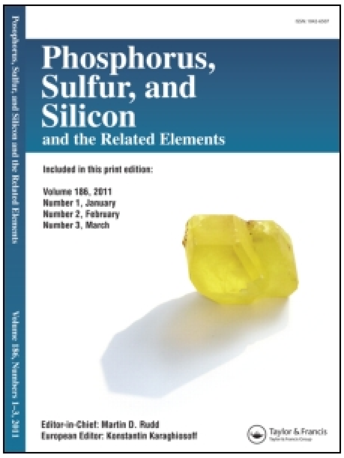

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Kaia Tõnsuaadu[a]; Merike Peld[a]; Michel Quarton[b]; Villem Bender[a]; Mihkel Veiderma[a]
[a] Department of Basic and Applied Chemistry, Tallinn Technical University, Tallinn, Estonia [b] Laboratory of Solid State Crystal Chemistry, University P. and M. Curie, Paris Cedex, France

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STUDIES ON SO_4^{2-} ION INCORPORATION INTO APATITE STRUCTURE

Kaia Tõnsuaadu,[a] *Merike Peld,*[a] *Michel Quarton,*[b]
Villem Bender,[a] *and Mihkel Veiderma*[a]
Department of Basic and Applied Chemistry, Tallinn Technical University, Tallinn, Estonia[a] *and Laboratory of Solid State Crystal Chemistry, University P. and M. Curie, Paris Cedex, France*[b]

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Calcium sulphate-apatites were synthesised by precipitation from aqueous solutions with different fluorine content and analyzed by chemical, x-ray diffraction (XRD), Raman, and Fourier transform infrared (FTIR) analyses. Their thermal stability was studied by differential scanning calorimetry (TG/DSC) and high-temperature XRD. It was established that the introduction of SO_4^{2-} *into apatite structure and the thermal changes depend on the fluorine content in the apatite structure. At temperatures above 600°C the structure of apatite reorganizes and* $CaSO_4$ *forms a separate phase.*

Keywords: Apatite; fluorine; substituted; sulfate; thermal stability

Apatite (Ap) is known as a mineral in the structure of which different substitutions can occur. Replacement of PO_4^{3-} ions with SO_4^{2-} ions has been found in the structure of natural Aps. The main goal of this work was to study the introduction of SO_4^{2-} ions into Ap structure on precipitation and the thermal stability of such Aps.

The Aps were synthesized by precipitation from aqueous solutions with a constant S:P ratio and different fluorine content at pH 9–10 and $T = 80°C$.[1] The products were characterized by chemical, x-ray diffraction (XRD), Raman, and Fourier transform infrared (FTIR) methods. The thermal stability was studied by differential scanning calorimetry (TG/DSC) and high-temperature XRD.

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Address correspondence to Kaia Tõnsuaadu, Department of Basic and Applied Chemistry, Tallinn Technical University, Ehitajate tee 5, 19086 Tallinn, Estonia.

TABLE I Chemical Composition of Sulfoapatites

Sample	Formula	mol CaF_2/mol Ap
AS1	$Ca_{9.34\ 0.66}(PO_4)_{4.79}(SO_4)_{1.04}(CO_3)_{0.16}(OH)_{1.78}F_{0.22}$	—
AS2	$Ca_{9.64\ 0.36}(PO_4)_{5.30}(SO_4)_{0.62}(CO_3)_{0.07}(OH)_{1.62}F_{0.38}$	0.07
AS3	$Ca_{9.70\ 0.30}(PO_4)_{5.40}(SO_4)_{0.49}(CO_3)_{0.11}(OH)_{1.04}F_{0.96}$	0.02
AS3,5	$Ca_{9.61\ 0.39}(PO_4)_{5.22}(SO_4)_{0.67}CO_3)_{0.11}(OH)_{1.01}F_{0.99}$	0.24
AS3,75	$Ca_{9.43\ 0.57}(PO_4)_{4.85}(SO_4)_{0.91}(CO_3)_{0.25}(OH)_{0.79}F_{1.21}$	0.51
AS4	$Ca_{9.35\ 0.65}(PO_4)_{4.72}(SO_4)_{1.08}(CO_3)_{0.21}(OH)_{0.69}F_{1.31}$	0.29
ASC1	$Ca_{9.01\ 0.99}(PO_4)_{4.02}(SO_4)_{0.51}(CO_3)_{1.47}(OH)_{1.27}F_{0.73}$	1.04
ASC2	$Ca_{9.09\ 0.91}(PO_4)_{4.19}(SO_4)_{0.89}(CO_3)_{0.92}(OH)_{0.72}F_{1.28}$	0.78

All synthesized samples had the apatitic structure. The formulas of the Aps, derived from the results of chemical analyses, are given in Table I. The samples with fluorine contain a certain amount of CaF_2. The lowest amount of SO_4^{2-} ions incorporated into Ap structure (0.49 mol/mol Ap) was found at F^- content 0.96 mol/mol Ap, and the highest amount (1.04–1.08) was established in hydroxyapatite (AS1) and fluorapatite (AS4). Simultaneous incorporation of CO_3^{2-} ion is also possible and depends on its content in the solution.

The incorporation of SO_4^{2-} ions into Ap structure increases the unit cell parameter *a* by about 0.15 Å in the case of HAp. The increase in *a* is less marked in fluorine containing Aps.

The thermal analysis (Figure 1) revealed that reorganization of the sulfate-Aps structure takes place almost at the same temperatures as that of carbonate-Aps, at 650–830°C. A sharp exothermic peak appears at 824°C if (F) $>$ 0.7 mol/mol Ap in a sample, and is shifted to lower temperatures with an increase in fluorine content. An endothermic effect at 920–940°C is a result of $CaSO_4$–CaF_2 fusion.

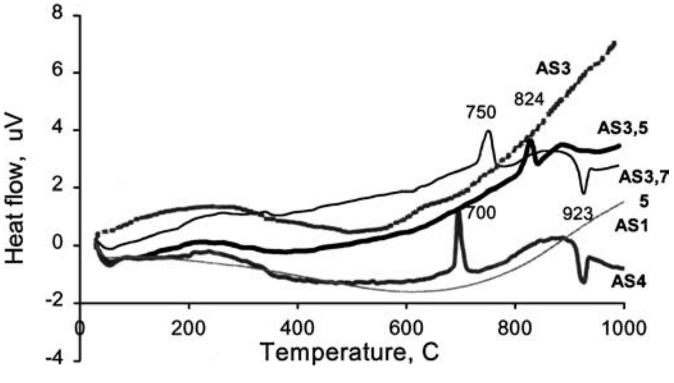

FIGURE 1 DSC curves of sulfate-apatites (heating rate 10 deg min^{-1} in air flow 30 ml min^{-1}).

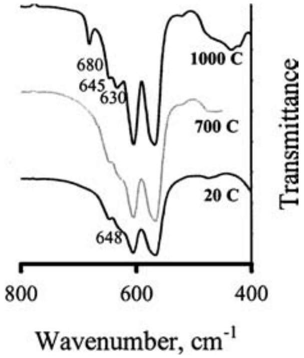

FIGURE 2 FTIR spectra of sample AS1.

In the IR and Raman spectra (Figures 2 and 3), peaks characteristic of SO_4^{2-} ion in hexagonal structure $\nu_4 = 648$ (IR) and $\nu_1 = 1007$ cm^{-1} (R) were found.[2,3] As a result of thermal changes, the ν_4 peak of SO_4 in orthorhombic $CaSO_4$ appears at 680 cm^{-1} in IR spectra and the ν_1 peak appears at 1018 cm^{-1} in Raman spectra. The high-temperature XRD analysis of sample AS4 confirmed the formation of $CaSO_4$ at temperatures above 700°C. As a result of calcination, the parameter a of the unit cell of the fluorine-rich Aps decreases and presents at 1000°C almost the value of the FAp one ($a = 9.373$ Å). Some SO_4^{2-} ions remain in the HAp structure also at 1000°C.

The introduction of SO_4^{2-} ions into the Ap structure depends on the fluorine and carbonate content in the solution. The FAp structure has a stricter atomic arrangement and the substitutes are displaced at lower temperatures than from HAp.

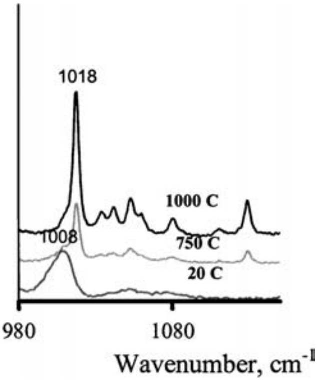

FIGURE 3 Raman spectra of sample AS4.

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