BIOCOMPATIBLE MATERIALS BASED ON SYNTHETIC APATITES CO-DOPED WITH SILVER AND LUTETIUM IONS

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Apatite based (CaHap and CaFap) materials were synthesized by saline–melt method at moderate temperature. Their structure and composition have been studied by X-ray phase analysis (XRPA) and IR spectroscopy of diffuse reflectance. The specimens of materials were identified as partially substituted (OH^- by Cl^- and F^- by OH^- in CaHap and CaFap, respectively) compounds. Annealing of apatite based materials in Ag^+- and Lu^{3+}- containing solutions resulted in sorption of the above mentioned ions, which was suggested by XRPA, electron spectroscopy of diffuse reflectance, and chemical analysis.

Apatites due to their universality are applied in many fields of activity. They can be used as sensor controls, sorbents, phosphors, biocompatible implants, etc. Apatites include compounds with general formula $M_{10}(PO_4)_6X_2$, where M is Ca, Sr, Ba, Pb; X is OH, F, Cl. In nature, calcium apatites are rather widespread, being a component of bones and teeth of vertebrates.

Methods of obtaining of apatites by solid-phase synthesis ("dry" synthesis) and by interaction in aqueous solutions ("wet" synthesis) are well known [1, 2]. Each of these methods possesses, alongside with advantages, a number of disadvantages. We have developed a technique for obtaining of calcium hydroxylapatite (CaHap) and calcium fluorapatite (CaFap) in saline melts at moderate temperatures (500-700°C). Thus, there occurs an intensification of process of synthesis, due to acceleration of movement of particles in a melt in comparison with a solid. The method with use of saline melts as media for synthesis (basically of complex oxides) and growing-up of single crystals is known for quite a long time [3]. A chloride melt of NaCl-KCl of equimolar composition, having a fusion temperature of 665°C, is used as medium for synthesis.

$CaCO_3$, CaO, $Ca(OH)_2$ (in case of CaHap) or CaF_2 (in case of CaFap), and $NaPO_3$ have been taken as initial components for carrying out synthesis of apatites in chloride melt [4]. It is shown that at interaction of $CaCO_3$, CaO, $Ca(OH)_2$, and CaF_2 with melt of NaCl-KCl, a decrease of temperature occurs due to formation of incongruently melting compound $KCaCl_3$ (its formation is proved by diagram of the state of system KCl-$CaCl_2$ [5]). Interaction of $NaPO_3$ with NaCl-KCl melt leads to formation of glassy-like compound $Na_6P_4O_{13}$. At reception of apatites the ratio batch mixture: saline melt was 1:1. Synthesis was carried out in a muffle furnace at the temperature 700ºC during 2 h. Interaction occurs by the following schemes

$$6NaPO_3 + 6CaO + 3CaCO_3 + Ca(OH)_2 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 3Na_2CO_3, \quad (1)$$

$$6NaPO_3 + 6CaO + 3CaCO_3 + CaF_2 \rightarrow Ca_{10}(PO_4)_6F_2 + 3Na_2CO_3 \quad (2)$$

The obtained materials were tested using the X-ray phase and structure analysis, electron and IR-spectrophotometery, and chemical analysis. A DRON-3 automated diffractometer in a discrete regime (step scan (0.02-0.05)˚, counting time (4-8) s) using the filtered copper radiation (anode voltage 30 kV, current 20 mA, entrance slits 2.4 mm, detector slit 0.1 mm).

The angle interval (2θ) of diffraction spectra registration for the phase analysis was 25-85˚. The diffraction spectra for crystal structure determination were registered in a whole angle range. The preliminary treatment of the diffraction spectra was carried out by full profile analysis. The centers of gravity of the peaks and their integrated intensities have been determined within the accuracy of ± (0.001÷0.005) and ± (5÷15)%, respectively. The phase analysis and structure calculations were carried out using own apparatus and software complex developed earlier.

IR-reflectance spectra in the interval of wavenumbers 4000 – 400cm^{-1} were recorded with the use of Thermo Nicollet Nexus FTIR (OMNIC) using a SMART Collector diffuse reflectance adapter. More than 50 scans with a step interval of 8 cm^{-1} were performed for the data collection.

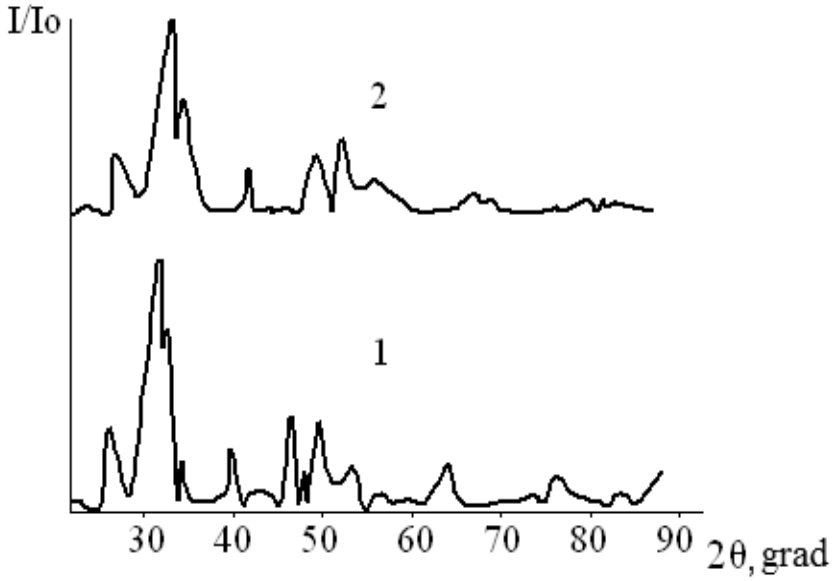

Fig. 1. Diffraction spectra of CaHap (curve 1) and CaFap (curve 2) synthesized in NaCl-KCl melt.

Figure 1 shows diffractograms of CaHap and CaFap; their kind specifies synthesized samples in high degree of crystalline and structural perfection of products of synthesis. However, parameters of crystal lattices of materials significantly differ from standard values; namely, the parameters *a* and *b* are appreciably more in comparison with demanded ones, and the parameter *c* in case of CaHap is less (table). It may be a result of a deviation from stoichiometry of the structure of apatites.

Results of quantitative X-ray phase analysis of materials based on apatites.

Type of material	Parameters of the lattices, Å		
	a	*b*	*c*
CaHap [1]	9.4180	9.4180	6.8810
CaHap (initial)	9.4718	9.4718	6.8576
CaHap (doped)	9.4789	9.4789	6.8654
CaHap (doped&washed)	9.4729	9.4729	6.8593
CaFap [1]	9.3680	9.3680	6.8830
CaFap (initial)	9.3735	9.3735	6.8833
CaFap (doped)	9.3719	9.3719	6.8806
CaFap (doped&washed)	9.3734	9.3734	6.8830

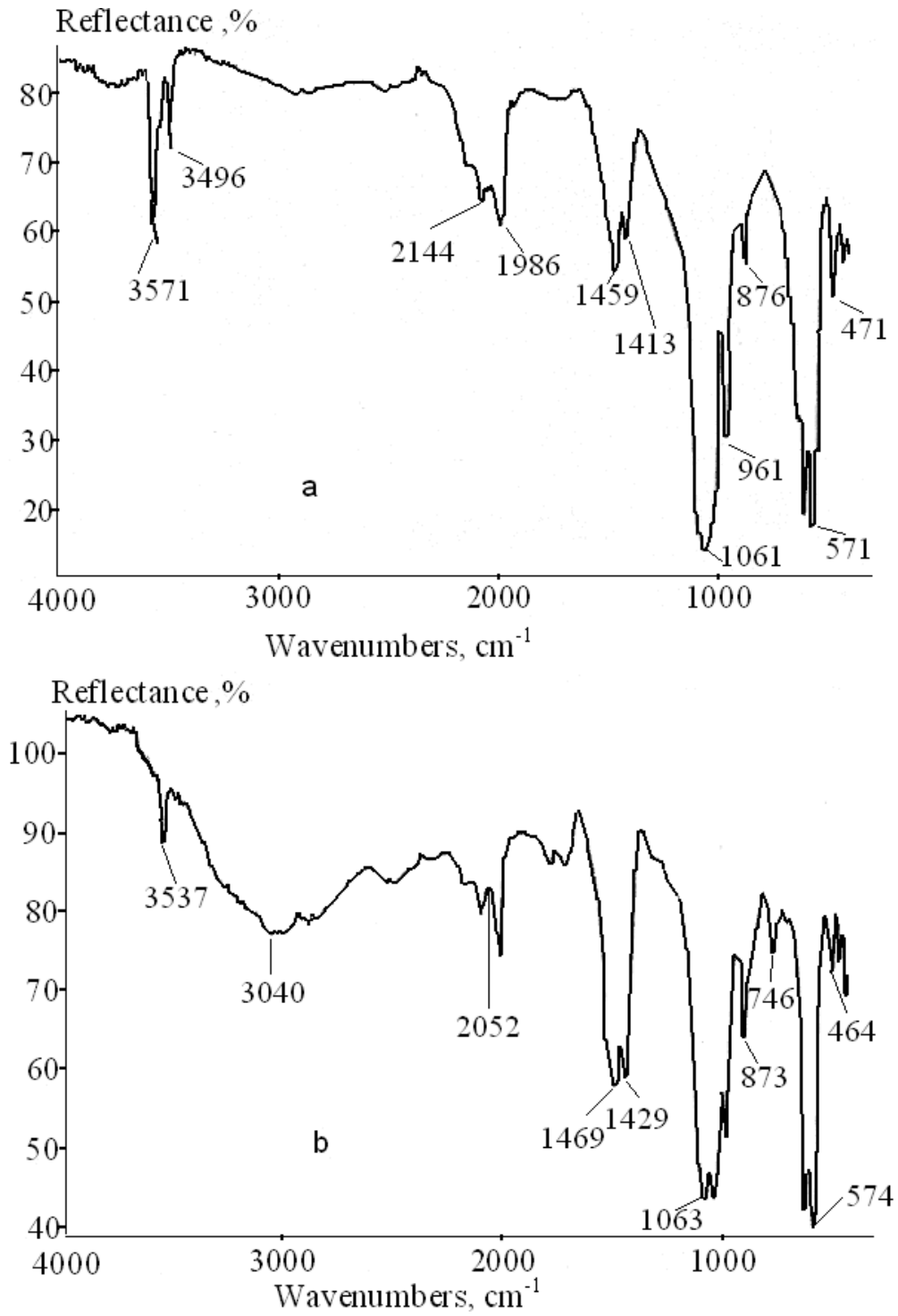

Fig. 2. IR–reflectance spectra of CaHap (a) and CaFap (b) synthesized in saline melt NaCl-KCl.

As stated above, IR diffuse-reflectance spectra of apatites (Fig. 2) serve. In additions to the characteristic for grouping PO_4^{3-} absorption bands in a range of 1100-450 cm^{-1}, other features are also available on them. As might be expected, a sharp peak of absorption characteristic of OH^- ions is shown on IR-reflectance spectra of CaHap at frequencies about 3570 cm^{-1}. However, it is accompanied by a less expressed peak near 3500 cm^{-1}. As it is shown by the author of [3], its occurrence can be caused by the presence of strong hydrogen bond

OH ••• Cl. Considering that synthesis of CaHap (as well as CaFap) was carried out in chloride melt, occurrence of Cl^- ions in the structure of calcium hydroxylapatite by partial substitution of groupings OH^- is quite possible. It can serve also an explanation of distortion of the lattice parameters of CaHap. Partial substitution for CO_3^{2-} ions in the anionic sublattice can be another explanation for the distortion of the lattice parameters. Actually, substitution of hydroxyl (OH^-) by CO_3^{2-} ions (A-type) should lead to the above described distortions of the lattice parameters for CaHap. However, the position of the peaks (at 1459, 1413, and 876 cm^{-1}) in the CO_3^{2-} absorption band rather indicates on a B-type of substation (i.e., substation of PO_4^{3-} groups by CO_3^{2-} ones) which, in turn, should lead to the inverse phenomenon – to some reduction of the parameters *a* and *b*.

With the use of the rule of additivity of lattice parameters (the Vegard's law) at isomorphic substitution

$$a_i(b_i, c_i) = a_1(b_1, c_1)\ (1-x) + a_2(b_2, c_2)\ x, \tag{3}$$

where a_1, b_1, c_1 are the parameters of a lattice of "owner", i.e., of the original lattice, and a_2, b_2, c_2 are the parameters of lattice of "visitor", i.e., the lattice of the contamination or dope, *x* is the molar fraction of the "visitor" (degree of substitution, i.e., the fraction of the replaced anions), the value $x \approx 0.25$ is estimated. This value is in a qualitative accordance with the ratio of intensities of absorption peaks for "free" and "hydrogen-bond connected" OH^- groups on IR-spectrum for CaHap. As to CaFap, its IR-spetrum, as a whole, is similar to IR-spectrum for CaHap. The difference consists in much higher intensity of an absorption band of CO_3^{2-}-groups in the case of CaFap, which counts in favor of higher degree of substitution of PO_4^{3-} (as the position of peaks in the band CO_3^{2-} has not significantly changed). The interesting fact is occurrence of wide "hydrates" bands with a minimum at 3040 cm^{-1}, as well as a sharp absorption band peak for OH^- ions at 3537 cm^{-1} (its shift is probably caused by strong hydrogen bond OH ••• F). Substitution of ions F^- for OH^-, obviously, is a principal cause of change of lattice parameters of CaFap in comparison with standard values. Using the technique described above, we have estimated the substitution degree $x \approx 0.12$. Thus, synthesized samples of apatites represent carbonate-replaced (mainly of B-type) CaHap and CaFap with partial substitution in OH^- and F^- sublattices, accordingly, for Cl^- ••• OH^- ions. This substitution should affect various properties of the synthesized apatites.

The apatites synthesized in saline melt were earlier tested as sorbents of ions of heavy metals, in particular, Pb^{2+} and Cu^{2+} [6]. In the present work, we made a shot at preparation of argentiferous apatites as perspective biocompatible materials with antimicrobial characteristics. Treatment of the synthesized apatites in $AgNO_3$ solution (0.1 mol/dm^3) led to a fast (within 1-1.5 h) entire fracture of sorbents. Products of this destruction are Ag_3PO_4, $Ca_{10}(PO_4)_6(OH)_2$/ $Ca_{10}(PO_4)_6F_2$, and unidentified phases. The fracture process is obviously caused by discrepancy of charges and the sizes of Ca^{2+} and Ag^+ ions. Electron diffuse reflectance spectra in the UV-range of products of a spectrum for destruction, presented in Fig. 3 suggest this fact.

For prevention of undesirable processes of apatite structure destruction, instead of $AgNO_3$ as a sorbent, we used a mixture of $AgNO_3$ and Lu $(NO_3)_3$ in a solution with concentration of 0.0096 and 0.018 mol/dm^3, respectively. It was supposed that the combination of Ag^+ and Lu^{3+} ions, in which

$$Z_{Ag}{}^{+} + Z_{Lu}{}^{3+} = 2Z_{Ca}{}^{2+},\ r_{Ag}{}^{2+} + r_{Lu}{}^{3+} = 2r_{Ca}{}^{2+}, \tag{4}$$

where $Z_{i\ and}\ r_i$ are the ionic charge and radius, respectively, will allow breaking of a discrepancy barrier.

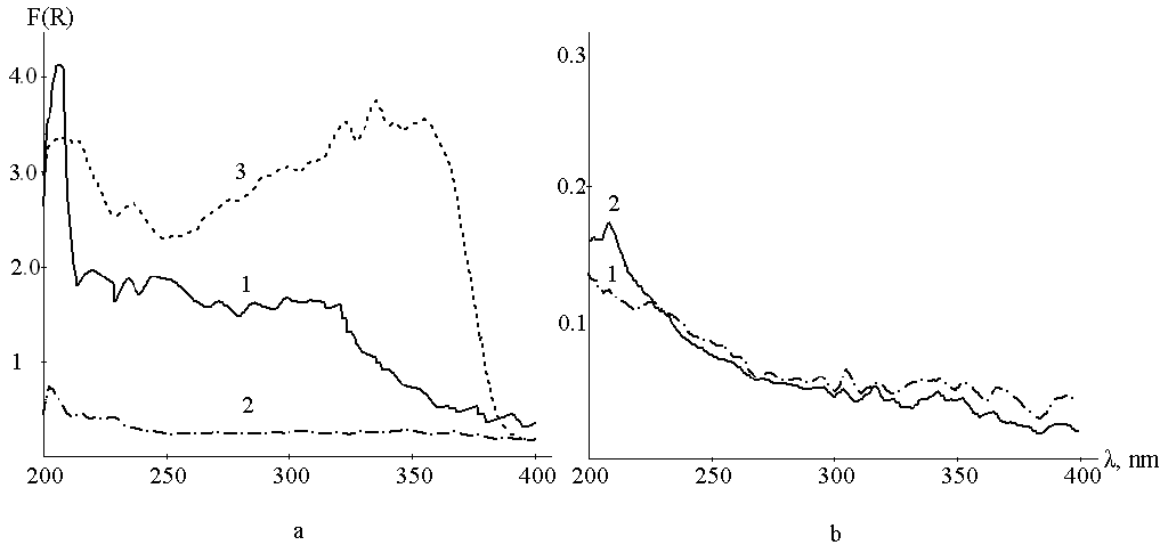

Fig. 3. Diffuse reflectance spectra for products of Ag^+ incorporation into CaHap (*1*) and CaFap (*2*): a) 0.1 mol/dm^3 $AgNO_3$ solution (*3* depicts pure $AgNO_3$ powder), b) 0.025 mol/dm^3 $AgNO_3$ + 0.045 mol/dm^3 $Lu(NO_3)_3$ solution.

It is established that at interaction of a sorbent (CaHap or CaFap) with a solution of the resulting composition, appreciable destruction of apatite structure is not observed. Thu, significant (to $C_{Ag}{}^+$ = 0.0057 mol/dm^3 for CaHap and $C_{Ag}{}^+$ = 0.0055 mol/dm^3 for CaFap) weakening of the solution occurs, which is indicative of a successful sorption of its components. Electronic diffuse reflectance spectra in the UV-range for samples after sorption (without washing) (Fig. 3b), on which absorption bands of rather high (F (R) ≈1 and more) intensity are observed, also testify to this process. It is necessary to note that washing of samples by water leads to gradual desorption (at least of Ag^+ ions), that is expressed in considerable reduction of intensity of adsorption bands. As follows from the table, a change in the lattice parameters of apatites is observed in the process of sorption; namely, in the case of CaHap, the parameters *a, b,* and *c* appreciably grow, and in the case of CaFap the inverse phenomenon takes place. After careful washing of sorbents, the lattice parameters of CaHap and CaFap approach those for initial materials. The reasons of the specified change in the lattice parameters still have no explanation. It is possible that sorption of ions from solution on CaHap and CaFap has equivalent character. The NO_3^- ion might occupy different positions in cases of either CaHap or CaFap: in the first case it is the position of the "free" hydroxyl (OH^-) ion.

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