In situ synthesis, structural chemistry and vibrational spectroscopy of Zn-doped Ca$_3$Mg$_4$(VO$_4$)$_6$

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Abstract
The phase formation of the solid solution Ca$_3$Mg$_{4-x}$Zn$_x$(VO$_4$)$_6$ (0≤x≤4) was studied in situ using differential scanning calorimetry and high-temperature X-Ray powder diffraction (XRPD). XRPD analysis shows the appearance of unavoidable secondary pyrovanadate phases using conventional synthesis methods. The local structure of the solid solution was verified by vibrational spectroscopy. The analysis of the infrared and Raman spectroscopy data allows establishing the main features between vanadate garnets and their isostructural analogs among natural silicates.

Keywords
crystal structure
vibrational spectroscopy
X-ray diffraction
ceramics
differential scanning calorimetry
pyrovanadate garnet

1. Introduction
A wide range of compounds with the general formula A$_3$B$_2$V$_3$O$_{12}$ that belong to calcium vanadate garnets is known nowadays. This system includes complex oxides with substitution of calcium ions in A position by alkaline, (Li, Na, K), alkaline-earth (Sr) and other metal cations like Cu, Ag, Cd, Pb [1, 2]. Heterovalent substitution in B position in the garnet structure A$_3$B$_2$V$_3$O$_{12}$ (B = Mg$^{2+}$, Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$) has been analyzed by many researched groups [1-3]. Ca$_3$Mg$_3$Zn(VO$_4$)$_6$ was first characterized as a garnet having the crystal symmetry of space group I43d [4]. The lattice comprises the VO$_4$ tetrahedra sharing edges with deformed CaO$_6$ dodecahedrons. The crystal structure of most of garnet-related vanadates is described with the symmetry of space group Ia3d [1]. These compounds attract increasing attention due to a cation deficiency, where the vacancy concentration in A position varies from 1/10 to 3/10 [5-8]. The nonstoichiometry values in B position were evaluated for Ca$_3$Co$_3$(VO$_4$)$_6$ [9].

Inorganic materials based on calcium vanadates have been studied as a new series of low-temperature co-fired ceramics [3] with promising microwave characteristics below 100 °C [10-14]. The optical and photophysical properties of compounds doped with In, Ta [15], and lanthanide ions [16-18] have been considered in view of their application in solid-state lighting. Ca$_3$Mg$_4$(VO$_4$)$_6$ is characterized by cationic transport [19], whereas the vanadates Ca$_3$Mg$_{4-x}$Co$_x$(VO$_4$)$_6$ (15≤x≤4) demonstrate predominantly electronic conductivity about 10$^{-2}$ S·cm$^{-1}$ at 850 °C [20].

Different chemical routes are used to synthesize vanadates as single crystals as well and in polycrystalline forms [11-14, 20, 21]. Among them, solid-state method can be carried out in a quartz ampule upon annealing at 975 °C [4]. The melting point of V$_2$O$_5$ is, nevertheless, about 650 °C, and, typically, vanadium oxide melt interacts with quartz. Some single-crystal fiber methods are also employed for preparation of calcium vanadates [22, 23]. However, most of the approaches for the synthesis of target compounds of this class of inorganic solids are highly time-consuming and require special equipment. The widely reported method implies a solid-state reaction [24-26]. For example, the synthesis of Ca$_3$Mg$_4$(VO$_4$)$_6$ (M = Mg and Zn) can be done taking MgCO$_3$, ZnO, CaCO$_3$ and either NH$_4$VO$_3$ or V$_2$O$_5$ as initial reagents with further annealing of the reaction mixture at 800–850 °C. The attempt to obtain Ca$_3$Zn$_{4-x}$Mg$_x$(VO$_4$)$_6$ (0≤x≤3) via a solid-state reaction results in the appearance
of ZnO as a second phase [10]. The problems of synthesis of the single-phase powders are reported not only for the above-mentioned system but for other compositions of garnet-type vanadates [1, 27, 28].

Wet-chemical synthesis procedure provides high homogeneity of its products [29, 30]. Many modified sol-gel methods using the corresponding nitrates as initial reagents are often applied to prepare vanadate-based solid solutions [15, 31, 32]. Other changes in the chemical routes to synthesize different inorganic solids include also mechanoc hemical treatment, variation of educts and raw materials, additional intermediate grindings and heat treatments, alternation in temperature of annealing. The observations listed above forces us to pay more attention to phase formation of the vanadate subclass of inorganic compounds. This can be accompanied by possible vaporization of vanadium oxides [33]. Ca$_3$Mg$_6$Zn$_x$(VO$_4$)$_6$ ($0 \leq x \leq 4$) is chosen as a model solid solution among garnet-related vanadates. Differential scanning calorimetry (DSC) analysis supplemented by gas emission analysis, in situ X-ray diffraction and evaluation of the local structure employing vibrational spectroscopy facilitate the solution of the problems in chemistry of vanadate-based materials more comprehensively than was reported earlier [4, 5, 10, 20, 31, 32]. The present study is also relevant to understanding of the synthesis processes of other garnet-type compounds such as silicates, hafnates, zirconates, germanates, etc.

2. Experimental

2.1. Reagents

The target ceramic samples of Ca$_3$Mg$_{6−x}$Zn$_x$(VO$_4$)$_6$ ($0 \leq x \leq 4$) were synthesized via a salt decomposition reaction using CaCO$_3$ (99%), MgCO$_3$ (99.999%), ZnO (99%), V$_2$O$_5$ (99.999%) or NH$_4$VO$_3$ (98%), HCOOH (98%, concentration 99%) and C$_6$H$_5$O$_7$·H$_2$O (99%) as initial reagents. Those taken in a stoichiometric ratio were dissolved in distilled water with HCOOH. Ethanol was used as a grinding medium. Next, CaH$_2$O$_7$·H$_2$O was added with subsequent stirring and heating at 70–80 °C on a hot plate. Homogeneous water reagent solutions were slowly evaporated into a gel, which then formed a dry residue.

2.2. In situ synthesis

DSC and thermal gravimetric analysis (TG) were performed to estimate the optimal temperature of heat treatment of the final product. Thermal analysis was conducted with a Netzsch STA 449C Jupiter simultaneous analyzer operating with the heating rate of 10 K/min. In situ phase formation was studied by collecting of the X-ray powder diffraction (XRPD) patterns upon heating of the reagents 5CaO·4MgO·3V$_2$O$_5$ and 5CaO·4ZnO·3V$_2$O$_5$ taken with the stoichiometric ratios. Room temperature XRPD patterns before heating and after the phase formation were recorded using a Shimadzu XRD-7000 Maxima diffractometer and Cu Kα radiation in the 2θ range between 10° and 90°. High temperature (HT) XRPD in the 2θ range between 15° and 60° was employed with Ni-filter instead of a graphite monochromator and a Shimadzu HA-1001 sample heating attachment (the scanning rate 1 °/min; the 2θ step of 0.02°). The temperature uncertainty was maintained at less than 1 °C. The xerogels obtained during the HT XRPD experiments were placed on a Pt plate. The samples were heated from 20 °C up to 700 °C at the rate <10 °C/min. Further heating was carried out from 700 °C to 785 °C in the steps of 15 °C and the rate <5 °C/min. The samples were maintained for 1 h prior to every measurement at the temperatures listed. Heat treatment at 785 °C was continued for over 12 h. Further heating was carried out on MgO-containing sample from 850 °C to 950 °C with the step 50 °C and the rate <5 °C/min with the dwell time of 1 h at every step. The scanning temperatures were selected according to the DSC curves of the precursor samples. The highest scanning temperature (820 °C) was chosen for Ca$_3$Zn$_x$(VO$_4$)$_6$.

2.3. Characterization

XRPD patterns were collected at room temperature using a Rigaku DMAX-2200 diffractometer operating with Cu Kα radiation over the angular range 15°≤2θ≤80° with the step increment Δ2θ = 0.02°. The XRPD patterns were compared with those in the ICSD database (2021). Rietveld refinement of the crystal structures was performed using the XRPD data collected on a Bruker D8 ADVANCE diffractometer with position-sensitive detector VANTEC-1 operating with Cu Kα radiation (the angular range 10°≤2θ≤5134°; the step increment Δ2θ=0.021°). The XRPD patterns were compared with those in the PDF4+ICDD (2018) [34]. The crystallographic computing system JANA2006 [35] was employed for Rietveld refinements (Figs. S1–S5). Raman spectra were recorded on a Renishaw Ramascope U1000. This setup comprised a confocal Leica DML microscope, 50× Olympus objective lens (the numerical aperture of 0.55), a notch filter, and a cooled charge-coupled device detector. A Renishaw HeNe laser operating at 632.8 nm and 4 mW at the sample was employed as an excitation source. Typical spectra acquisition time was 300 s and the resolution was 1 cm$^{-1}$. The Raman spectrum of silica was used for spectral calibration. Fourier transform infrared (FTIR) measurements were carried out on a Bruker vacuum spectrometer Tensor 27 using KBr pellets. The FTIR spectra were collected in a transmittance mode in the range from 400 cm$^{-1}$ to 1000 cm$^{-1}$ with the resolution of 2 cm$^{-1}$. The FTIR spectra in the range of 50–600 cm$^{-1}$ were recorded using ATR technique with a diamond optical element employed at a Bruker Vertex 70v spectrometer. Vibrational spectroscopy was performed at room temperature.

3. Results and Discussion

Decomposition of the precursor colloidal solution upon heating in air is an exothermic process with the mass loss
mainly between 200 °C and 730 °C (Fig. 1). The total mass loss of the precursor mixture of Ca₃Mg₅(VO₄)₆ is 61.02 wt%, whereas the value of 52.57 wt% was obtained in the case of Ca₅Zn₇(VO₄)₁₂ up to 730 °C. Following the DSC data of a dried mixture of reagents, one can observe the water desorption at ~220 °C (Fig. 1) with the maximum of the DSC signal at 250 °C. It is accompanied by emission of CO₂ and NO₂ after decomposition of organics and (H₃N)⁺ groups with energy uptake. The slow exothermal process at 270 °C associated with the prolonged emission of H₂O, CO₂, NO₂ and NO was reported in earlier papers [31]. However, the next stages depicted in the DSC plots differ due to the other precursors chosen for synthesis. At 350 °C, there is an exothermal stage with the ongoing emission of the gases listed above (CO₂ and NO₂). After the known exothermal effect at 372 °C [31], a well pronounced exothermal peak near 450 °C correlates with emission of CO₂, NO₂ and H₂O. This can evidently be explained by the exhaust that forms during the decomposition of the available organic matrix. The energy output at 510–528 °C is accompanied by emission of CO₂, NO and NO₂. Extraction of CO₂ and NO occurs up to 730 °C with energy consumption. The observed disagreement between the obtained results and those reported earlier [31] arises from two main reasons. First, this difference may be caused by the reactants used to synthesize the target compositions. Second, the DSC data are analyzed in this study, whereas only the DTA results were presented previously [31]. The DSC curves of the dried precursor of Ca₅Zn₇(VO₄)₁₂ demonstrate several exothermal peaks at 396 °C, 451 °C, 528 °C and 727 °C and one endothermal one at 689.5 °C (Fig. 1). Some of the processes listed above can be evaluated more accurately employing in situ X-ray diffraction as an additional method.

The XRPD patterns of dried sol-gel precursors show the phase formation of CaCO₃ at 360 °C which is stable up to 785 °C (Fig. 2 and 3). Its appearance is accompanied by the emission of CO₂ from the decomposition of an organic matrix. The pyrovanadates CaMgV₂O₇ and Mg₃V₂O₇ are formed at 360 °C along with calcium carbonate (Fig. 2). The exothermal process near 450 °C is assigned to the formation of the intermediates α-Zn₃V₂O₇ and Ca₃V₂O₇ whose crystal structures are characterized by monoclinic symmetry (Fig. 1–3). The energy output at 510 °C (or 566 °C in Ref. [31]) corresponds to the phase with a cubic structure (space group Ia3d). Extraction of CO₂ observed up to 730 °C with energy consumption is caused by the start of calcite decomposition, which ends at 785 °C, according to the XRPD data (Fig. 1–3).

The mixture of phases is observed from 460 °C to 950 °C in the magnesium-containing powder sample (Fig. 2), whereas the zinc-containing sample is characterized by coexistence of the phases like CaCO₃, pyrovanadates, garnet-type vanadate in the temperature range 460–820 °C (Fig. 3).

Fig. 1 DSC and TG curves with mass spectrometry analysis of the gaseous phase during heating of the xerogel powders Ca₃Mg₅(VO₄)₆ (left) and Ca₅Zn₇(VO₄)₁₂ (right) prepared by the sol-gel process

Fig. 2 HT XRPD profiles of Ca₃Mg₅(VO₄)₆ prepared via a sol-gel process: * - Ca₅Mg₅(VO₄)₆, ● - Mg₃V₂O₇, ● - CaMgV₂O₇, Δ - Ca₃V₂O₇ (P2₁/c), V - Ca₅V₂O₇ (P,1), ▲ - CaCO₃
In turn, the phase transition in Zn$_2$V$_2$O$_7$ implies the change of space group $\text{C}2/c \rightarrow \text{C}2/m$ at 620 °C [36]. Ca$_2$V$_2$O$_7$ undergoes also the phase transition $\text{P}\overline{1} \rightarrow \text{P}2_1/c$ above 900 °C. CaMgV$_2$O$_7$ melts incongruently at 885 °C, whereas Ca$_3$V$_2$O$_7$ and Mg$_2$V$_2$O$_7$ are thermally stable even at 950 °C.

The coexistence of Ca$_3$Mg$_3$(VO$_4$)$_6$ (space group $\text{Ia} \overline{3}d$) and CaMgV$_2$O$_7$ (space group $\text{P}2_1/c$) is detected at room temperature in the reaction products (Fig. 2). In this way, one can carry out synthesis at 850 °C and, after short-term heat treatment, can obtain the target product with contamination of Ca$_3$V$_2$O$_7$. The presence of satellite pyrovanadates was revealed in many earlier studies on evaluation of the most efficient chemical route to synthetize garnet-type vanadates [3, 5, 15]. The elimination of these satellite pyrovanadates is a complex problem which is often dismissed when the target chemical products of Ca$_3$Mg$_3$(VO$_4$)$_6$ (M = Mg, Zn, Co, etc.) are synthesized. Fortunately, the impurity-free samples can be obtained. However, this usually requires a long duration of thermal treatment [4, 5]. Indeed, the heat treatment at 980 °C for 150 h allows a single-phase sample of Ca$_3$Mg$_3$(VO$_4$)$_6$ to be prepared. This temperature of the final annealing during the synthesis procedure corresponds to the melting point of Mg$_2$V$_2$O$_7$.

The XRPD analysis shows that polycrystalline Ca$_3$Mg$_{2-x}$Zn$_x$(VO$_4$)$_6$ (0 ≤ x ≤ 4) with some quantity (2–3 wt%) of pyrovanadate phases is formed via the sol-gel process (Fig. 4). The crystal structures of Ca$_3$Mg$_{1.5}$Zn$_{0.5}$(VO$_4$)$_6$ (0 ≤ x ≤ 4) were refined using the Rietveld method (Table S1; Supporting Information). The solid solution Ca$_3$Mg$_{2-x}$Zn$_x$(VO$_4$)$_6$ (0 ≤ x ≤ 4) crystallizes in the cubic space group $\text{Ia} \overline{3}d$, Z = 8 (Supporting Information: Fig. S1–S5). The fractional atomic coordinates and refinement parameters are listed in Table 1. Magnesium and zinc cations have close radii that promotes the formation of solid solutions [38]. Both Mg and Zn ions occupy the octahedral position (16d) and the formation of the solid solutions is proved by a linear change in the cell parameter and volume when zinc concentration increases (Fig. 4). The lattice parameter $a$ refined for Ca$_3$Mg$_{2-x}$Zn$_x$(VO$_4$)$_6$ deviates from the linear dependence because of a relatively large amount of CaMgV$_2$O$_7$ impurity (Supporting Information: Table S1).

The site occupancy factor of Ca$^{2+}$ positions is chosen to be about 5/6 that is close to the data reported by Ronniger and Mill [6]. Cation deficiency from 1/10 to 3/10 is not surprising and was also observed in other garnet-type vanadates [6, 39]. Therefore, a study of the local structure of these compounds becomes highly relevant in view of high deficiency in the cation sublattice.

Eight molecules of Ca$_3$Mg$_{2-x}$Zn$_x$(VO$_4$)$_6$ (M$^{2+}$ = Mg, Zn) per primitive cell in the $\text{Ia} \overline{3}d$, (006) structure support 3×8×19,5 = 468 modes of vibration with $\chi = 0$ involving the zero-frequency translational motion of the crystal. These vibrations are classified according to irreducible representations of the point group of the elementary cell [40]. Given that the number of equivalent sites in any set is defined by the order of the point group divided by the order of the site symmetry subgroup for the primitive or primitive rhombohedral lattices, the number is greater for the centered lattices. The body-centered unit cells have twice as many points as the primitive ones (Table 1).

Fig. 3 HT XRPD profiles of Ca$_3$Zn$_x$(VO$_4$)$_6$ prepared via a sol-gel process: * – Ca$_3$Zn$_x$(VO$_4$)$_6$, △ – Ca$_3$V$_2$O$_7$, (P2$_1$/c), ▲ – CaCO$_3$, ▼ – α-Zn$_2$V$_2$O$_7$, ▼ – β-Zn$_2$V$_2$O$_7.

Fig. 4 XRPD patterns of Ca$_3$Mg$_{2-x}$Zn$_x$(VO$_4$)$_6$ (0 ≤ x ≤ 4) (a), concentration dependence of the lattice parameters in Ca$_3$Mg$_{2-x}$Zn$_x$(VO$_4$)$_6$ (0 ≤ x ≤ 4) (b)
The vibration modes of the full symmetry group are characterized by the following irreducible representations of $O_h$:

\[ \Gamma^{\text{crys}} = 3A_{1g} + 5A_{1u} + 5A_{2g} + 5A_{2u} + 8E_g + 10E_u + 13F_{1g} + 18F_{1u} + 14F_{2g} + 15F_{2u} \]  

Three acoustic modes are described by $\Gamma^{\text{acoust}} = F_{1u}$ and the remaining ones,

\[ \Gamma^{\text{acoust}} = 3A_{1g} + 5A_{1u} + 5A_{2g} + 5A_{2u} + 8E_g + 10E_u + 13F_{1g} + 17F_{1u} + 14F_{2g} + 15F_{2u} \]

are active. The modes of the $F_{1u}$ symmetry are infrared active and the combination of $A_{1g}$, $E_g$ and $F_{2g}$ is Raman active. Infrared and Raman activities are presented in Table 2.

Vibrational modes can be classified in two main categories \([41, 42]\), i.e., internal modes of the tetrahedral VO$_4$ unit with the molecular symmetry $S_4$ and external modes, which include translations of Ca$^{2+}$, Mg$^{2+}$, Zn$^{2+}$ and [VO$_4$]$^{3-}$ ions, and librations of [VO$_4$]$^{3-}$. In a lattice of $A_{23}B_2$(VO$_4$)$_3$, zone-center Raman active vibrational modes can be distinguished for Ca$^{2+}$ cations (A-site in $A_{23}B_2$(VO$_4$)$_3$) and VO$_4$ tetrahedra, whereas Mg$^{2+}$/Zn$^{2+}$ cations (B-site) do not produce Raman active vibrations.

Table 1 Fractional atomic coordinates and isotropic thermal displacement parameters ($B$) of Ca$_3$Mg$_{1-x}$Zn$_x$(VO$_4$)$_6$, 0.5<=$x$<4 (SG $Ia\overline{3}d$, $Z$ = 8)

<table>
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<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$R_{\text{wp}}$</th>
<th>$B$</th>
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<td>Mg</td>
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<td>0.2897(1)</td>
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<td>Mg</td>
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SOF stands for site occupancy factor

Table 2 Classification of the $k = 0$ unit cell modes* for Ca$_3$Mg$_{1-x}$Zn$_x$(VO$_4$)$_6$, $M^{III}$ = Mg, Zn (SG $Ia\overline{3}d$, $Z$ = 8)

<table>
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<tr>
<td>A$_{1g}$</td>
<td>1</td>
<td>2</td>
<td>xx + yy + zz</td>
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<td>2</td>
<td>3</td>
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<tr>
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<td>3</td>
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</tr>
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</tr>
<tr>
<td>E$_{g}$</td>
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<td>2</td>
<td>xx + yy + 2zz</td>
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<td>4</td>
<td>v3xx – v3yy</td>
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<tr>
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<td>4</td>
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<td>T</td>
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<tr>
<td>F$_{3g}$</td>
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<td>6</td>
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<tr>
<td>F$_{3u}$</td>
<td>3</td>
<td>6</td>
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</tr>
<tr>
<td>Overall</td>
<td>3</td>
<td>36</td>
<td>108</td>
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* The $F_{1u}$ modes are infrared and the $A_{1g}$, $E_u$ and $F_{2u}$ modes are Raman active.
Translations and librations of the VO₄ unit are associated with the representations below:

\[ \Gamma'(\text{VO}_4) = A_{1u} + A_{2g} + E_g + E_u + 2F_{1g} + 3F_{1u} + \]
\[ 3F_{2g} + 2F_{2u} \] (3)

\[ L(\text{VO}_4) = A_{1g} + A_{2u} + E_g + E_u + 3F_{1g} + 2F_{1u} + \]
\[ 2F_{2g} + 3F_{2u} \]. (4)

Once acoustic modes are subtracted, the external modes are distributed among the irreducible representations \( A_{1g} + 2A_{2u} + 2A_{2g} + 3A_{1u} + 3E_g + 5E_u + 7F_{1g} + 10F_{1u} + \)
\[ 7F_{2g} + 9F_{2u} \). Therefore, the internal modes of the tetrahedral VO₄ unit can be characterized by

\[ \Gamma \text{_{crist}}^{\text{libr}} = 2A_{1g} + 3A_{1u} + 3A_{2g} + 2A_{2u} + 5E_g + 5E_u + \]
\[ 6F_{1g} + 7F_{1u} + 7F_{2g} + 6F_{2u} \]. (5)

In Ca₂₅MIII₂(VO₄)₃ (MIII = Mg, Zn), the symmetry of the VO₄ tetrahedron changes due to the site symmetry and crystal field effects, and all the internal modes are split. The latter are summarized in Table 3.

FTIR and Raman spectroscopy techniques are employed to study possible structural changes when Mg²⁺ cations are substituted for Zn²⁺ in the solid solution Ca₅Mg₄₋₅Znₓ(VO₄)₆. Both types of vibrational spectra of Ca₅Mg₄₋₅Znₓ(VO₄)₆ (0≤x≤4) are similar and do not indicate any significant changes in the crystal structure (Fig. 5). Whereas 25 Raman and 17 infrared modes are active according to the group theory, not all of them can actually be detected [10]. This discrepancy originates from the negligible changes in polarizability and dipole moment, which do not give rise to observable Raman and infrared modes [43]. According to the previous studies on garnet compounds [41, 44, 45], the Raman lines between 910 cm⁻¹ and 950 cm⁻¹ and infrared bands in the range of 700–950 cm⁻¹ correspond to the internal anti-symmetric (ν₁) stretching vibrations of [VO₄]³⁻ ions, whereas the symmetric (ν₁) stretching modes of [VO₄]³⁻ are revealed only in the Raman spectra between 690 cm⁻¹ and 875 cm⁻¹. Typical weak Raman lines at ~450 cm⁻¹ with the shoulder at ~430 cm⁻¹ are expected for the VO₄ bending vibrations. An observed general order of mode frequencies, i.e., \( L(\text{VO}_4) > \Gamma' \) (the metal cation) \( > \Gamma \) (VO₄) is also presented in most garnet-type silicates. A very strong Raman peak (as well as some weak ones) at ~320 cm⁻¹ is attributed to the librational VO₄ modes which can be also distinguished as the infrared band in the range of 340–380 cm⁻¹ (Fig. 5).

**Table 3** Correlation table for the internal vibrations of [VO₄]³⁻ in Ca₅MIII₄₋₅(VO₄)₆, MIII = Mg, Zn (SG Ia₃d, Z = 8)

<table>
<thead>
<tr>
<th>[VO₄]³⁻</th>
<th>Normal modes of free [VO₄]³⁻ with ( T_d ) symmetry</th>
<th>Splitting of normal modes of ( T_d ) symmetry due to site symmetry and factor group effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>site symmetry and factor group</td>
<td>( \nu_1 (A_1) )</td>
<td>( \nu_3 (F_3) )</td>
</tr>
<tr>
<td>( S_4 )</td>
<td>( A )</td>
<td>( B )</td>
</tr>
<tr>
<td>( O_h )</td>
<td>( A_{1g} + A_{2u} + E_g + E_u + F_{2u} )</td>
<td>( A_{1g} + A_{1u} + F_{2u} + 2F_{1u} )</td>
</tr>
<tr>
<td>( T_d )</td>
<td>( A_{1u} + A_{2g} + E_g + E_u + 2F_{1g} )</td>
<td>( A_{1u} + A_{1g} + A_{2g} + A_{1u} + 2E_g + 2F_{1u} + 3F_{1g} + 2F_{2u} )</td>
</tr>
</tbody>
</table>
The Raman line at ~245 cm\(^{-1}\) is assigned to translation modes of Ca\(^{3+}\). Meanwhile, T'(Ca\(^{3+}\)) and T'(Mg\(^{2+}/Zn\(^{2+}\)) modes are associated with the infrared band at 190–250 cm\(^{-1}\). Very weak Raman lines below 200 cm\(^{-1}\) correspond to external translations of VO\(_4\) tetrahedrons. The latter stand in the line with the T'(SiO\(_4\)) modes analyzed previously for A\(_2\)B\(_2\)(SiO\(_4\))\(_3\) (A = Mg, Ca, Mn, Fe; B = Al, Cr, Fe) [44, 45]. Substitution of Mg\(^{2+}\) by Zn\(^{2+}\) in Ca\(_3\)Mg\(_4\)Zn\(_4\)(VO\(_4\))\(_6\) leads to the monotonic increase of the unit cell parameter (Fig. 4b) and a slight shift (not exceeding ~10 cm\(^{-1}\)) of most of the vibrational bands towards lower wavenumbers (Fig. 5). The similar dependencies of vibrational frequencies on the lattice parameter were earlier found in silicate garnets [44, 45]. Given that the density of modes is relatively high to allow a clear assignment of all the lines, it is obviously not complete. Therefore, first-principle calculations in the density functional theory (DFT) framework based on the geometry optimization of Ca\(_3\)Mg\(_4\)Zn\(_4\)(VO\(_4\))\(_6\) (M = Mg, Zn) are needed to perform an accurate assignment of vibrational bands and will be discussed elsewhere.

4. Conclusions

High-temperature X-Ray diffraction supported by DSC technique allowed studying Ca\(_3\)Mg\(_4\)Zn\(_4\)(VO\(_4\))\(_6\) (0 ≤ x ≤ 4) so as to provide more detailed and reliable data on the phase formation of garnet-type vanadates. The synthesis of Zn-doped Ca\(_3\)Mg\(_4\)(VO\(_4\))\(_6\) is accompanied by the appearance of Ca\(_3\)V\(_2\)O\(_7\), Mg\(_2\)V\(_2\)O\(_7\) or Zn\(_2\)V\(_2\)O\(_7\). These satellite pyrovannadate phases are stable up to 950 °C and disappear only above their melting point. The single-phase samples of Ca\(_3\)Mg\(_4\)(VO\(_4\))\(_6\) and Ca\(_3\)Zn\(_4\)(VO\(_4\))\(_6\) can be obtained following heat treatment for 150 h at 980 °C and at 750 °C, respectively. The formation of the solid solution Ca\(_3\)Mg\(_{4-x}\)Zn\(_x\)(VO\(_4\))\(_6\) (0 ≤ x ≤ 4) was confirmed by XRPD and vibrational spectroscopy. The findings in structural chemistry contribute to understanding of the impact of synthesis procedures on crystal engineering of vanadates and other garnet-type oxides.

Supplementary materials

Supplementary materials in the online format are available at the website of this paper. These data contain:

**Table S1:** Phase composition and lattice parameters of Ca\(_3\)Mg\(_{4-x}\)Zn\(_x\)(VO\(_4\))\(_6\) (0 ≤ x ≤ 4). **Fig. S1:** Rietveld refinement of Ca\(_3\)Mg\(_4\)(VO\(_4\))\(_6\) from XRPD data. **Fig. S2:** Rietveld refinement of Ca\(_3\)Mg\(_4\)Zn\(_4\)(VO\(_4\))\(_6\) from XRPD data. **Fig. S3:** Rietveld refinement of Ca\(_3\)Mg\(_2\)Zn\(_2\)(VO\(_4\))\(_6\) from XRPD data. **Fig. S4:** Rietveld refinement of Ca\(_3\)Mg\(_2\)Zn\(_2\)(VO\(_4\))\(_6\) from XRPD data. **Fig. S5:** Rietveld refinement of Ca\(_3\)Zn\(_4\)(VO\(_4\))\(_6\) from XRPD data.

**References**


**Funding**

This study was funded by the Research Programs No. AAAA-A19-119090190041-7 and No. AAAA-A19-11902190044-1 (IHTE UB RAS).

**Acknowledgments**

We are grateful to Dr. Olga G. Reznitskikh (ISSC UB RAS), Dr. Elena A. Sherstobitova (IMP UB RAS) and Dr. Nikolai I. Moskalenko (IHTE UB RAS) for technical assistance. The crystallographic and spectroscopic studies were carried out in the Shared Access Centers at IMET UB RAS and IHTE UB RAS, respectively.

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**Conflict of interest**

The authors declare no conflict of interest.

**Additional information**

Webpages of Institute of High-Temperature electrochemistry: [http://www.ihte.uran.ru/?page_id=3106](http://www.ihte.uran.ru/?page_id=3106)