1454–1458 cm^{-1} and the ν_2 shifts from 876 to 879 cm^{-1} [1, 10] (Fig. 5). Therefore, the bonds of CO_3^{2-} in Ap structure are related to structural water and the evolvement of water makes them more labile. Relocation of CO_3^{2-} ion into A-position on the hexagonal axis can be an-

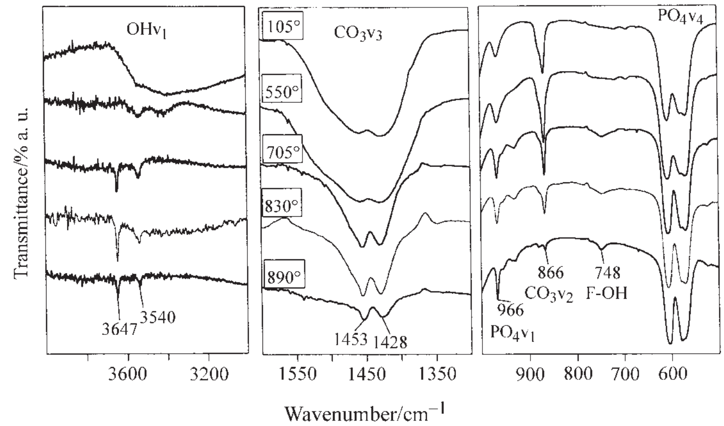

Fig. 5 IR spectra of sample F4C2 calcined at different temperatures

ticipated as the peaks at 1502 and 1542 cm^{-1} appear [10]. No significant changes are observed in the spectra of HAps and SAps. In the IR spectra of Aps used for metal ions sorption no additional changes were observed either.

On calcination of CAps at higher temperatures the intensities of CO_3^{2-} ν_2 and ν_3 modes decrease: first the side bands and then, above 830°C, the bands at 1458 and 876 cm^{-1} assigned to CO_3^{2-} groups related to OH^- and the bands at 1428, 1454 and 867 cm^{-1} assigned to CO_3^{2-} groups related to F^- (Fig. 5). At the same time OH^- bands at 3647 cm^{-1} from $Ca(OH)_2$ appear in the spectra of calcined samples in addition to OH^- bands at 3540 cm^{-1} that belong to the apatite structure. $Ca(OH)_2$ originates from the moisture binding with CaO.

In the IR spectra of calcined SAps, the intensity of the peaks characteristic of SO_4^{2-} ion in Ap hexagonal structure ν_4=648 cm^{-1} decreases and the peak of SO_4 in orthorhombic $CaSO_4$ appears at 680 cm^{-1} as a result of thermal changes [11].

Conclusions

It was shown that all thermal effects taking place during the calcination of apatites are related to structural changes and their temperatures are characteristic of that particular type of substitution.

The structural changes in apatite established by thermal analysis with complementary data of IR spectroscopy and XRD were as follows:

1) Evolvement of lattice water between 20–500°C was accompanied by reorganization in the apatite structure. The temperature depends on the carbonate content and the kind of cations bound with apatite by sorption, rising with an increase in the CO_3^{2-} content and dropping in case of cationic substitutions.

2) Displacement of SO_4^{2-} ions in the temperature range 700–1000°C, the exact value of which depends on the fluorine content in the apatite.

3) Displacement of CO_3^{2-} ions and evolvement of CO_2 at 600–950°C. The temperatures of CO_2 evolvement depend on the carbonate and fluorine content in the apatite. The data of thermal analysis indicate on the existence of different positions for carbonate ions in the apatite structure.

4) No significant effect of Na^+ substitution in apatite structure on the thermal changes was detected.

The results obtained allow the conclusion that thermal analysis can be used for characterization of structural substitutions in apatite.

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