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# Fluorwavellite from Petroshnitsa river valley, Republic of Macedonia

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The first finding of fluorwavellite $Al_{2.90}(PO_4)_2(OH)_2.[F_{0.88}(OH)_{0.12}]5H_2O$ ($+0.10H^+$) from the Balkan Peninsula was studied by XRD, FTIR, Raman spectroscopy and thermal analysis. The unit cell volume of the sample is comparably smaller than that of the wavellite and fluorwavellite studied so far. The vibrational modes of water molecules and hydroxyl groups are detected in their Raman and IR spectra. The results on the thermal decomposition of the fluorine analogue with wavellite structural topology are reported for the first time and different types of water were defined.

**Keywords:** fluorwavellite, crystal structure, Raman spectroscopy, FTIR spectroscopy, thermal behavior.

## INTRODUCTION

New data on lithostratigraphy, petrology and ore mineralogy of the volcanic rocks, exposed along the Petroshnitsa river valley, Republic of Macedonia have been recently reported [1]. In the same study, the complex sulfide mineralization was described as generated during a two-stage mineralization process. Quartz-wavellite and wavellite veins that fill cracks in the intensively quartzified latite – trachytes are referred to the first hydrothermal stage. The preliminary chemical analyzes of the wavellite crystals show a significant amount of fluorine, suggesting the presence of the newly described fluorine analogue of wavellite $Al_3(PO_4)_2(OH)_2(OH_{0.5-x}F_{0.5+x}).5H_2O$ [2]. This mineral is identical to the wavellite in terms of structural topology and morphology. The crystal structure is composed of two different chains of corner sharing Al octahedra, additionally connected by $PO_4$ tetrahedra [3]. The F atoms replace part of the OH groups, linking the Al octahedra.

The aim of the study is to determine the structural and physicochemical characteristics of the first fluorwavellite finding in the Balkan area.

## METHODS

*Single crystal* (colorless prismatic crystals with dimensions 0.6 × 0.3 × 0.25 $mm^3$) of the studied sample was carefully selected and mounted on a glass capillary. Diffraction data were collected at room temperature by xscan technique, on an Agilent Diffraction SuperNova Dual four-circle diffractometer equipped with Atlas CCD detector using mirror-monochromatized MoKα radiation from a micro-focus source (λ = 0.7107 Å). The determination of cell parameters, data integration, scaling and absorption correction was carried out using the CrysAlis Pro program package [4]. The structures were solved by direct methods (SHELXS-2014) [5] and refined by full-matrix least-square procedures on F2 (SHELXL-2014). The heavy atoms (P, Al, O) and part of the hydrogen atoms were positioned from difference Fourier maps. It was not possible to obtain the positions of the hydrogen atoms for hydroxyl groups with oxygen atoms, numbered as O5 O9 and O10. The non-hydrogen atoms were refined anisotropically while the hydrogen atoms were constrained to ride on their parent atom with Uiso(H) values of 1.2Ueq ($H_2O$) and 1.5Ueq (OH). A summary of the fundamental crystal and refinement data is provided in Table 1.

*Differential thermal analysis and Thermogravimetry* (DTA-TG) were carried out on the DTA-TG analyzer SETSYS2400, SETARAM at the following conditions: temperature range from 20 to

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**Table 1.** Data collection and structure refinement parameters

| | |
|---|---|
| Diffractometer | Agilent Diffraction SuperNova |
| X-ray radiation | Mo*K*α (λ = 0.71075 Å) |
| Temperature (K) | 290 |
| Chemical Formula | $Al_{2.90}(PO_4)_2(OH)_2[F_{0.88}(OH)_{0.12}] \cdot 5H_2O$ $(+0.10H^+)$ |
| Formula Mass | 408.85 |
| Crystal system | Orthorhombic |
| Space Group | *P c m n* |
| Unit cell parameters (Å) | *a* = 9.6111(4) |
| | *b* = 17.3422(7) |
| | *c* = 6.9804(3) |
| Unit cell volume (Å$^3$) | 1163.48(8) |
| No. of formula units per unit cell, Z | 4 |
| Density | 2.334 |
| F(000) | 826 |
| Crystal size (μm) | 60 × 30 × 25 |
| Θ range | 3.794–29.334 |
| Index ranges | $-8 \le h \le 12$; $-23 \le k \le 22$; $-7 \le l \le 9$ |
| Reflections collected/unique | 3144 / 1412 |
| Reflection with I > 2\s(I) | 1186 |
| Completnes to Θ (%) | 0.99 |
| Min. and max transmission | 0.94958 , 1 |
| Refinement method | Full-matrix least squares on $F^2$ |
| Parameters refined | 112 |
| GoF | 1.094 |
| R indices [$F_o > 4\sigma F$] | *R* = 0.0341, *wR* = 0.0867 |
| R indices (all data) | *R* = 0.0436, *wR* = 0.0945 |
| Largest diff. peak / hole (e / Å$^3$) | +0.567 / –0.457 |

1000 °C, in a static air atmosphere, with a heating rate of 10 C min$^{-1}$ and 10–15 mg samples mass.

*Raman spectrum* was collected in backscattering geometry using HORIBA JobinYvon Labram HR spectrometer, Olympus BH2 microscope, 633-nm line of He-Ne laser, CCD detector, and x50 objective.

*FTIR spectrum* of the powder KBr pallet was collected using Tensor 37 Bruker spectrometer, averaging over 64 scans in the 400–4000 cm$^{-1}$ spectral range.

## RESULTS AND DISCUSSION

Spherulitic wavellite aggregates with radial structure (Fig. 1) with a maximum diameter of about 15 mm are formed in the cracks and veins of the hosted volcanic rocks. A colorless needle shaped prismatic crystal was selected for the single crystal analyses. The obtained structural parameters are comparable with that of the previously reported data for wavellite and fluorwavellite (Table 2).

The studied sample exhibit similar structural topology to that of fluorwavellite, where one of the OH groups is partially replaced by fluorine atoms. Atomic coordinates and selected bond distances are presented in Tables 3 and 4. The structural packing of the studied compound is shown in Fig. 2.

**Fig. 1.** Hemispherical fluorwavellite aggregates up to 15 mm in diameter.

**Table 2.** Unit cell parameters for wavellite and fluorwavellite, available in the structural databases

| | Wavellite single crystal data | Wavellite – F rich single crystal data | Fluorwavellite single crystal | Fluorwavellite powder data | Fluorwavellite single crystal data |
|---|---|---|---|---|---|
| Ref. | [3] | [6] | [2] | | **this study** |
| Formula | $Al_3(PO_4)_2(OH)_3$ $5H_2O$ | $Al_3(PO_4)_2(OH)_2$ $[F_{0.53}OH)_{0.47}]$ $5H_2O$ | $Al_3(PO_4)_2(OH)_2[F_{0.90}(OH)_{0.10}]$ $5H_2O$ | | $Al_{2.90}(PO_4)_2(OH)_2[F_{0.88}$ $(OH)_{0.12}]5H_2O$ $(+0.10H^+)$ |
| Unit cell parameters | | | | | |
| SGc | *Pcmn* | *Pcmn* | *Pcmn* | *Pcmn* | *Pcmn* |
| a (Å) | 9.621(2) | 9.6422(7) | 9.6311(4) | 9.6482(4) | 9.6111(4) |
| b (Å) | 17.3630(40) | 17.4146(15) | 17.3731(12) | 17.362(12) | 17.3422(7) |
| c (Å) | 6.994(3) | 7.0094(2) | 6.9946(3) | 6.9848(3) | 6.9804(3) |
| V (Å$^3$) | 1168.34 | 1176.98 | 1170.35 | 1170.04 | 1163.48(8) |

**Table 3.** Fractional atomic coordinates and displacement parameters

| | x | y | z | $U_{eq}$ | Occupancy |
|---|---|---|---|---|---|
| Al1 | 0.22334(12) | 0.25 | 0.37577(15) | 0.0064(4) | 0.927(6) |
| Al2 | 0.24385(8) | 0.51608(4) | 0.64131(10) | 0.0061(3) | 0.977(4) |
| P | 0.06048(6) | 0.40754(3) | 0.39593(8) | 0.00697(19) | 1 |
| O1 | 0.14113(18) | 0.42751(9) | 0.5790(2) | 0.0096(4) | 1 |
| O2 | 0.08827(19) | 0.32319(10) | 0.3445(3) | 0.0147(4) | 1 |
| O3 | –0.09569(17) | 0.41666(9) | 0.4354(2) | 0.0096(4) | 1 |
| O4 | 0.10083(17) | 0.45839(10) | 0.2256(2) | 0.0116(4) | 1 |
| O5 | 0.195(9) | 0.25 | 0.634(13) | 0.0167(15) | 0.11(6) |
| F | 0.2237(11) | 0.25 | 0.6299(12) | 0.0167(15) | 0.89(6) |
| O6 | 0.32037(18) | 0.51776(10) | 0.3952(2) | 0.0098(4) | 1 |
| H6 | 0.415066 | 0.52118 | 0.391898 | 0.015 | 1 |
| O7 | 0.3689(2) | 0.32919(11) | 0.4017(3) | 0.0214(5) | 1 |
| H71 | 0.390826 | 0.356574 | 0.495244 | 0.026 | 1 |
| H72 | 0.373627 | 0.365274 | 0.299845 | 0.026 | 1 |
| O8 | 0.34954(19) | 0.61041(10) | 0.6972(3) | 0.0137(4) | 1 |
| H81 | 0.365236 | 0.606614 | 0.826778 | 0.016 | 1 |
| H82 | 0.294536 | 0.645815 | 0.696278 | 0.016 | 1 |
| O9 | 0.1920(13) | 0.75 | 0.720(6) | 0.060(8) | 0.53(5) |
| O10 | 0.220(2) | 0.75 | 0.603(5) | 0.052(5) | 0.47(5) |

**Table 4.** Comparing Selected bond distances

| Distance | Wavellite [3] | Fluorwavellite [2] | This study |
|---|---|---|---|
| Al1 – F | | 1.7817(17) | 1.7770(30) |
| Al1 – F | | 1.7982(16) | 1.7940(30) |
| Al1 – $OH_2$ (x2) | 1.8336(42) | 1.8346(13) | 1.8290(20) |
| Al1 – $OH_2$ (x2) | 1.9835(46) | 1.9715(15) | 1.9690(20) |
| Al1 – OH | 1.8031(45) | | 1.8300(90) |
| Al1 – OH | 1.7758(44) | | 1.8600(90) |
| Al2 –OH | 1.8795(32) | 1.8747(12) | 1.8703(18) |
| Al2 –OH | 1.8826(32) | 1.8793(12) | 1.8754(18) |
| Al2 –O | 1.8947(41) | 1.8807(13) | 1.8763(19) |
| Al2 –O | 1.8969(41) | 1.8973(12) | 1.8906(19) |
| Al2 –O | 1.9268(39) | 1.9210(13) | 1.9164(19) |
| Al2 –$OH_2$ | 1.9799(43) | 1.9686(14) | 1.9660(20) |

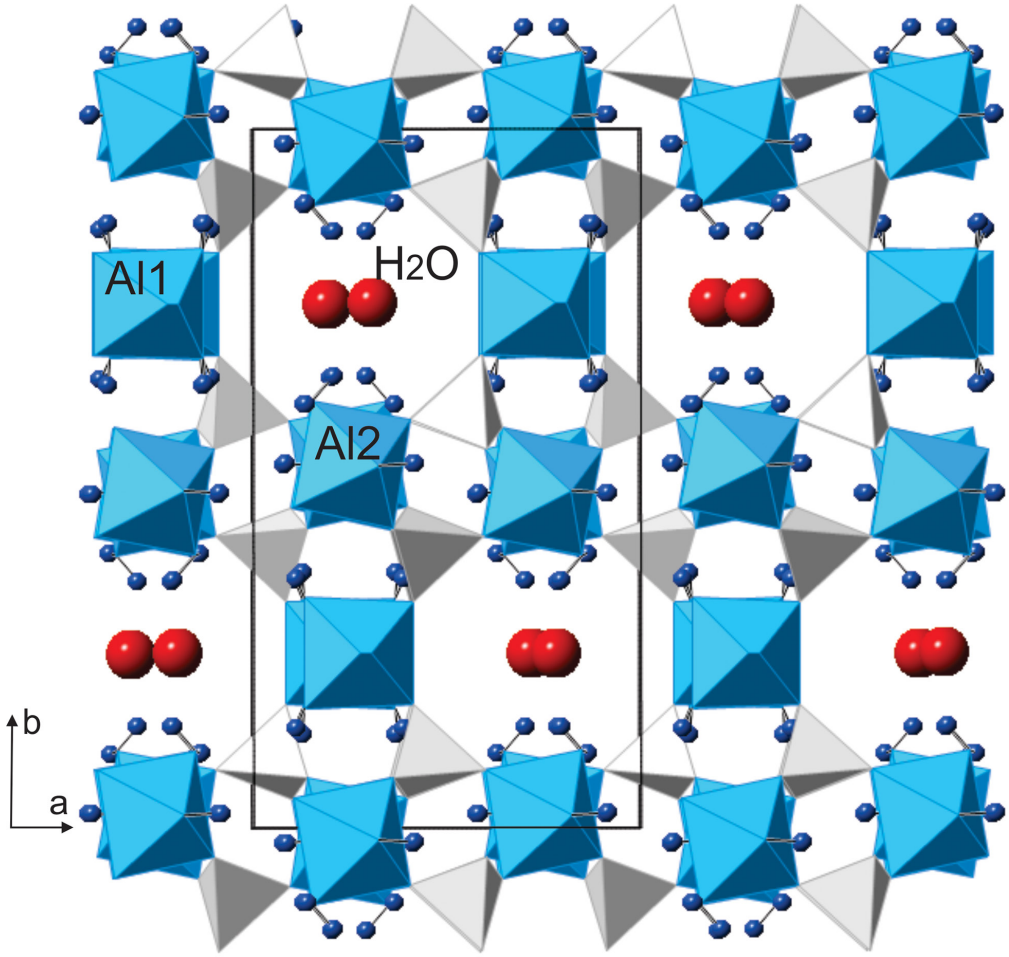


**Fig. 2.** Structural packing of the fluorwavellite under study.

Our structural refinement confirms splitting of the common (OH, F) position as it is shown on Fig. 3. Considering the difference in the size of the hydroxyl group ion and the fluorine atom, it could be expected that the replacement of the OH groups by F will reduce the unit cell volume. However, this is not unambiguously visible from the data known so far. Most probably the structure density is also affected by the conditions of formation, as fluorwavellite is formed in a variety of environments.

The Raman spectra of fluorwavellite crystals (Fig. 4) reveal intensive peak at 1022 $cm^{-1}$, assigned to the symmetrical stretching vibration of the phosphate group and other peaks at 410, 543 and 636 $cm^{-1}$ due to bending modes of phosphate group. Peaks at lower frequencies are assigned to Al-O lattice vibrations. In the range of O-H stretching vibrations several peaks can be distinguished. The most intensive and sharp peak at 3508 $cm^{-1}$ is assigned to stretching vibrations of hydroxyl group, while

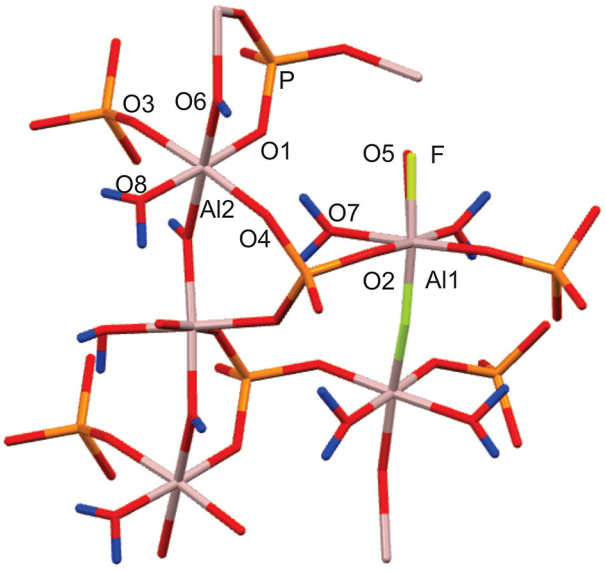


**Fig. 3.** Structural motive showing the common (OH, F) position splitting.

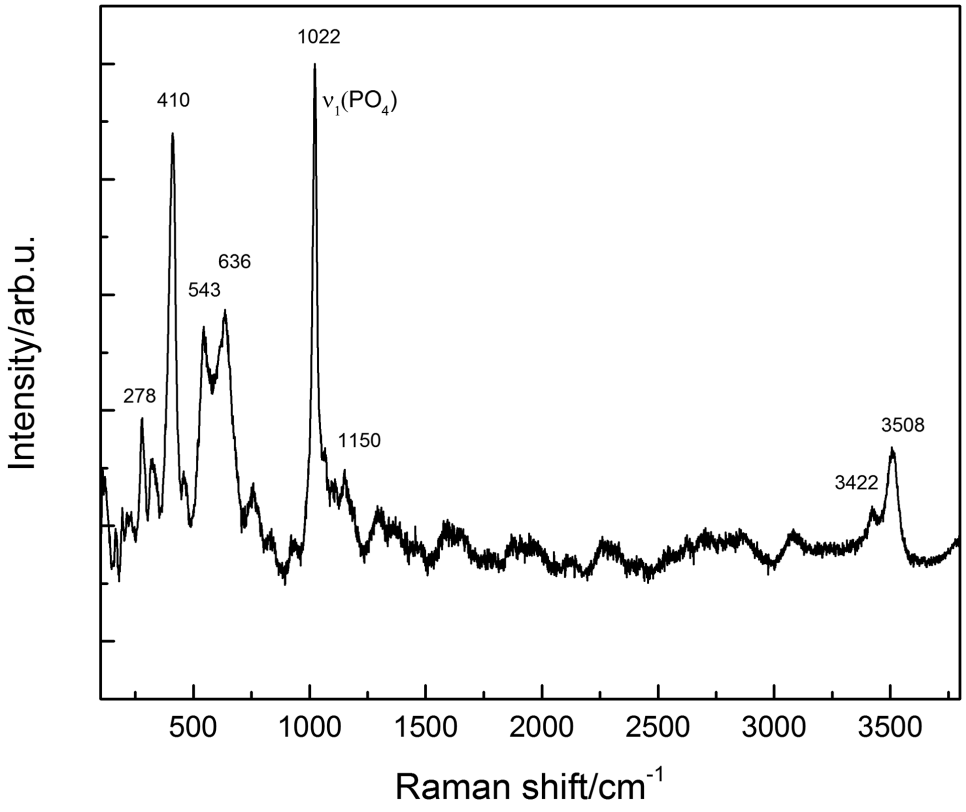


**Fig. 4.** Raman spectra of fluorwavellite crystals.

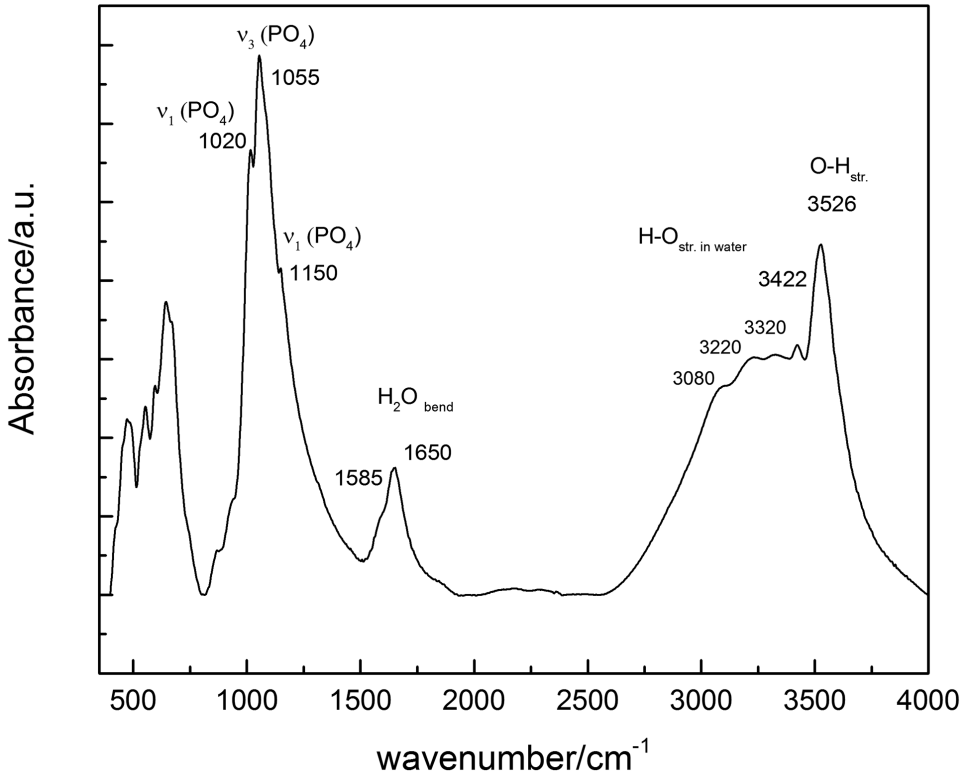


**Fig. 5.** IR spectra of fluorwavellite crystals.

broader overlapping bands at 3422 and around 3100 $cm^{-1}$ can be related to different water molecules. A strong and sharp peak at 3526 $cm^{-1}$ due to stretching vibrations of OH groups occurs in the same spectral range of IR spectra (Fig. 5). This peak is slightly shifted to higher wavenumbers as compared to previously reported spectral data for wavellite [6]. Several broader absorption bands could be resolved at around 3422, 3320, 3220 and 3080 $cm^{-1}$ due to OH stretching in water molecules, while bending modes are detected at 1650 and 1585 $cm^{-1}$. This indicates the presence of different water molecules with varying degrees of hydrogen bonding.

Thermal decomposition data of both wavellite and fluorwavelite have not been found so far in the literature. DTA and TG curves, as well as DTG (first derivative of TG) and DDTG (second derivative of TG) curves are presented on Fig. 6. Three endothermal and two exothermal effects can be separated on the DTA curve. First endothermal one is around 97°C and related to the release of physisorption water. The second effect maximizes at 215 °C and corresponds to 21.6 wt% mass loss from the TG curve. This event involves the dehydration of the structure expressed by evolving of 5 molecules of water. Theoretically, this loss is 21.85 wt%, which is in a good agreement with our data. The first water

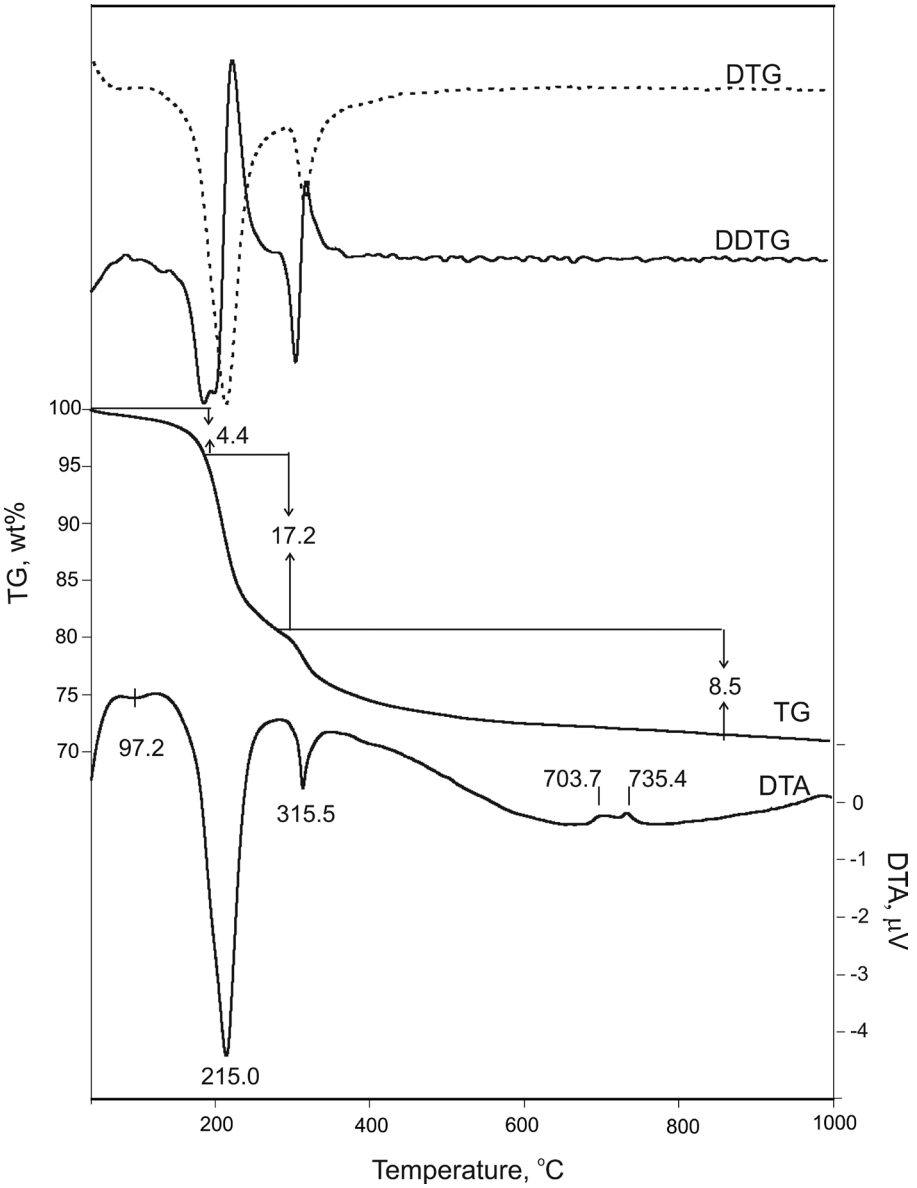


**Fig. 6.** DTA-TG(DTG and DDTG) curves of the fluorwavellite under study.

molecule (4.4 wt% mass loss) could be separated only when the DDTG curve was applied. This water is situated by hydrogen bonds in the structure cavities. The remaining four water molecules are released (17.2 wt%) at a later stage as they are more strongly linked through coordination bonds to the aluminum atoms of the structural octahedrons. The third endothermal effect (maximum of 315.5 °C) is mainly due to the process of dehydroxylation. Probably the defluoridation process starts simultaneously with dehydroxylation. Both exothermal effects at 704 and 735 °C represent the heat released at the formation of new phases, most probably aluminum phosphate and oxides.

## CONCLUSIONS

Fluorwavellite from hydrothermal veins crossing early Oligocene volcanic rocks, part of the Kratovo-Zletovo volcanic area, Republic of Macedonia was studied. This is the first described finding of the mineral for the Balkan region.

Structural and spectroscopic data reveal similarity to fluorwavellite, already described by other localities.

Thermal decomposition data of flourwavellite were reported for the first time and respectively different types of water were defined.

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# ФЛУОРВАВЕЛИТ ОТ ДОЛИНАТА НА РЕКА ПЕТРОШНИЦА – РЕПУБЛИКА МАКЕДОНИЯ

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(Резюме)

Първата находка на флуорвавелит $Al_{2.90}(PO_4)_2(OH)_2.[F_{0.88}(OH)_{0.12}]5H_2O$ $(+0.10H^+)$ от Балканския полуостров беше изследвана чрез XRD, FTIR, Raman спектроскопия и термичен анализ. Обемът на елементарната клетка на пробата е сравнително по-малък от този на образци на вавелит и флуоравелит, изследвани досега. В рамановите и инфра-червени спектри се констатират вибрационни характеристични линии на водни молекули и хидроксилни групи. За първи път се съобщават резултати от термичното разлагане на флуорния вавелитов аналог, като се диференцират различните типове вода в структурата.