



Raman spectroscopy and structural study of baryte-hashemite solid solution from pyrometamorphic rocks of the Hatrurim Complex, Israel

Rafał Juroszek^{a,*}, Biljana Krüger^b, Kamila Banasik^a, Yevgeny Vapnik^c, Irina Galuskina^a

^a Faculty of Earth Sciences, Department of Geochemistry, Mineralogy and Petrography, University of Silesia, Będzińska 60, 41-200 Sosnowiec, Poland

^b University of Innsbruck, Institute of Mineralogy and Petrography, Innrain 52, 6020 Innsbruck, Austria

^c Department of Geological and Environmental Sciences, Ben-Gurion University of the Negev, POB 653, Beer-Sheva 84105, Israel

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ABSTRACT

A number of the baryte, BaSO₄, - hashemite, BaCrO₄, solid solution compounds were synthesized previously. In this study, Raman spectra of naturally occurring phases belonging to the baryte-hashemite series from the pyrometamorphic rocks of the Hatrurim Complex were investigated. The Raman spectrum of natural hashemite, obtained for the first time, shows the position of the fundamental bands for the chromate anion vibrations. The bands related to the stretching vibrations (ν_1 , ν_3) occur at 864 cm⁻¹ and in 871–909 cm⁻¹ regions, whereas the bending vibrations (ν_2 , ν_4) are visible in the 346–360 cm⁻¹ and 400–422 cm⁻¹ range, respectively. Received results allowed to observe a gradual shift of bands in baryte-hashemite solid solution as a consequence of the substitution by different cations. The position of bands depends on the Cr/S ratio in analysed samples, and it is determined by differences in atomic mass, and ionic radii between Cr⁶⁺ and S⁶⁺, which affect changes in the strength and length of bonds. The occupancy of the same atomic position by two different cations enables to notice variations of polyhedra geometry, and unit cell parameters despite that baryte and hashemite are isostructural and crystallize in the same *Pnma* space group. We also confirm that the immobilization of the toxic (CrO₄)²⁻ ion in the baryte structure may occur directly without oxygen state reduction, we propose to using a baryte-hashemite solid solution as a reservoir for the incorporation of Cr as an environmental pollutant.

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1. Introduction

Hashemite, BaCrO₄, and baryte, BaSO₄, are minerals belonging to the baryte group, which form a complete solid solution series [1]. Hashemite is isostructural with baryte with Cr-S substituting in the tetrahedral site. Both minerals crystallize in orthorhombic system in the *Pnma* space group [2–4]. In the crystal structure, each Ba ion is surrounded by twelve oxygen ions belonging to seven distinct CrO₄ groups in hashemite [2, 3] and SO₄ group in baryte [4]. Baryte is a well-investigated mineral [4–7] as opposed to hashemite, which is rare in nature and occurs only in late hydrothermal veins within pyrometamorphic phosphate carbonate rocks belonging to the Hatrurim Complex [8–11]. Firstly, hashemite was found and described as brown, tabular, prismatic crystals, associated with Cr-bearing ettringite, calcite, apatite, and bultfonteinite in the Daba stone quarries in Jordan [8]. Afterwards, Sokol and co-authors [9] recognised yellow hashemite crystals in relation to Cr⁶⁺-mineralization in Nabi Musa locality, Palestinian

Autonomy. Moreover, minerals of the baryte-hashemite series occur in Khushaym Matruk [10] and Maqarin [11] complexes in Jordan. There, they are associated with high-temperature, low-pressure combustion metamorphic rock altered by hyper-alkaline solutions containing Cr [10, 11].

The structural and electronic properties of synthetic barium chromate were investigated in detail [12–15], as well as, its Raman spectrum [13]. As a material, BaCrO₄ has been mainly studied for its potential applications as a photocatalyst and oxidizing agent [14, 16]. Furthermore, to understand a structural stability and phase transition properties, minerals with a baryte-type structure were investigated at the high pressure [14, 15]. A continuous baryte-hashemite solid solution, in a form of the small crystals, was precipitated under laboratory conditions [1, 17–19]. In a number of studies, XRD analyses and data of this solid solution were presented [18, 20]. However, to the best of our knowledge, there is no data on vibrational spectroscopy of naturally occurring hashemite and minerals of baryte-hashemite series. Single publications about FT-Raman spectroscopic study of synthetic baryte-hashemite solid solution were reported hitherto [18, 20]. Thereby, there is a need to supplement this lacking part of the spectroscopic knowledge for a natural solid solution. The Ba[(SO₄)-(CrO₄)] solid solution is interesting

* Corresponding author at: Będzińska 60, 41-200 Sosnowiec, Poland.
E-mail address: rjuroszek@us.edu.pl (R. Juroszek).

for many applications such as nanobelts and nanorod films [21, 22] and may have applications in ecology for the potential entrapment of the toxic $(\text{CrO}_4)^{2-}$ ion in an aqueous system [16, 19, 23].

The present study concentrated on hashemite samples collected from two localities: Nabi Musa (Judean Mountains, Palestinian Autonomy), and Nahal Morag (Negev Desert, Israel), which are characterized by different grades of isomorphous Cr/S substitution. Crystal structure modifications (caused by changes in chemical composition), as a distortion of the tetrahedra, are analysed for end-members, and $\text{Ba}[(\text{SO}_4)(\text{CrO}_4)]$ solid solution. The purpose of the research was to complete the missing spectroscopic data for naturally occurring hashemite and baryte-hashemite solid solution series. The results and detailed analyses presented in this paper, and compared with data of synthetic phases, confirm the anionic substitutions, and the gradual shift of Raman bands within the baryte-hashemite solid solution, and also fill the gap in the systematic knowledge.

1.1. Occurrence and Geological Settings

The Hatrurim Complex (or the “Mottled Zone”) is a unique rock complex, widespread over the territory of Israel, the Palestinian Autonomy, and Jordan (Fig. 1) [24–29]. It is found in 16 separate localities with high-temperature, low-pressure pyrometamorphic rocks, and products of their low-temperature hydrothermal alteration [30]. Rocks of the Hatrurim Complex formed as a result of combustion metamorphism [24, 26], but the origin of the combustibles is still uncertain. Some researchers correlated its formation with the combustion of dispersed organic matter contained in the sedimentary protolith, most likely Maastrichtian to Palaeocene chalk and marls of the Ghareb and Taqiye formations [24, 25, 31, 32]. In several current hypotheses, pyrometamorphism was triggered by the ignition of the methane gas released from the deep sedimentary layers, analogous to the mud volcanism [27–30]. In any case, >250 minerals have been identified in rocks of the Hatrurim Complex, and over the last decade, 28 new mineral species have been discovered [8, 9, 26, 33–45].

Nabi Musa is one of the several complexes with pyrometamorphic rocks belonging to the Mottled Zone [24, 26, 27, 30]. It is located in the Judean Mountains, near to the highway from Jerusalem to Jericho [9, 29]. The whole area, existing as an isolated hill, has a crater-like structure and consists of brown, and reddish brecciated rocks, found within massive, light yellow, fine-grained carbonate-bearing rocks

[29]. The latter rocks are represented by breccia, rich in calcite, aragonite, vaterite, gypsum, and tobermorite mainly [29]. Pyrometamorphic rocks from this locality consist of high-temperature minerals such as larnite, spurrite, gehlenite, brownmillerite, and contain characteristic dark-coloured veins of paralava [9, 29]. More detailed petrological and geological description of rocks from Nabi Musa complex was described by Sokol and co-authors [29]. In collected rock samples from Nabi Musa, hashemite occurs in cavities within hornfels composed mainly of gehlenite, flamite, brownmillerite, and fluorapatite.

Nahal Morag is a wadi situated in the eastern part of the Hatrurim Basin, a best-studied and largest Mottled Zone in the Negev Desert, Israel [46]. It is one of a few separate exposures of pyrometamorphic rock within the Hatrurim Basin, complex in Israel [24, 26, 29, 30, 47]. Hatrurim Basin is a synclinal structure filled by Late Cretaceous-Tertiary chalk, and marl sequences, which has been converted into calcium-silicate, and calcium-aluminium-silicate assemblages in high-temperature conditions [24–27, 30, 47]. Unmetamorphosed and protolith rocks, as well as, pyrometamorphic rocks in the Hatrurim Basin, were divided into several lithological units by Burg et al. [26]. The most common and widespread pyrometamorphic rocks in this complex are represented by gehlenite-larnite-bearing rocks, and spurrite marbles [24, 26, 47]. In Nahal Morag locality, hashemite occurs in Ca-rich paralava composed of rankinite, wollastonite, cuspidine, fluorapatite, and minerals of gehlenite-akermanite, andradite-schorlomite, larnite-flamite series. Phases such as barioferrite, magnetite, zadovite, perovskite, kalsilite, and nepheline are accessory minerals.

2. Material and Methods

2.1. Samples Description

Rock samples studied in this work were collected from the outcrops of the Hatrurim Complex in Israel, and the Palestinian Autonomy during fieldworks in 2014 and 2015. Hashemite and baryte crystals occur in veins and cavities of these rocks. Scanning electron microscopy (SEM), and Raman spectroscopy investigations were performed without crushing the samples. Two thin sections from Nabi Musa (NBM4b, NBM2014-6), and two from Nahal Morag (YG15-20A, YG15-20B) rock samples, and mounts with 15 hashemite crystals from Nabi Musa locality were made for SEM, and electron microprobe analyses (EMPA). These probes were also used for Raman spectroscopy analyses. Because

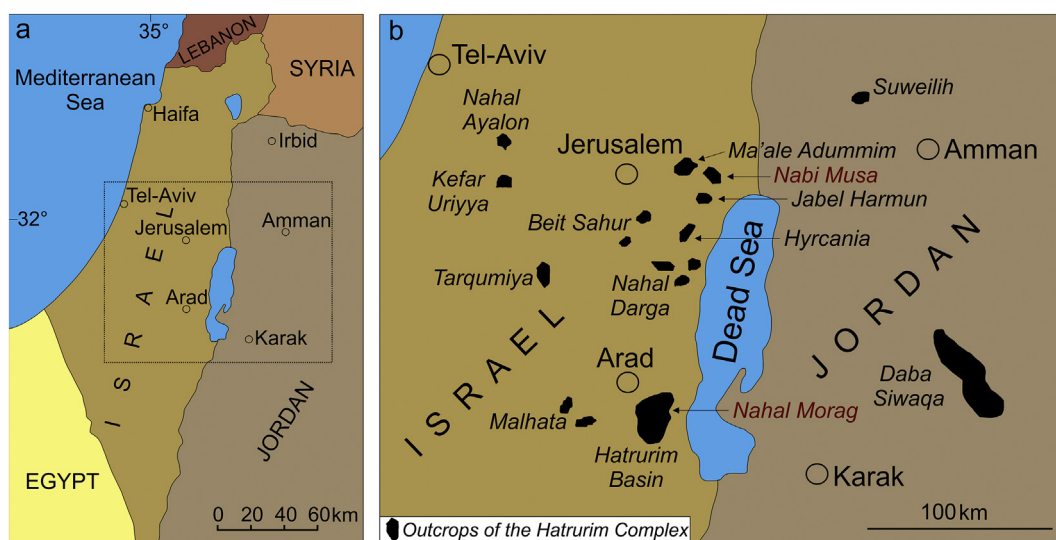


Fig. 1. Schematic map of the Middle East (a). The framed part is magnified in b. Schematic map of the Hatrurim Complex outcrops along Israel-Jordan border (b). Localities described in this study are marked in red. (After Burg et al. [26]). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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