

Chabazite [idealized formula $\text{Ca}_2\text{Al}_4\text{Si}_8\text{O}_{24}\cdot 12\text{H}_2\text{O}$] is one of the most widespread natural zeolites. A consensus on positions of water molecules and exchangeable cations in chabazites had not been obtained, although attempts to determine their positions have been made intensively. However, our previous study (Nakatsuka *et al.*, 2007) successfully determined their positions at room temperature, in a natural chabazite [$\text{Ca}_{1.57}\text{Na}_{0.49}\text{Al}_{3.39}\text{Si}_{8.55}\text{O}_{24}\cdot 12.47\text{H}_2\text{O}$] from Komuro, Oh-hito, Shizuoka Prefecture, Japan, using a single crystal X-ray diffraction method. Consequently, we revealed the presences of five water sites (OW1-OW5) and four exchangeable-cation (Ca1-Ca4) sites. However, locations of hydrogen atoms in chabazites could not be determined. Determining their positions is quite important for gaining insights into the interactions between water molecules and framework and between water molecules. X-ray diffraction study at low temperature is useful for reducing thermal vibrations of atoms and should make the determination of hydrogen positions easy. Here, we perform the single crystal X-ray diffraction study at 123 K using the same sample as that of our previous study (Nakatsuka *et al.*, 2007) and try to determine hydrogen positions. Moreover, we discuss the crystallographic configurations of water molecules and exchangeable cations at low temperature. In the present study, we found five water sites and four exchangeable-cation sites, as well as the case of room temperature (Nakatsuka *et al.*, 2007). Three (OW1, OW3, OW4) of five water sites found at 123 K are the same as those at room temperature, whereas the remaining two water sites (OW2, OW5) are different from those at room temperature. At present, we are examining hydrogen positions on difference Fourier map.

Keywords: zeolite crystal chemistry, microporous materials, low-temperature single-crystal diffractometry

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Structural behaviour and thermal phase transitions of borosilicates with large cations

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The knowledge of borosilicate structures with tetrahedral boron and silicon is very limited in comparison with the number of related aluminosilicate structures. Present work aims at studying the crystal structures and phase transformations as a function of temperature and chemical composition in ternary borosilicate systems with large (K, Rb, Cs, Sr) cations. During the years microporous compounds RBSi_2O_6 (R = K, Rb, Cs) isotopic with cubic leucite (ANA) are studied extensively by us. Structural (cubic $I-43d$ \leftrightarrow cubic $Ia3d$) transitions of K-Rb, K-Cs and Rb-Cs boroleucites are presented as a function of composition and temperature. Compared with natural aluminosilicates (ANA), borosilicates exhibit lower melting points and smaller coefficients of thermal expansion. Recently a new low symmetrical presumably orthorhombic polymorph of KBSi_2O_6 was prepared in hydrothermal conditions. High-temperature X-ray diffraction (HTXRD) showed that this modification undergo a series of reversible displacive transitions first into tetragonal and then to the cubic phase. Above 1000 °C Cs-rich ANA borosilicates decompose, releasing a gas phase and forming stoichiometrically different $\text{CsBSi}_5\text{O}_{12}$ phase. Its structure was refined in CAS framework type. $\text{CsBSi}_5\text{O}_{12}$ also decomposes above 1070 °C via liberating a gas phase. After treatment at 1100 °C its XRD pattern contained the maxima of SiO_2 only. In $\text{SrO-B}_2\text{O}_3\text{-SiO}_2$ system $\text{Sr}_3\text{B}_2\text{SiO}_8$

(unindexed pdf 32-1224) was prepared by solid state reaction; it was indexed in orthorhombic space group $Pcmn$: $a=3.924(1)$, $b=5.416(2)$, $c=12.427(7)$ Å. According to HTXRD $\text{Sr}_3\text{B}_2\text{SiO}_8$ expands anisotropically. This research is supported by Russian Foundation for Basic Researches (08-03-91952) and by grant of Russian President for young scientists (MK-3661.2007.5).

Keywords: zeolite-like borosilicates, high-temperature x-ray diffraction, crystal structure determination

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Zeolite-based (guest-host) systems: Structure, interactions and optical properties

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Zeolites are characterised by a porous framework built from SiO_4 and AlO_4^- tetrahedra whose global negative charge is balanced by exchangeable cations sparse throughout the structure. The use of molecular sieves (zeolites, microporous metallophosphates) possessing large cages and channels of uniform sizes enables the incorporation of guest molecules that may seat in well defined positions. Contrary to usual applications as selective sorbants or catalysts where the (guest-host) system has only a transient character and where adsorbed molecules are highly mobile, in (chromophore-zeolite) systems a permanent and controlled arrangement of molecules is advisable. In all cases detailed understanding of the guest-host interactions (hydrogen bonding, ion pairs) is a primary step to tailor-made functional materials at a molecular level. Despite frequent defects or disorder induced by the sample preparation, diffraction remains the main source for structural information (framework topology, cationic distribution in the cavities, interaction of the guest entity with the framework), supplemented by local spectroscopies (XAFS, UV-Visible) or Monte-Carlo simulations. We will present examples of X-Ray and neutron diffraction studies on (guest@zeolite) systems used as pigments, exhibiting Second Harmonic Generation properties, or whose colour is sensible to water sorption. The influence of sample preparation over optical properties (guest molecules loading rate, structural defects, cationic distribution) will be discussed.

Keywords: zeolites-microporous materials, guest-host structures, structure determination using X-ray and neutron di