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Investigation of vibration anharmonicity in the crystal lattice of the mixed composition apatites

V.L.Karbivskyy, A.P.Shpak, N.A.Kurgan, V.V.Vishnyak, O.P.Dimitriev, V.H.Kasiyanenko

G.Kurdyumov Institute for Metal Physics, National Academy of Sciences of Ukraine, 36 Vernadsky blvd., 03680 Kyiv, Ukraine

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The study results of the influence of lattice crystal field on the structure of the IR vibrational bands in the tetrahedral sublattice of the crystal $(PO_4)^{3-}$ with the isomorphous anionic substitution of compounds $Ca_{10}(PO_4)_{6-x}(VO_4)_x(M)_2$, where $M = OH^-$, F^-, Cl^-, $x = 0$, 1, 3, 5, 6 were considered. It was established that the decrease in of IR absorption half-width characterizing XO_4 tetrahedra is associated with a decrease in the interaction between the tetrahedra of the same type, and as a consequence, the suppression of vibration anharmonicity in quasi-free tetrahedra. High sensitivity of chlorapatites matrix to changes of vibrations in tetrahedral sublattice by doping affects the thermal stability of compound.

Рассматриваются результаты исследования влияния кристаллического поля решетки на структуру ИК-колебательных полос тетраэдрической подрешетки кристалла $(PO_4)^{3-}$ при изоморфных анионных замещениях соединений $Ca_{10}(PO_4)_{6-x}(VO_4)_x(M)_2$, где $M = OH^-$, F^-, Cl^-, $x = 0$, 1, 3, 5, 6. Установлено, что уменьшение полуширины полосы ИК поглощения, характеризующей XO_4 тетраэдры, связано с уменьшением взаимодействия между тетраэдрами одного типа, и, как следствие, подавлением ангармонизма колебаний у квазисвободных тетраэдров. Высокая чувствительность хлороапатитов матрицы к изменениям колебаний тетраэдрической подрешетки при допировании отражается на термической стабильности соединения.

1. Introduction

It is known that the widening of oscillatory bands in the absorption spectra of the crystal lattice is associated mainly with the anharmonicity of the vibrational modes [1–3]. A necessary condition for harmonic oscillations is oscillators independency. At the oscillators interaction, the anharmonic component of their vibrations has occurred, that results in a widening of the oscillatory modes. The real observation of anharmonicity contribution to the oscillatory bands widening in the spectra is often complicated by the influence of other factors, such as decrease of the local environment symmetry of oscillators [4], resulting in degeneracy of vibration symmetry and the split absorption lines. The contribution of the anharmonic component in the widening of oscillatory bands, however, can be seen in the crystals permitting the substitution of ions without distorting the crystal lattice structure. These crystals include apatites. The crystal structure of hydroxy, fluoro- and chlorapatite belongs to the space group $P6_3/m$ and includes the tetrahedral sublattice permiting replacement of phosphorus to vanadium or arsenic [5–7]. In our synthesized mixed composition apatites, VO_4 and PO_4 tetrahedra alternate in the tetrahedral sublattice. Relationship between these elements can be set arbitrarily, that is permited by the complete isomorphous substitution.

2. Experimental materials and methods

Powdered polycrystalline samples of apatite $Ca_{10}(PO_4)_{6-x}(VO_4)_x(M)_2$, where $M = OH^-$, F^-, Cl^-, $x = 0, 1, 3, 5, 6$ were synthesized by method described in [7].

IR spectra were obtained on double-beam spectrophotometer "SPECORD M80". To provide the study, the samples were prepared by compressing into the mixed tablets of the compound and powdered KBr. Tablets of pure KBr powder were also prepared to measure of the sample phonon transmission. Transmission spectra were recorded in the absorption range of the tetrahedral sublattices $(PO_4)^{3-}$ and $(VO_4)^{3-}$ with vibrational modes lying in the 1600 cm^{-1} to 400 cm^{-1} range. In the region of slow electromagnetic waves, sharp KBr powder absorption begins, therefore, the measurement in the range <400 cm^{-1} is not correct. The measurements were made at a constant level of signal/noise ratio in the whole measurement range. To optimize the recording of the spectra, an electromagnetic radiation attenuator was also installed in comparison channel, so that the absorption background level of KBr pellet approaching to 80 %. During the measurements, the sample chamber was additionally blown through with dry air for thorough drying of water vapor.

Investigations by differential-thermal analysis method were carried out on Q-1500D derivatograph of MOM company (Hungary). Samples of equal mass (~ 1 g) were investigated in a thermogravimetric platinum crucibles in the temperature range 294–1773 K with a heating rate of 7.5 K/min in air (limited space), in conditions of free convection.

3. Results and discussion

Transmission spectra of the studied apatite samples are shown in Fig. 1–3. Spectrum of initial phosphate hydroxyapatite (Fig. 1) is characterized by two intense groups of bands around 1030 cm^{-1} and 550 cm^{-1}. It is known that nine possible variations of XO_4 group in the case of equivalence all X–O bonds, i.e. tetrahedral symmetry T_d, give only two bands of IR spectrum: one band of υ_3 vibrations and another of υ_4 ones, the vibrations υ_2 and υ_1 being active only in Raman spectra [8]. If only three of four bonds are equal (symmetry $C_{3\upsilon}$), then totally symmetrical vibration υ_1 becomes active and the splitting of three

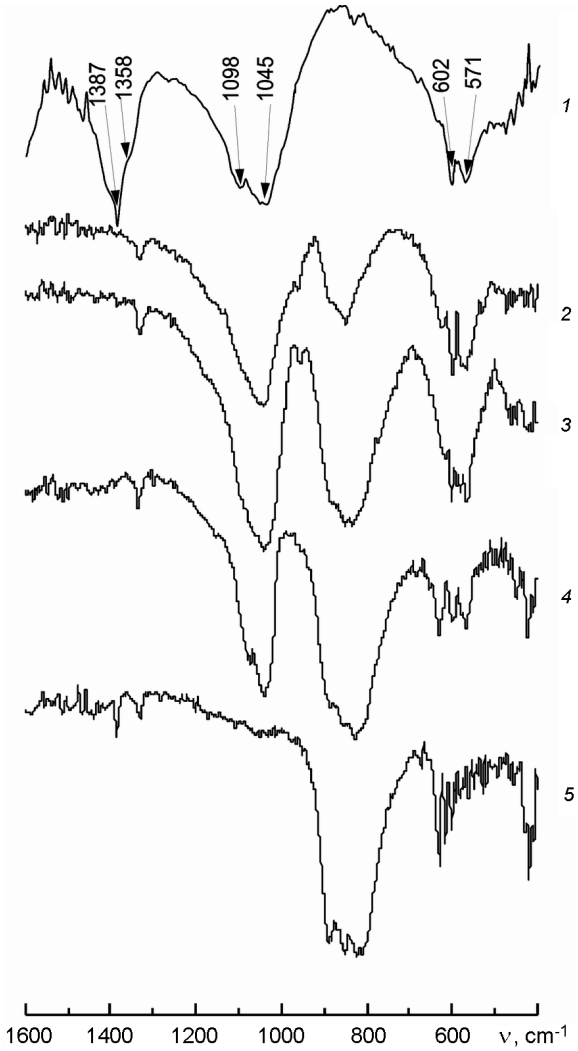

Fig. 1. IR absorption spectra of apatites $Ca_{10}(PO_4)_{6-x}(VO_4)_x(OH)_2$: (*1*) $x = 0$, (*2*) $x = 1$, (*3*) $x = 3$, (*4*) $x = 5$, (*5*) $x = 6$.

degenerate vibrations υ_3 and υ_4 is removed partially. When there is a non-equivalence of the two X–O bonds with respect to the other two (point symmetry $C_{2\upsilon}$), degeneration of vibrations υ_3 and υ_4 is removed completely. Finally, in the case, when all four bonds are different (symmetry C_s), there is another change in the spectrum — the removal of doubly degenerate vibration υ_2 [8, 9]. Thus, as shown in Fig. 1, the bands that correspond to vibrations of the PO_4 group are split. This indicates a decreasing of surrounding symmetry of the $(PO_4)^{3-}$ anion in apatite sublattice. Since the vibration υ_4 ~ 571 cm^{-1} splits into two components, the environment symmetry must meet a point group $C_{3\upsilon}$. This result is conformed the fact

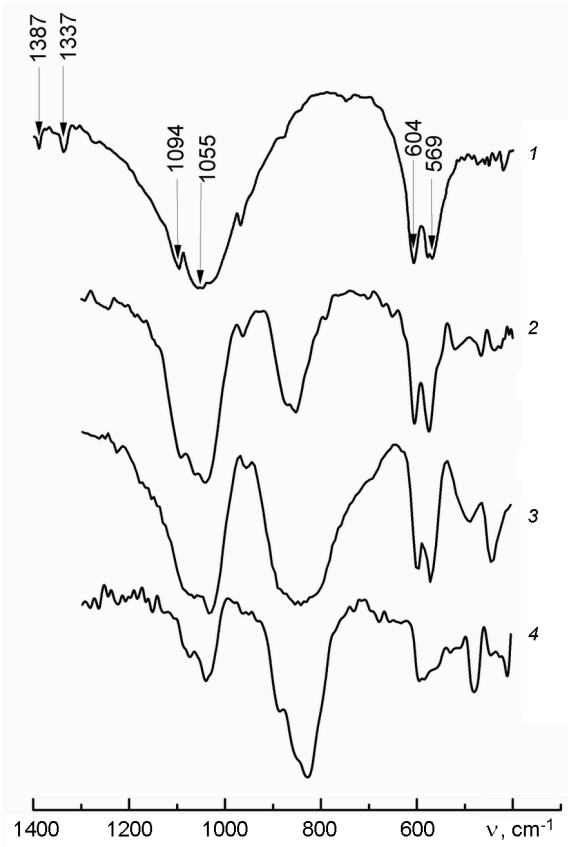

Fig. 2. IR absorption spectra of apatites $Ca_{10}(PO_4)_{6-x}(VO_4)_x(F)_2$: (*1*) $x = 0$, (*2*) $x = 1$, (*3*) $x = 3$, (*4*) $x = 5$.

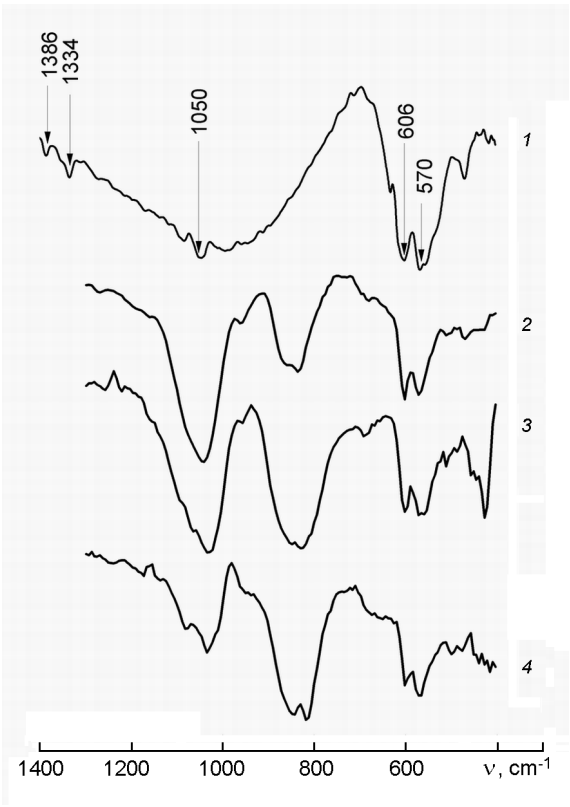

Fig. 3. IR absorption spectra of apatites $Ca_{10}(PO_4)_{6-x}(VO_4)_x(Cl)_2$: (*1*) $x = 0$, (*2*) $x = 1$, (*3*) $x = 3$, (*4*) $x = 5$.

that the 5-valent phosphorus atom makes three single and one double bond with an oxygen environment.

Completely other changes in the spectrum are observed for the group VO_4. As is known, the vibrations of the free group VO_4 which are active in the IR spectrum should be determined at the frequencies $\upsilon_3 = 825$ cm^{-1} and $\upsilon_4 = 480$ cm^{-1} [5–6]. In the spectrum of $Ca_{10}(VO_4)_6(OH)_2$, near the indicated frequency values, there are two groups of absorption bands. In the spectra of mixed composition samples is observed the simple superposition of the above-considered bands, with the change in the bands relative intensity belonging to different tetrahedral groups. Similar changes are observed and described for fluoro- (Fig. 2) and chloro-containing apatites, with some distinction in the case of chloro-containing apatites (Fig. 3).

For chlorinated apatites, the blurring of the two groups of intense bands around 1500 cm^{-1} is observed (Fig. 3). Changing of the bands intensity is proportional to change of the elements concentration P and V in the apatite structure. Neither new bands nor widening of the bands belonging to the original crystal structures were observed in the spectra, thus evidencing that the lattice symmetry in the samples of mixed composition is virtually identical to the symmetry of the original forms.

Vibrational modes υ_3 for phosphorus and vanadium apatite are significantly separated and do not overlap. From the absorption spectra (Fig. 1–3) it is seen that with the changing balance of phosphate and vanadium tetrahedra, in the apatite sublattice half-width absorption band of the tetrahedra decreases with a decrease in their concentration (Table).

For the chloro-containing apatites of any topotetrahedral matrix doping level, of a significant decrease the tetrahedra absorption band (from ~400 cm^{-1} down to 90 cm^{-1}) is observed for the boundary concentrations (Table). Similar effects are observed for fluoro- and hydroxyapatites, but they are less expressed. Decrease of the width occurs from ~200 cm^{-1} down to ~95 cm^{-1}.

Thus, with decreasing ratio of one type tetrahedron to another to a value of 1:5 the concentration of first ones becomes sufficiently low, so that they are in isolation

Table. Half-width of the absorption band υ_3 in mixed apatites

Compound	Half-width of the absorption band of sublattice $(PO_4)^{3-}$, cm^{-1}	Half-width of the absorption band of sublattice $(VO_4)^{3-}$, cm^{-1}
$Ca_5(PO_4)_3OH$	210	–
$Ca_{10}(PO_4)_5(VO_4)OH_2$	150	90
$Ca_{10}(PO_4)_3(VO_4)_3OH_2$	130	135
$Ca_{10}(PO_4)(VO_4)_5OH_2$	95	140
$Ca_5(VO_4)_3OH$	–	140
$Ca_5(PO_4)_3F$	220	–
$Ca_{10}(PO_4)_5(VO_4)F_2$	110	78
$Ca_{10}(PO_4)_3(VO_4)_3F_2$	130	152
$Ca_{10}(PO_4)(VO_4)_5F_2$	87	108
$Ca_5(PO_4)_3Cl$	420	–
$Ca_{10}(PO_4)_5(VO_4)Cl_2$	105	85
$Ca_{10}(PO_4)_3(VO_4)_3Cl_2$	120	122
$Ca_{10}(PO_4)(VO_4)_5Cl_2$	98	108
$Ca_5(VO_4)_3Cl$	–	410

from each other and we can assume that the interaction of characteristic vibration modes between them is not occurred. In this cast, the half-width of absorption lines decreases about a half as compared to the original "undiluted" form. This decrease of the absorption band half-width is associated with a decrease of interaction and, consequently, with the suppression of vibration anharmonicity in the quasi-free tetrahedra.

The residual widening of the absorption band seems to be due to the interaction with the surrounding tetrahedra having a different vibration frequency as well as to internal factors in the tetrahedron (e.g., decreasing the local symmetry, etc.).

High sensitivity of chloroapatite matrix to changes of tetrahedral sublattice vibrations at doping should be reflected and thermal stability, as revealed by us in by differential thermal analysis studies.

Investigations by differential thermal analysis (Fig. 4, 5) have shown that with increasing content of VO_4 groups in calcium chloroapatite, the changes in the thermal stability of compounds in the direction of its decreasing occurs. With the substitution of three or more anionic groups PO_4 by VO_4

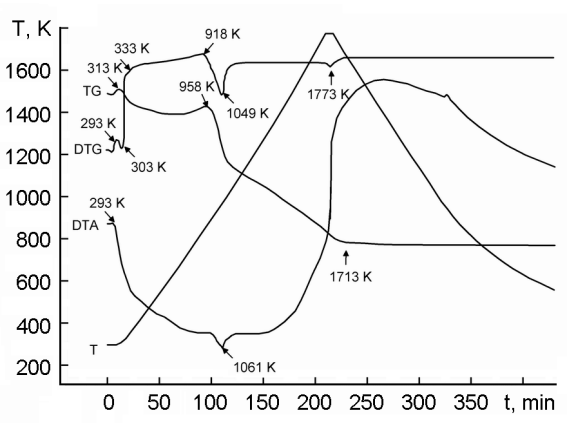

Fig. 4. Thermogram of compound $Ca_{10}(PO_4)_5(VO_4)(Cl)_2$.

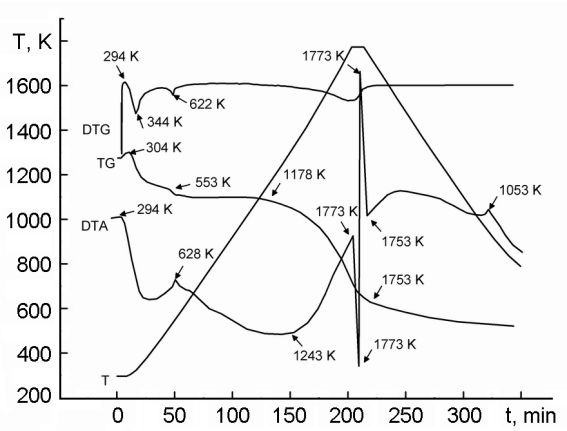

Fig. 5. Thermogram of compound $Ca_{10}(PO_4)(VO_4)_5(Cl)_2$.

a complete fusion of the sample at 1773 K is observed, as evidenced by the appearance of a step in the TG curve of 1178–1773 K, and endothermic and exothermic peaks in the 1773 K (DTG and DTA curves) (Fig. 5). All other compounds under study did not undergo some significant changes in the course of heating in the studied temperature range.

Thus, it was established, that anharmonicity of vibration in the apatite lattice may change depending on the concentration of that type oscillators in crystal structure. These changes are local and by means of various replacements, it is possible to create necessary spatial distribution of anharmonic component in the crystal that opens the prospect of controllable change of heat conductivity, temperature expansion factor and other parameters of the crystal which depend on the anharmonicity of vibration of the lattice.

4. Conclusions

The decrease the of IR absorption band half-width, characterizing XO_4 tetrahedra, is associated with a decreasing interaction between the tetrahedra of the same type and, consequently, with the suppression of vibration anharmonicity in quasi-free tetrahedra. The vibration anharmonicity in the apatite crystal lattice may change depending on the concentration of that type tetrahedra. These changes are local and it is possible by means of various replacements in the crystal to create necessary spatial distribution of anharmonic component that offers the possibilites of controllable change of heat conductivity, temperature expansion factor and other parameters in the crystal which depend on the vibration anharmonicity of of the lattice.

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Дослідження ангармонізму коливань у кристалічній гратці апатиту змішаного складу

В.Л.Карбівський, А.П.Шпак, Н.А.Курган, В.В.Вишняк, О.П.Димітрієв, В.Х.Касіяненко

Розглядаються результати дослідження впливу кристалічного поля гратки на структуру ІЧ-коливальних смуг тетраедричної підгратки кристала $(PO_4)^{3-}$ при ізоморфних аніонних заміщеннях сполук $Ca_{10}(PO_4)_{6-x}(VO_4)_x(M)_2$, де $M = OH^-, F^-, Cl^-$, x = 0, 1, 3, 5, 6. Встановлено, що зменшення напівширини смуги ІЧ-поглинання, що характеризує XO_4 тетраедри, пов'язано зі зменшенням взаємодії між тетраєдрами одного типу, та, як наслідок, пригніченням ангармонізму коливань у квазівільних тетраедрів. Висока чутливість хлороапатитів матриці до змін коливань тетраедричної підгратки при допуванні відображається на термічній стабільності сполуки.