Centrosymmetric and acentric whitlockite-type phosphates and vanadates among \( \text{Ca}_3(\text{VO}_4)_2 - \text{Ca}_3(\text{PO}_4)_2 - \text{Y}_2\text{O}_3 \) compositions

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Abstract. Identifications and studies of whitlockite-type phases for the first time are fulfilled in the cation-anion mixed phosphate-vanadate ferroelectric systems \( \text{Ca}_{10.5}(\text{V}_{1-x}\text{P}_x\text{O}_4)_7 \), \( \text{Ca}_9\text{Y}(\text{V}_{1-x}\text{O}_4)_7 \), \( \text{Ca}_{10.5-1.5}\text{Y}(\text{VO}_4)_7 \) and \( \text{Ca}_{10.5-1.5}\text{Y}(\text{PO}_4)_7 \). These systems are the sections of a more extensive multi-component system \( \text{Ca}_3(\text{VO}_4)_2 - \text{Ca}_3(\text{PO}_4)_2 - \text{Y}_2\text{O}_3 \), but are all built on the basis of well-known individual compounds of the type of mineral whitlockite. The solid solutions formed between them are also of ferroelectric whitlockite-type, but some compositions are not ferroelectric, and according to the nonlinear optical phase analysis possess centrosymmetric structure. Ferroelectric phase transitions were detected in the region of 1000–1300 K by the method of dielectric spectroscopy. A precision X-ray study of some compositions of solid solutions using synchrotron radiation revealed a significant deviation in the cationic-anionic arrangement from being completely disordered. Partial ordering of structural tetrahedral groups of \( \text{PO}_4^{3-} \) and \( \text{VO}_4^{3-} \) determines a significant increase in nonlinear optical activity in the mixed anions whitlockite-type compounds.

1. Introduction

Tricalcium vanadate \( \text{Ca}_3(\text{VO}_4)_2 \) [1] is a forefather of the extensive family of high-temperature ferroelectric (FE) and nonlinear optical phosphates and vanadates with the structure of the mineral whitlockite [2,3]. Like natural mineral whitlockite, all other representatives of this family regularly have a noncentrosymmetric structure described by a polar space group (sp. gr.) \( R\overline{3}c \) [4]. The ferroelectric and nonlinear optical properties of members of this family are most pronounced in compounds \( \text{Ca}_9\text{MIII}(\text{XO}_4)_7 \), where \( \text{X} = \text{P} \) or \( \text{V} \), and \( \text{MIII} \) – trivalent cation [2–7]. Moreover, vanadates are characterized by a higher optical nonlinearity and temperature of the FE phase transformations.

Compounds of the \( \text{Ca}_9\text{MIII}(\text{XO}_4)_7 \) group are capable of forming solid solutions both between themselves [8], and with tricalcium vanadate. It is more convenient to present its formula as \( \text{Ca}_{10.5}(\text{XO}_4)_7 \) [9]. This formula embraces all structural positions \( M1-M6 \) occupied by divalent and trivalent cations which can be clearly identified. These positions are divided into the closest octahedral site (\( M5 \)), three more extensive three-fold sites (\( M1, M2 \) and \( M3 \)) and two additional sites (\( M4 \) and \( M6 \)) [10]. The \( M4 \) and \( M6 \) sites can be either both empty, as in \( \text{Ca}_9\text{MIII}(\text{XO}_4)_7 \), or the \( M4 \) site is partially occupied, in the case when \( \text{MIII} \rightarrow \text{Ca} \), so \( \text{Ca}_{10.5}(\text{VO}_4)_7 \equiv \text{Ca}_3(\text{VO}_4)_2 \). All whitlockite-type compounds with the latter formula are certainly noncentrosymmetric, sp. gr. \( R\overline{3}c \), and the compounds themselves are ferroelectrics [11]. It should be noted that, above the FE phase transition, they
transform into a centrosymmetric ion-conducting state, corresponding to the through motion of Ca$^{2+}$ through the $M_4$ and $M_6$ sites, which are equally occupied by Ca$^{2+}$ and become structurally identical [3]. From a structural point of view, whitlockite-type compounds Ca$_{M^{	ext{III}}}$($XO_4$)$_7$ have more prerequisites for a centrosymmetric structure, since $M_4$ and $M_6$ positions are equally empty. The temperatures of transitions FE - centrosymmetric paraelectric phase in this group are lower than in Ca$_3$(XO$_4$)$_2$ ($X = P, V$) [12]. In addition, among the compounds Ca$_9$RE(P$_2$O$_7$)$_3$, where $M^{	ext{III}}$ are represented by rare earth elements, there are a significant number of antiferroelectrics with centrosymmetric structures even under normal conditions [2]. Such centrosymmetric whitlockite-type phosphates have no analogues among vanadates.

In this contribution we report on synthesis and characterization of whitlockite-type phases in the phosphate and vanadate systems, including the mixed in the anionic and cationic parts: Ca$_{10.5}$($V_1-x$P$_x$O$_4$)$_7$, Ca$_9$Y($V_1-x$P$_x$O$_4$)$_7$, Ca$_{10.5}$Y$_x$($VO_4$)$_7$ and Ca$_{10.5}$Y$_x$($PO_4$)$_7$. Special attention is paid to determining the presence or absence of an inversion center in their crystal structure. The latter, as is known, determines the possibility of the formation of nonlinear optical and ferroelectric properties in substances.

2. Experimental section

2.1. Materials and general methods

The solid solutions Ca$_{10.5}$($V_1-x$P$_x$O$_4$)$_7$, Ca$_9$Y($V_1-x$P$_x$O$_4$)$_7$, Ca$_{10.5}$Y$_x$($VO_4$)$_7$ and Ca$_{10.5}$Y$_x$($PO_4$)$_7$ were synthesized by solid state route from stoichiometric amounts CaCO$_3$ (99.99%), Ca(HPO$_4$)$_2$•2H$_2$O (99.99%), NH$_4$VO$_3$ (99.98%) and Y$_2$O$_3$ (99.9%) in air at 1273 K for 150 hours with intermediate grinds every 50 hours.

Powder X-ray diffraction (PXRD) patterns were collected on a Thermo Termo ARL powder diffractometer (Cu K$_{\alpha 1}$+K$_{\alpha 2}$), Bragg–Brentano geometry, Peltier-cooled CCD detector at RT in a range of 2$\theta$ = 5°–65° with a step of 0.02°. The second harmonic generation (SHG) signal was measured with a Q-switched YAG:Nd laser at $\lambda_{\text{exc}}$ = 1064 nm in the reflection mode for powder series. The experimental set-up and arrangement have been described in [13]. The powders were ground in ethanol for 30 minutes before the formation of a suspension and then dried in air. The similar procedures were used to prepare quartz powders, which were used as references. To separate the powders into fractions according to crystallite size, time-controlled deposition of powders in an ethanol solution was used. Certification of particle size distribution was carried out by constructing histograms of light scattering of powders in solutions, measured using a laser analyzer CILAS 1180.

For electrical properties, examinations the ceramic pellets with 8 mm in diameter and 2–3 mm thickness were prepared. Electrodes were applied to the flat surfaces of the disks by burning colloidal platinum containing paste SPI-Chem. The upper heat treatment temperature was 1273 K, temperature exposure was 1 hour. The dielectric constant and dielectric loss measurements were carried out by a two-contact method using Novocontrol Beta-N Impedance Analyser with Probostar A-cell at frequencies from 0.3 Hz to 1 MHz in a 293–1273 K temperature range.

Synchrotron PXRD data for Ca$_9$Y($P_1-x$V$_x$O$_4$)$_7$, $x = 0 - 1$ and Ca$_{10.5}$($P_0.5V_0.5O_4$)$_7$ were measured with a large Debye-Scherrer camera at the BL15XU beamline of SPring-8. The intensity data were collected in a 20 range from 1° to 62° with a step of 0.003°. The incident beam was monochromatized at $\lambda = 0.65298$ Å. The sample was packed into a Lindemann glass capillary with the inner diameter of 0.1 mm, that was rotated during the measurement. The absorption coefficient was also measured. Rietveld analysis [14] was performed using JANA2006 programme package [15].

3. Results and Discussion

3.1. System Ca$_{10.5}$Y$_x$($PO_4$)$_7$

Obtained XRD patterns for Ca$_{10.5}$Y$_x$($PO_4$)$_7$ compositions with $x = 0, 0.167, 0.333, 0.500, 0.667, 0.833, 1$ are similar to more simple whitlockite-type compounds [2-7], all reflections in the XRD were in accordance with JCPDSPDF-2 №46402 data. The unit cell parameters $a$, $c$ and $V$ are given in table 1. The volume $V$ of the unit cell shows non-monotonic change during Ca$^{2+}$ → Y$^{3+}$ substitution.
Although substitution with smaller cations usually leads to a decrease in unit cell parameters [16,17], in this case the replacement adduct to formation of vacancy in the \( M_4 \) site according to the scheme 
\[
3\text{Ca}^{2+} = 2\text{Y}^{3+} + \Box
\]
[18]. So, a decreasing of the unit cell parameters is observed, as a result.

| \( x \) | \( a, \text{Å} \) | \( c, \text{Å} \) | \( V, \text{Å}^3 \) | \( I_{2\omega}/I_{2\omega}(\text{SiO}_2) \) | \( T, \text{K} \) |
|---|---|---|---|---|---|
| 0.000 | 10.4024(1) | 37.380(1) | 3503.0(1) | 1.85 | 1203 |
| 0.167 | 10.4182(3) | 37.384(2) | 3514.0(2) | 1.75 | 1159 |
| 0.333 | 10.4323(1) | 37.376(1) | 3522.8(1) | 1.35 | 1123 |
| 0.500 | 10.4297(2) | 37.386(7) | 3522.0(3) | 1.20 | 1073 |
| 0.667 | 10.4306(1) | 37.376(1) | 3519.0(2) | 0.70 | 1043 |
| 0.833 | 10.4346(1) | 37.390(2) | 3525.6(2) | 0.35 | 863 |
| 1.000 | 10.4309(1) | 37.360(2) | 3520.3(1) | 0.3 | 863 |

Taking into account smaller ionic radii of the \( \text{Y}^{3+} \) (\( r_{\text{VI}} = 0.89 \text{ Å} \)) in comparison with \( \text{Ca}^{2+} \) (\( r_{\text{VI}} = 1.00 \text{ Å} \)), the yttrium ions occupy smaller sites, ranking from the sequence \( M_5 > M_1 > M_2 > M_3 \). The range of substitution in the \( M_3 \) site is the smallest: \( M_3 < 0.01 \) [19]. The occupation of \( M_5 \) site by \( \text{Y}^{3+} \) ions increases the lattice cell, while the location in the \( M_1, M_2 \) sites reduces them [20]. Thus, cell volume changes are associated with the redistribution of substitutional cations in crystallographic positions.

The SHG study on powders with a grain size of 5 \( \mu \text{m} \) showed low-intensity SHG signals characteristic to phosphates compounds (table 1). The signal intensity for \( \text{Ca}_9\text{Y}(\text{PO}_4)_7 \) coincides with the references data, and monotonically decreases in the solid solution with declining yttrium concentration.

For compound with \( x = 0.667 \) temperature dependence of SHG signal was measured (figure 1). The SHG signal intensity gradually decreases with rising temperature until it disappears. The declining of the response occurs at temperature \( T_c \), corresponding to the transition from a noncentrosymmetric to a centrosymmetric state. Subsequent cooling will restore the signal. A smooth decay of the signal near \( T_c \) shows that this transition is close to a second-order type. This fact complicates the study of phase transition by scanning calorimetry method.

![Figure 1](image.png)

Figure 1. Temperature dependences of SHG signal for \( \text{Ca}_{10.5-1.5x}\text{Y}_x(\text{PO}_4)_7, x = 0.667 \) in the heating-cooling circle.
The temperatures of phase transitions in the \( \text{Ca}_{10.5-1.5}x\text{Y}_x(\text{PO}_4)_7 \) solid solution decreasing with enrichment of yttrium content, which corresponds to the previously obtained results [2]. The temperatures of phase transitions obtained by the SHG method are given in the table 1.

The temperature of phase transitions was also measured by dielectric spectroscopy, and the ferroelectric nature of solid solution was confirmed. The temperature dependences of the dielectric constant and the dielectric loss tangent of \( \text{Ca}_{10.5-1.5}x\text{Y}_x(\text{PO}_4)_7 \) solid solution are shown in the figure 2. The dielectric constant \( \varepsilon \) has a maximum in the range 1163-1229 K. Though temperature positions of the maximum do not depend on the frequency of the electric field, the peaks are significantly broadened, similar to a diffuse phase transition in \( \text{Ca}_3(\text{PO}_4)_2 \) [21]. As a whole, the forms of the \( \varepsilon(T) \) and the \( \tan\delta(T) \) curves correspond to the behavior of ferroelectrics.

![Figure 2](image-url)

**Figure 2.** Dielectric constant \( \varepsilon \) and the loss tangent for \( \text{Ca}_{10.5-1.5}x\text{Y}_x(\text{PO}_4)_7 \ (x = 0.167) \) at the frequency of the measuring field: 750 kHz (1), 1.5 MHz (2) and 3 MHz (3).

3.2. System \( \text{Ca}_{10.5-1.5}x\text{Y}_x(\text{VO}_4)_7 \)

All the compounds obtained in this system have unit cell parameters \( (a, c, \text{ and } V) \) close to those of whitlockite vanadates \( \text{Ca}_9\text{RE}(\text{VO}_4)_7 \) and the characteristic spatial symmetry of the \( R3c \) group, confirmed by the presence of the second harmonic generation. Unit cell parameters increase with increasing content of yttrium (table 2). The SHG study was carried out on samples of the same dispersion (20 \( \mu m \)). The data are given in table 2. The signal intensity for \( \text{Ca}_3(\text{VO}_4)_2 \) was 8 units of quartz standard, nonlinearly increasing with increasing of \( Y^{3+} \) content to 60 units.
Table 2. The unit cell parameters and SHG signal of Ca_{10.5-1.5}Y_x(VO_4)_7:

| x         | a, Å   | c, Å   | V, Å³  | I_{2ω}/I_{2ω}(SiO_2) |
|-----------|--------|--------|--------|-----------------------|
| 0         | 10.7929(2) | 37.922(2) | 3825.7(1) | 8                     |
| 0.167     | 10.8048(8)  | 37.934(3)  | 3835.3(5)  | 12                    |
| 0.333     | 10.8098(6)  | 37.917(2)  | 3837.1(4)  | 13                    |
| 0.500     | 10.8105(2)  | 37.895(2)  | 3835.3(1)  | 18                    |
| 0.667     | 10.8197(2)  | 37.908(1)  | 3843.2(1)  | 40                    |
| 0.833     | 10.8308(2)  | 37.907(5)  | 3850.9(3)  | 50                    |
| 1.000     | 10.8369(9)  | 37.916(3)  | 3856.2(6)  | 60                    |

The dielectric constant for Ca_{9.5}Y_{0.667}(VO_4)_7 has a sharp temperature maximum at 1223-1273 K, which is characteristic of the FE phase transition. The position of the maximum does not depend on the frequency of the electric field. The temperature minimum on the tanδ(T) curve precedes the ε maximum, which also corresponds to the ferroelectric behavior.

Figure 3. Dielectric constant ε and the loss tangent for Ca_{9.5}Y_{0.667}(VO_4)_7 at the frequency of the measuring field: 93 kHz (1), 187 kHz (2) and 375 kHz (3)

The phase transition temperature of Ca_{9.5}Y_{0.667}(VO_4)_7 is just between $T_c = 1383$ K for Ca_{10.5}(VO_4)_7 and Ca_{9}Y(VO_4)_7 (1213 K). Taking into account the structural mechanism of ferroelectric-to-paraelectric phase transition in the whitlockites [6,20], one may conclude that an additional population of $M4$ position by calcium atom prevents from free reorientation of the $X1O4$ tetrahedron which is adjacent to $M4$ positions. In such neighborhood reorientation of $X1O4$ tetrahedron to centrosymmetry requires more thermal energy, and therefore the phase transition into centrosymmetric paraelectric phase in Ca_{10.5}(VO_4)_7 is higher in temperature.
3.3. System $\text{Ca}_{10.5}(P_{x}V_{1-x}O_{4})_7$

Fragments of XRD patterns of $\text{Ca}_{10.5}(P_{x}V_{1-x}O_{4})_7$ ($x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1$) presented in the figure 4. All samples obtained are single phase and do not contain additional phases besides similar to $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Ca}_3(\text{VO}_4)_2$ (JCPDS №48-247). Dependences of unit cell parameters $a$, $c$ and volume $V$ from vanadium concentration are shown in figure 4. The growth of all three parameters with $x$ is a sequence of the incorporation larger in compared with phosphorus vanadium atom into the structure.

**Table 3.** Unit cell parameters and SHG values for powders of different dispersion in solid solution $\text{Ca}_{10.5}(P_{x}V_{1-x}O_{4})_7$.

| $x$  | $a$, Å | $c$, Å | $V$, Å³ | SHG (17 μm) | SHG (3 μm) |
|------|--------|--------|---------|-------------|------------|
| 0.0  | 10.7922(9) | 37.928(5) | 3825.8(9) | 8.0 | 4 |
| 0.2  | 10.7124(3) | 37.760(1) | 3752.7(2) | 14 | 5 |
| 0.4  | 10.6259(3) | 37.607(1) | 3677.4(2) | 16 | 7 |
| 0.5  | 10.5738(8) | 37.519(3) | 3632.9(6) | 15 | 6 |
| 0.6  | 10.5251(2) | 37.449(1) | 3592.8(2) | 7.0 | 5 |
| 0.8  | 10.4439(3) | 37.379(1) | 3530.9(2) | 2.5 | 1.3 |
| 1.0  | 10.3677(7) | 37.201(2) | 3463.1(4) | 1.2 | 0.6 |

All obtained compounds have the sp. gr. $R3c$ usual for most of whitlockite-type compounds. The indication of powder patterns led to a hexagonal whitlockite cell (table 3). The nonmonotonic nature of the change in the parameters $\text{Ca}_{10.5}(P_{x}V_{1-x}O_{4})_7$ near $x = 0.5–0.6$ is noteworthy. Apparently, in this concentration range, the distribution of phosphorus and vanadium over possible anionic positions $E_1$-$E_3$ is mostly ordered. This also corresponds to a marked increase in the nonlinear optical activity of the solid solution, which is clearly manifested on powders with different crystallite sizes (table 3). It is significant also that the luminescence of guest europium atoms in this system [22] has a maximum intensity near $x = 0.7$. The destruction of the $V$ – $V$ relaxation mechanisms proposed in [22] is probably due to an increase in the distance between the vanadium – oxygen tetrahedra as a result of their alternation with the phosphorus – oxygen.

![Figure 4. Concentration dependences of unit cell parameters $a$, $c$, $V$ in $\text{Ca}_{10.5}(P_{x}V_{1-x}O_{4})_7$.](image-url)
To refine the crystal structure of Ca$_{10.5}$(P$_{0.5}$V$_{0.5}$O$_4$)$_7$, the structure of calcium phosphate was used as an initial model [23]. At the first stage, f-curves for phosphorus were calculated and the coordinates of calcium were refined. Next, vanadium atoms were introduced and bound by coordinate and atomic displacement parameters. The coordinates of all atoms were clarified. The refinement R-factors show good agreement between the calculated and experimental curves. The adjusted unit cell parameters, taking into account the differences in the chemical composition of the samples, are in satisfactory agreement with the data in figure 4. The calculated composition is close to theoretical.

The cations of phosphorus and vanadium occupy all three positions E1, E2, E3. However, the position distribution of the uneven positions E1, E2 is predominantly occupied by vanadium cations, while phosphorus cations preferably occupy the positions E3, E2. In calcium phosphate Ca$_3$(PO$_4$)$_2$ and vanadate Ca$_3$(VO$_4$)$_2$, the average distances E1-O, E2-O, E3-O are approximately the same (1.540 Å, 1.536 Å – for phosphate and 1.691 Å, 1.700 Å, 1.694 Å – for vanadate). However, for Ca$_{10.5}$(P$_{1-x}$V$_x$O$_4$)$_7$ significant asymmetry is observed: predominantly occupied by vanadium E1, E2 (1.538 Å, 1.536 Å – for phosphate and 1.691 Å, 1.700 Å, 1.694 Å – for vanadate). However, for Ca$_{10.5}$(P$_{1-x}$V$_x$O$_4$)$_7$ significant asymmetry is observed: predominantly occupied by vanadium E1, E2 (1.538 Å, 1.536 Å – for phosphate and 1.691 Å, 1.700 Å, 1.694 Å – for vanadate). However, for Ca$_{10.5}$(P$_{1-x}$V$_x$O$_4$)$_7$ significant asymmetry is observed: predominantly occupied by vanadium E1, E2 (1.538 Å, 1.536 Å – for phosphate and 1.691 Å, 1.700 Å, 1.694 Å – for vanadate).

A series of solid solutions in the Ca$_{9}$(P$_{1-x}$V$_x$O$_4$)$_7$ system begins and ends with double-phosphate and vanadate calcium-yttrium having the polar whitlockite-type structure. It was previously assumed that between them there is a continuous series of solid solutions. However, large single crystals of compositions close to x = 0.5 grown by the Czochralski method [8] showed no SHG effect. This indicated that the crystals are centrosymmetric (CS). It was of interest to study in detail the structural features of the samples in this system, provided they were obtained by standard solid-state synthesis. For a more reliable refinement of their structure of powders in the system Ca$_{9}$(P$_{1-x}$V$_x$O$_4$)$_7$, x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1, their X-ray diffraction patterns were obtained using synchrotron radiation. A detailed X-ray phase analysis showed that all the obtained samples contained a small amount of YVO$_4$ impurity. The position of the peaks in the diffraction patterns is close or coincides with their location for Ca$_{9}$(PO$_4$)$_7$ and Ca$_{9}$(VO$_4$)$_7$. Table 4 shows the unit cell parameters $a$, $c$ and volume $V$ from the vanadium concentration. All three parameters naturally rising with increasing x, which is due to the larger size of the vanadium anions in comparison with phosphorus. The asymmetric distribution over the positions, as well as a significant distortion of the bond lengths, leads to an increase in optical nonlinearity.

### Table 4. Unit cell parameters, SHG and $T_c$ values for Ca$_{9}$(P$_{1-x}$V$_x$O$_4$)$_7$ system (0 ≤ x ≤ 1).

| x  | SG   | a, Å  | c, Å  | V, Å$^3$ | SHG  | $T_c$, K |
|----|------|-------|-------|---------|------|----------|
| 0  | $R3c$| 10.43116(3) | 37.3335(1) | 3517.98(1) | 0.30 | 823 |
| 0.1| $R3c$| 10.47607(4) | 37.3354(1) | 3548.53(2) | 0.15 | - |
| 0.2| $R3c$ | 10.52250(9) | 37.3736(3) | 3583.72(5) | 0 | CS-phase |
| 0.3| $R3c$ | 10.56593(6) | 37.4111(2) | 3616.99(3) | 0 | CS-phase |
| 0.4| $R3c$ | 10.60703(5) | 37.4648(2) | 3650.41(2) | 0 | CS-phase |
| 0.5| $R3c$ | 10.64756(5) | 37.5203(2) | 3683.81(3) | 0.15 | CS-phase |
| 0.6| $R3c$ | 10.68738(2) | 37.5978(2) | 3719.07(1) | 0.35 | - |
| 0.7| $R3c$ | 10.72038(4) | 37.6555(1) | 3747.83(2) | 0.8 | - |
| 0.8| $R3c$ | 10.74430(3) | 37.7014(1) | 3769.15(8) | 1.8 | 1123 |
| 0.9| $R3c$ | 10.78648(7) | 37.7998(3) | 3808.72(4) | 4.0 | 1193 |
| 1.0| $R3c$ | 10.83206(1) | 37.8877(5) | 3849.92(1) | 6.0 | 1207 |

Weakening to null of the SHG signal intensity for mixed yttrium calcium phosphate vanadates dramatically contrasts in comparison with its augmentation with described above Ca$_{9}$(P$_{1-x}$V$_x$O$_4$)$_7$ system, and makes it possible to reliably establish the existence of a centrosymmetric whitlockite-type phase at 0.2 ≤ x ≤ 0.5. This centrosymmetric phase exists only in yttrium-rich compositions.
According to SHG data even 15-20 at.% shortage of yttrium leads to disappearance of centrosymmetry at the P5\(^{±}\)-V5\(^{±}\) substitution.

SHG intensities for the non-centrosymmetric compounds \(x = 0, 0.1, 0.2, 1\) demonstrate temperature dependences typical for ferroelectrics (figure 5). With increasing temperature, the SHG gradually decreases until disappearance at the Curie point \(T_c\) corresponding to the FE transition into the centrosymmetric paraphase. Upon subsequent cooling, the signal is reversibly restored. The smooth decay of the signal near \(T_c\) for Ca\(_9\)Y(VO\(_4\))\(_7\) \((x = 0)\) shows that this transition is close to the second order FE transition found on the single crystal in [20]. As phosphorus enrichment occurs, the \(T_c\) this decreases. As evidenced by a stepwise change in the SHG near the \(T_c\), the phase transition acquires the features of a first-order transformation. A slight change in SHG with temperature up to a sharp disappearance of the effect at \(T = T_c\) in the case of Ca\(_9\)Y(PO\(_4\))\(_7\) \((x = 1)\) indicates a first-order transition. The temperatures of phase transitions obtained by the SHG method are given in the table 4.

![Figure 5. SHG temperature dependences for noncentrosymmetric compositions in the system Ca\(_9\)Y(P\(_{1-x}\)V\(_x\)O\(_4\))\(_7\), \(x = 1\) (1), 0.9 (2), 0.8 (3), 0 (4).](image)

The crystal structure of the whitlockite-type phase was refined for two compositions according to the SHG data located in the centrosymmetric region \(0.2 \leq x \leq 0.5\).

The structure of Ca\(_9\)Y(PO\(_4\))\(_{4.511}\)(VO\(_4\))\(_{2.489}\) was refined in two models: centrosymmetric (CS) and noncentrosymmetric (NCS). The initial NCS model was Ca\(_9\)Y(VO\(_4\))\(_7\), for which the coordinates of all large cations were refined based on the measured array. Then, f-curves for Ca and V were constructed and yttrium and phosphorus atoms were introduced, linking them with the corresponding atoms. The final refinement of all atoms to the R-factor value of 3.16 was carried out. As the initial CS model, we used the data for Ca\(_9\)Y(P\(_{4/7}\)V\(_{3/7}\))O\(_7\) single crystals from [8]. The final refinement of all atoms to the R-factor value of 3.03 was carried out.

A similar model calculation was performed for the composition Ca\(_9\)Y(PO\(_4\))\(_{3.5}\)(VO\(_4\))\(_{3.5}\), the structure of which was refined in the Ca\(_9\)Y(P\(_{4/7}\)V\(_{3/7}\))O\(_7\) model [8]. For both compositions, the best agreement between the calculated and experimental data was obtained for the CS model. The choice of the CS model also relies on the absence of a noticeable SHG effect in powders of the corresponding compounds.

4. Conclusion
Structural features, corresponding to the transformation from NCS to CS type structure are of great scientific and practical interest. Previous study shown that mixed vanadate-phosphate is a suitable matrix for synthesis of new CS-type whitlockites. Present investigation confirms that the problem of a
stabilization of CS-type structure may be solved using only cation ordering in the whitlockite-type host. It is demonstrated that among whitlockite-type compounds with NCS structure in the system Ca₉(VO₄)₂-C₅₃(PO₄)₂-Y₂O₃ there is a specific concentration region where CS phase is stabilized at room temperature. This fact greatly relieves future examination of crystal structure characteristics of paraelectric phases for a number of whitlockite-type ferroelectrics with ferroelectric-to-paraelectric phase transitions in the region of 1000 K or above.

The sections studied in this paper Ca₁₀.₅(VO₄)₇, Ca₉Y(VO₄)₇, Ca₁₀.₅₋₁.₅ₓYₓ(PO₄)₇ and Ca₁₀.₅₋₁.₅ₓYₓ(PO₄)₇ are characterized by homovalent substitutions in the anionic part (P - V) and heterovalent in the cationic part (Ca - Y). Heterovalent substitutions are accompanied by a change in the filling of the M4 cation position near the XO₄-tetrahedron, whose polar orientation determines the non-centrosymmetric structure in the ferroelectric phase. The temperature of transition from the ferroelectric to the paraelectric phase (Tc) depends on the stereochemical possibility of reorientation of half of the XO₄ tetrahedra. This possibility is limited if a calcium cation is located in the nearby M4 position. This results in higher Tc for Ca₁₀.₅ₓ(XO₄)₇ (X = P, V) against a plurality of Ca₉MIII(XO₄)₇ compounds with significantly lower ferroelectric transition temperatures. Note also that filling the M4 position due to electrostatic compression of the corresponding oxygen polyhedron reduces the volume of the entire unit cell, which also prevents its symmetrization and shifts the existence of the CS phase to the high temperature region.

The systems with isovalent anionic substitution of P5+-V5+ studied in this work make significant refinements of the "composition-structure-properties" correlations described above. Systems Ca₉Y(P₁₋ₓVₓO₄)₇ and Ca₁₀.₅(P₁₋ₓVₓO₄)₇ demonstrate completely different behavior of the unit cell parameters, intensity of the SHG, and phase transitions temperatures. A continuous solid solution of a whitlockite-like structure with a polar space group R3c is formed in the Ca₁₀.₅(P₁₋ₓVₓO₄). The P⁵±/V⁵±- mixing leads to an increase in the second harmonic effect with a pronounced maximum at x=0.6. Regular increase in optical nonlinearity is not here unexpected, since it is achieved due to the greater electron polarizability of vanadium ions with respect to phosphorus. The presence of the maximum SHG in the system Ca₁₀.₅(P₁₋ₓVₓO₄)₇ at x = 0.6 can be associated with the initial localization of vanadium chiefly in the T1 position, primarily responsible for the nonlinear optical susceptibility of the whitlockites [13,24].

It may be resumed that the CS-type state in whitlockites in the Ca₃(VO₄)₂-C₅₃(PO₄)₂-Y₂O₃ system is controlled by a partial ordering of V⁵⁺ and P⁵⁺ cations among tetrahedral sites with further orientational disorder of T1-tetrahedron around center of symmetry. That becomes possible because of the absence of any cations in M(4)-site and increasing of the unit-cell parameters by the insertion of V cations. However, the field of stability of CS state decreases with the Y→Ca substitution. The further structural investigations of compounds belonging to Ca₃(VO₄)₂-C₅₃(PO₄)₂-Y₂O₃ system with the structural solutions are necessary to understand the crystal chemical features of CS-type whitlockite.

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