

КРИСТАЛЛОХИМИЯ ЩЕЛОЧНОЗЕМЕЛЬНЫХ ГИДРОАРСЕНАТОВ:
КРИСТАЛЛИЧЕСКАЯ СТРУКТУРА И КОЛЕБАТЕЛЬНЫЕ СПЕКТРЫ
НОВОЙ ПОЛИМОРФНОЙ РАЗНОВИДНОСТИ Ba(AsO₃OH)

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CRYSTAL-CHEMISTRY OF EARTH ALKALINE HYDROGEN ARSENATES:
CRYSTAL STRUCTURE AND VIBRATIONAL SPECTRA OF A NEW
Ba(AsO₃OH) POLYMORPHIC VARIETY

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An ongoing study concerning the hydrothermal synthesis, crystallography and properties of arsenate and vanadate(V) compounds in the system $M1O-M2O-X_2O_5-H_2O$ ($M1 = Sr^{2+}, Cd^{2+}, Ba^{2+}, Bi^{3+}, Hg^{2+}$; $M2 = Mg^{2+}, Mn^{2+,3+}, Fe^{2+,3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$; $X = As^{5+}, V^{5+}$) yielded a large number of new $M1^{2+}-(H-)-M2^{2+}-(H-)$ - and $M1-M2-(H-)$ arsenates and vanadates (Đorđević and Karanović, 2008 and references therein) that are characterized structurally, and, in part, also by spectroscopic techniques. Among them, new polymorphic variety of Ba(AsO₃OH) has been obtained. Here are reported its hydrothermal synthesis, and crystal structure. Ba(AsO₃OH) represents one new structure type. Its crystal structure was determined from a racemic twin by single-crystal X-ray diffraction at 120 and 293 K [space group $P2_1$, $a = 7.2149(14) / 7.2370(2)$, $b = 7.7028(15) / 7.7133(2)$, $c = 21.7385(43) / 21.8079$ Å, $\beta = 95.95(3) / 96.073(1)^\circ$, $V = 1201.6(4) / 1210.51(5)$ Å³, $Z = 12$]. The structure refinement of the data collected at 120 K did not reveal significant changes and did not indicate any phase transition. The crystal structure of Ba(AsO₃OH) has a layered character and can be divided into four types of regularly alternating layers parallel to (001). Each layer shares common O atoms and OH groups with adjacent layers. All these layers host different kinds of BaO₇(OH)₂ and BaO₈(OH)₂ polyhedra and isolated, slightly distorted AsO₃OH tetrahedra. These tetrahedra are linked through three O atoms and one OH group to four Ba atoms in the same layer *i.e.* AsO₃OH tetrahedra are chelating to two Ba atoms and bridged by another two Ba atoms. The OH group acts as hydrogen bond donor toward the oxygen atoms positioned in the same or adjacent layers. In all layers neighboring BaO₇(OH)₂ and BaO₈(OH)₂ polyhedra form zigzag chains along *b*-axis sharing edges or trigonal faces. These polyhedra are additionally connected by hydrogen bonds involving all hydroxyl

groups. Raman and infrared spectra were acquired to obtain further information on both anion groups and especially on the very short hydrogen bond distances, where the donor and acceptor atoms are not equal due to (average) space-group symmetry. In order to compile the spectral data on protonated orthoarsanates the single crystal infrared spectra of Sr(AsO₃OH) and powder infrared spectra of orthorhombic variety of Ba(AsO₃OH) (Mihajlović & Effenberger, 2006) are given. Furthermore, structural similarities with other alkaline earth mono arsenates are discussed. Besides potentially interesting properties of arsenates (*e.g.*, ion conductivity, ion exchange and catalytic activities), continuous investigations on their crystal chemistry should be performed because arsenic is known to be one of the most toxic elements in nature. A better knowledge of As immobilization mechanism in natural and experimental systems is necessary to develop its remediation process. Due to the difference in sorption efficiency, and in toxicity between arsenites and arsenates, remediation processes often suggest immobilizing As in its highest oxidation state. However, arsenates are insufficiently studied, and their crystal-chemical behavior and stability fields are often unknown. No matter what the origin of the arsenates in the soils, the identification of its presence is essential.

Financial supports of the Austrian Science Foundation (FWF) (Grant T300-N19) and the Ministry for Science and Technological Development of the Republic of Serbia (Project No. 142030) are gratefully acknowledged.

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