



Spectroscopic characterization of rare hydrated ammonium borate mineral larderellite

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ABSTRACT

Two samples of larderellite $(\text{NH}_4)_2\text{B}_5\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ from Monte Rotonda (Italy) have been studied. Spectroscopic methods, like infrared and Raman spectroscopy, were used in combination with thermal analysis and X-ray diffraction. The main objective was vibrational characteristic of research mineral and, based on the obtained results, test how the long storage of minerals affect their structure. Raman and infrared spectroscopy confirm the presence of tetrahedral and trigonal boron structural units in the investigated samples. The most intensive Raman band is located at 149 cm^{-1} and is assigned to lattice vibration. The most intensive infrared bands, located at 1209 and 1273 cm^{-1} , are ascribed as in-plane modes (δ) of B–O–H. Bands associated with water bending mode (ν_2) and stretching vibration (ν_1) are observed at 1668 cm^{-1} (IR) and in the $3000\text{--}3500\text{ cm}^{-1}$ region (both Raman and IR spectrum). Thermal analysis showed differences between two research samples of larderellite connected with presence of adsorption water, that can indicate influence of conditions of minerals storage on properties of mineral.

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1. Introduction

Larderellite is a very rare mineral formed by hydrated ammonium borate $(\text{NH}_4)_2\text{B}_5\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. It is known mostly from two sites in the world: in Larderello, Italy [1–3] and second in Panarea (Eolie Islands) in the volcanic crater Isola located north of Sicily [4]. This kind of mineral was named after F. de Larderell, owner of the Tuscan borax industry from Montecerboli. Larderellite was described in details for the first time by Bechi in 1853 [5]. This mineral crystallized in open thermodynamic systems as a product of boric acid activity of fumaroles and commonly is associated with sassolite and ammonioborite [5–7].

The described mineral occasionally forms rhomboidal flattened tablets, consistent of {100} perfect cleavage with acute planes cutting one to another at an angle near to 68° . It is often white or yellowish (due to impurities), with hardness of 1–2 in Mohs scale and density about $1.09\text{--}1.10\text{ g/cm}^3$. In 1959 Marinelli determined space group and cell parameters of larderellite as follows: $a = 11.63\text{--}11.65$; $b = 7.615\text{--}7.63$; $c = 9.447\text{--}9.47\text{ \AA}$;

$\beta = 96^\circ 45' - 97^\circ 05'$; $Z = 4$ and the space group symmetry $P2_1/a$ [7,8].

In 1960 Clarc suggested that the chemical formula of this mineral is $\text{NH}_4\text{B}_5\text{O}_8 \cdot 2\text{H}_2\text{O}$ and he also confirmed data presented by Marinelli and Carron about density of this mineral and new chemical analyses carried out by Schaller and Vlisidis [6].

From a structural point of view larderellite is classified as pentaborate with chain structure. Its crystal structure is created by infinite double chain of $[\text{B}_5\text{O}_7(\text{OH})_2]_n^{4-}$ with interstitial ammonium (NH_4^+) and water (H_2O) groups linked through H-bonds, as it was earlier presented by Merlini and Sartori in 1969 [9] (Fig. 1). Hawthorne et al., in 1996 presented the classification of structures of borate minerals based on polymerization of coordination polyhedral into clusters, i.e. fundamental building blocks (FBB). In this classification scheme larderellite FBB consists of two $\langle 2\Delta \square \rangle$ rings where Δ and \square stand for BO_3^{3-} triangle and BO_4^{3-} tetrahedron respectively [10].

Thermal analyses of borates containing ammonia group were relatively rare. To this day characterization of larderellite was done by Waclawska and Anderson [11–14].

There have been a number of studies of the Raman and infrared spectra of borates. Larderellite has been rarely tested using Raman and infrared spectroscopy, but never characterized so far. Raman

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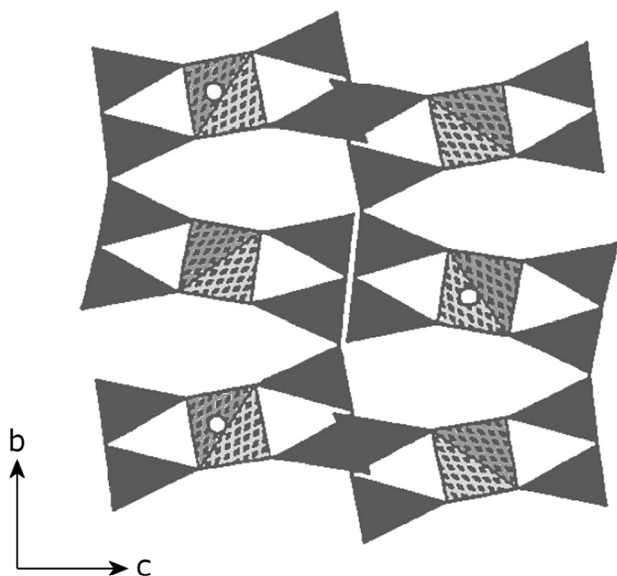


Fig. 1. Simplified fragment of larderellite crystal structure (after Hawthorne et al., 1996). Two infinite chains build of tetrahedra BO_4^{2-} connected with triangles of BO_3^{2-} and interstitial ammonium molecules (NH_4^+) (white circle) above and under tetrahedra.

spectra obtained from our measurement were compared with the infrared data downloaded from the Arizona State University database - RRUFF (no. R130392), collected in 1972 [15]; and with the IR spectra of the larderellite sample no. B48 and B49 from publication of Chukanov [16]. Measurements and analysis of vibration spectra were supplemented by XRD and thermal analysis of research samples. All these experiments allowed us to check whether long-term storage in museum conditions affect its physicochemical properties.

Next step, on the basis of obtained results, was checking whether long-term storage in museum conditions affect its physicochemical properties. For the sake of differences in storage of research minerals, two samples have been tested. One of them (MM II-5713) was enclosed in a glass bottle with natural cork plug but second (MM II-5712) was stored in open cardboard box.

2. Experimental

Research mineral samples are part of historical collection (from 1811 to 1945) of Mineralogical Museum of University of Wrocław, Poland. Research specimens came from Monte Rotonda near Lardarello in Italy and were collected in 1868. Descriptions from original metrics say: “*Larderellit, Monte rotonda bei Lardarello in Toscana. 1868, d. Gebhard, München*”. The examined material was homogenic, white and pearl luster containing aggregates of fine-grained larderellite. Specimen labeled MM II-5713 is very powdered, with large fragmented parts and single fragments sized 32×15 mm, 20×15 mm and smaller. Second sample (MM II-5712) is more uniform (about $70 \times 45 \times 30$ mm).

Samples intended for analysis have been separated by crushing and hand-picking under a binocular. Homogeneity of selected samples was checked on powder X-ray diffraction patterns obtained using X'Pert PRO X-ray SIEMENS D5005 diffractometer at the Institute of Geological Sciences, University of Wrocław, Poland. These diffractometric measurements were conducted with CoK_α radiation source (1.788965 Å) in the range of 2θ angles between 5° and 75° , with step of 0.04° , operating at 40 kV and 30 mA. Total measurement time of each scan was 1 h.

The Raman spectra were obtained using LabRAM 800 HR (UV–Vis–NIR) microRaman spectrometer at the Faculty of Materials Science and Ceramics at AGH University of Science and Technology in Cracow. Raman spectra were excited by 532 nm laser (power at the sample ~ 8 mW) at nominal resolution of 2 cm^{-1} and precision of $\pm 1 \text{ cm}^{-1}$ in the range of $4000\text{--}50 \text{ cm}^{-1}$. Sample MM II-5712 showed weak fluorescence and presented spectra were obtained by subtracting the “background” with the aid of Spectra-Calc software by Galactic Industries Corp.

The mid-infrared (MIR) spectra were recorded using Bruker Vertex 70v vacuum at the Faculty of Materials Science and Ceramics, AGH University of Science and Technology, using transmission technique and KBr pellets method. The spectra were recorded with a resolution 4 cm^{-1} and were averaged over 128 scans in the range of $4000\text{--}400 \text{ cm}^{-1}$. Decomposition of the spectra into component bands has been done on Spectra-Calc software by Galactic Industries Corp. The number of component bands and its approximate positions were estimated based on the second derivative of the spectra; no other parameters were adjusted. Fitting process was carried out to obtain residual RMS error lower than 2.

Thermal decomposition of samples was carried out on Institute of Geological Sciences of University of Wrocław using Perkin Elmer STA 6000 Thermal Analyzer in a flowing nitrogen atmosphere (20 ml/min), at a rate of $15^\circ\text{C}/\text{min}$ up to 980°C in Al_2O_3 crucible. For the thermal analysis two samples (MM II-5712–17 mg, MM II-5713–22 mg) were taken from the surface of research minerals and gently crushed to the same granularity. For interpretation of obtained results the Pyris software has been applied.

3. Results and discussions

Obtained X-ray diffraction data, in comparison with of larderellite's reference sample no 01-076-0795 (034704 ICSD) pattern (Fig. 2), shows that tested specimens are comparable with mineral of formula $(\text{NH}_4)\text{B}_5\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$. The X-ray diffraction pattern of sample MM II-5712 contains one peak for d-space value about 3.1, while for sample MM II-5713 we see two clearly separated peaks. This difference also occur in another reference pattern no 00-012-0633 (034704 ICSD).

Results of thermal analysis of MM II-5712 and MM II-5713 samples are shown in Figs. 3 and 4 respectively. Results show that thermal decomposition of this mineral is multistage in nature. The first stage of phase destruction occurs in temperatures $70\text{--}280^\circ\text{C}$ and is connected to release of water molecules and hydroxyl groups. Above this range (up to 400°C) ammonium groups were released along with water still remaining in the structure. As a result of gradual dehydration of larderellite new phases were formed, first above 100°C and the second above 210°C [13]. The results obtained for sample MM II-5712 almost overlap with those obtained by Waclawska [11]. In Waclawska's paper the first point of the mass change was at 170°C and the next loss of mass occurred at 220 and 260°C . The last stage of disintegration of crystal structure of larderellite took place at 415 , 429 and 500°C . It follows curves of sample MM II-5712 (Fig. 3) at temperature 163°C in derivative heat flow (DDSC) curve, where release of water and some hydroxyl groups occurs in structure of larderellite. This effect was accompanied by loss of 4.91 wt% and was well shown in thermogravimetry curve (TG). Next loss of mass in researched sample, amounting to about 3.7% due to loss of H_2O and OH, was observed at 216°C and 268°C . Temperature above 300°C followed violent loss of weight (circa 19%) marked by a step on DDSC curve. It is related to loss of H_2O and NH_3 from larderellite structure at 300 , 333 and 376°C . The effect observed at about 430°C was not accompanied by any change in the weight of sample related to removal of parts of gaseous products. The TG curve showed a total

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