MANGANESE MINERALS FROM THE POZHARITE LOCALITY, CENTRAL RHODOPES, BULGARIA: RAMAN AND INFRARED SPECTROSCOPY AND X-RAY DIFFRACTION DATA. T. N. Moroz¹, N. A. Palchik¹, T. N. Grigorieva¹, S. V. Goryainov¹, S. Entcheva².¹Institute of Geology and Mineralogy Siberian Branch of RAS (630090, Novosibirsk, Russia, moroz@igm.nsc.ru), ²Earth and Man Nationa Museum (Sofia, Bulgaria).

Introduction: The mineral and microelement composition and structures of manganese minerals from Pozharite locality, Enyovche deposit, Eastern Rhodopes (Bulgaria) have been studied by means of infrared, micro-Raman spectroscopy with used of visible and near-ultraviolet excitation and X-ray diffraction methods. Pozharite locality is a part of weathering zone of Pb-Zn scarn deposit Enyovche of Nedelinsko ore field. It represents a layer-like pyrolusite-psilomelane body formed after oxidation of johannsenite – hedenbergite skarns. The pyrolusite, psilomelane and Mn-calcite are major minerals in ores. 197 400 tons of Mn-ore and 64 389 tons of Mn metal were mining in the period of 1959-1971 years. The average manganese content varies from 31,0 to 36.1% [1]. It is the most representative deposit of rhodonite from Bulgaria. It is promising for the production of material for decorative purposes. The rhodonite mineralization forms a large layer-like body with dimensions of 100 by 250 m and an average thickness of about 7-8 m. The mineral forms dense fibrous aggregates of individuals with a length of 15-20 cm and a silky shine. It is often changed to black manganese oxides that form dendritic aggregates among rhodonite [2].

X-ray diffraction studies were carried out on an ARL X'TRA (Thermo Fisher Scientific (Ecublens) SARL) powder diffractometer (CuKα radiation). The spectra were recorded on a VERTEX 70 FT-IR (Bruker) spectrophotometer. The micro Raman spectra were measured by using Horiba Jobin IVon LabRAM HR800 spectrometer with 1024 pixel LN/CCD detector. Raman spectra were collected in backscattering geometry using Olympus BX41microscope. The exciting was performed with the visible 514.5 nm (2.41 eV) line of Ar ion laser and the near-ultraviolet 325 nm (3.8 eV) line of He-Cd laser.

As a mineral class, pyroxenes and pyroxenoid have a substantial range of structures and chemical compositions. Determination of their compositional and structural characteristics in rocks contributes greatly to understanding the petrologic processes that produced them. Raman spectroscopy is well suited for this determination [3].

Five-term chain rhodonite (Mn, Fe, Ca)[Si₅O₁₅] is a member of the pyroxenoid group of minerals, crystallizing in triclinic system. The different crystal systems are characterized by the certain number of diffraction groups containing from one to five space groups with the same rules of systematic absences, and triclinic system is one of them. In this case, two space groups (sp. gr.) $P1 = C_i^1$ and $P\bar{1} = C_i^1$ cannot be distinguished from the diffraction data. These groups can be distinguished in IR and Raman spectra. For the $C_i^1$ space group all vibrations are active in IR spectrum and Raman one. For the $C_i^1$ the alternative selection rule is realized: vibrations are active in IR spectrum are inactive in Raman one, and vice versa, vibrations active in Raman spectra are inactive in IR one [4]. Fig. 1 show that no coincidence bands in Raman and IR spectra. It is preferably for $P\bar{1} = C_i^1$ space group. Despite the twisted and deformed SiO₄ chains in the rhodonites, the Raman spectra are similar to those of the pyroxenes, showing the same characteristic type of vibration modes [5] (fig. 1, 2).

According to the analytical methods the samples of black and pink color have following characteristics. Raman spectra of pink samples show rhodonite with spectrum more similar to R060549 spectra rhodonite $(\text{Mn}_{0.76}\text{Ca}_{0.12}\text{Fe}_{0.07}\text{Mg}_{0.06})\text{Si}_{0.96}\text{O}_3$ from Gemological...
Institute of America [6], with calcite, pyroxmangite, augite impurities (fig. 1, 2). The Raman results show that samples of rhodonite have the disordered carbon matter (fig.1, insert).

Trace element composition was determined on a VEPP-3 energy dispersive X-ray fluorescence elemental analysis workstation at the Synchrotron Radiation (SR) Center of the Institute of Nuclear Physics, Siberian Branch, Russian Academy of Sciences. The greatest variety and amount of microelements are observed in black samples with ~ 68 % Mn, and especial high levels for K, Fe, Zn, Sr, Cr, Ni, As and Mo according SR X-ray fluorescence analysis data. X-ray powder diffraction show that the major minerals of black part of samples are 9.6Å manganese minerals, 7.2Å birnessite, 2.39Å vernadite, impurities of hollandite, ramsdellite, romanechite, chalcophanite, cryptomelane. The identification of many manganese minerals meets considerable difficulty [7,8]. An admixture of 9.6Å Mn minerals was preliminarily identified as either buserite I, buserite II, or todorokite. For more exact identification, selected samples were subjected to heat treatment at 105°C, which showed various extents of weakening of the 7.2 Å reflection in all X-ray diffraction patterns. The structure of 9.6Å mineral was not transformed into birnessite, evidence of absence of buserite I. The structures of buserite II and todorokite do not change at this temperature. Annealing up to 200°C for 1 h transforms the birnessite structure into 4.9Å manganese oxide. The retained intensity of the 9.6 Å reflection after annealing at 200°C implies the absence of asbolan and a possible presence of buserite-II and/or todorokite in the sample. After heat treatment at 200°C, one of the X-ray diffraction patterns featured broadening of the 9.6 Å reflection. This might be due to the formation of mixed-layered minerals, buserite-I + buserite-II or buserite-II + asbolan, which have different temperature stabilities. This effect can explain by stepwise removal of water from the todorokite structure which occurs over a wide temperature range depending on the degree of crystallinity. The occurrence of todorokite is verified by the appearance in IR spectra of a shoulder in the region of 760 cm\(^{-1}\) and the stretching vibrations of OH groups in the region of 3200 cm\(^{-1}\). Some of these phases, namely, vernadite and todorokite are identified by Raman spectroscopy (fig.2, insert).

Mineralogy and crystal chemistry of manganese minerals from Pozharite region Enovche side, Central Rhodope (Bulgaria) with the most representative deposit of rhodonite are multifarious. X-ray powder diffraction data and IR spectra of pink samples correspond to rhodonite with quartz, bustamite, and johannsenite impurities. Complex of physical chemical analytical methods show crystal-chemical peculiarities of studied rhodonite, allow identify of Mn silicates, carbonate, different manganese oxides, including 9.6 Å mineral todorokite.

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Fig. 2. Micro-Raman spectra of rhodonite (1); carbonate (2); and black part of sample (insert).