

**PS10.09.09 PHASE EQUILIBRIA AND STRUCTURES OF SOME CRYSTALLINE PHASES IN  $Rb_2O-B_2O_3$  SYSTEM.** S.K.Filatov, R.S.Bubnova\*, M.G.Krzhozhanovskaya, I.G.Polyakova\*. St.Petersburg University, Dept. of Crystallography, University Emb. 7/9, St.Petersburg, 199034. \*Institute of Silicate Chemistry RAS, Ul. Odoevskogo, 24, korp.2, St.Petersburg, 199155, Russia

The paper presents new data on phase equilibria and crystal structures of rubidium borates and summarises some common features of borate crystal structures, which may throw some light on the marked tendency of the borates to supercool to vitreous phase. Alkali borate systems are rich in chemical compounds, especially in the boron anomaly interval (70-75 mol. %  $B_2O_3$ ), where boron atoms are three- and fourfold coordinated. Tetrahedra and triangles condensed to rigid arrangements (diborate, triborate groups and others) form various (sometimes interlocking) frameworks. Up to now none of the rubidium borate structures has been determined.

Crystal data have been obtained by X-ray analysis and immersion and crystal optic method. Thermal expansion, phase transformations and melting processes of borates have been studied by powder high-temperature X-ray diffraction. Potentialities of this method and DTA for phase equilibria studying in glass forming systems are considered. Samples were prepared by solid state reaction as well as crystallisation of glasses.

New compounds  $Rb_3BO_3$  and  $Rb_3B_7O_{12}$  and new modifications  $\alpha$ -,  $\beta$ - $RbB_3O_5$  have been discovered. The new compound  $Rb_3B_7O_{12}$  is formed in the course of solid-state reaction above 620°C and melts according to peritectic reaction. The new low-temperature modification  $\alpha$ - $RbB_3O_5$  transforms to  $\beta$ - $RbB_3O_5$  on heating (at about 675°C).

New crystal data on  $Rb_2B_4O_7$ ,  $\alpha$ - and  $\beta$ - $RbB_3O_5$  obtained by X-ray analysis are presented. Distribution of boron-oxygen bond lengths and angles within arrangements is of special interest. Bond lengths show systematic variations depending on the location of adjacent bonds. The review of these variations within rigid arrangements is given for various structures of borates. The changes in angles between arrangements are also considered.

Rubidium diborate  $Rb_2B_4O_7$  is triclinic, space group  $\bar{P}1$ . This compound is isostructural to  $K_2B_4O_7$ .  $\alpha$ - $RbB_3O_5$  crystallises in orthorhombic space group  $P 2_1 2_1 2_1$ . It is isostructural to  $CsB_3O_5$ .  $\beta$ - $RbB_3O_5$  belongs to orthorhombic space group  $P 2_1 2_1 2_1$ .

## Materials X

### Pore Framework Structures

**MS10.10.01 CRYSTALLOGRAPHY OF MICRO-AND MESOPOROUS FRAMEWORK STRUCTURES** Hartmut Fuess, C. Kirschhock, C. Pophal, Fachbereich Materialwissenschaft Technische Hochschule Petersenstr. 20, 64287 Darmstadt

Whereas the crystal structures of microporous zeolitic materials have extensively been studied by X-ray, neutron and synchrotron radiation only a limited amount of knowledge on the structure of mesoporous materials is yet available. High resolution powder data of Direct Methods or Patterson techniques and the refinement of structural details like the localization of organic molecules in the voids and channels. Their position could be compared to molecular mechanics calculations [1].

Mesoporous materials like MCM-41 and similar structures based on  $AlPO_4$  and other oxides consist of large pores (ca. 4 nm) and walls of approximately 0.8nm - 1.2nm. X-ray powder patterns reveal the periodicity of the pores but show features of amorphous organisation with the walls. Wide-angle scattering and subsequent Fourier synthesis produce radial distribution functions which allow the calculation of a model of the arrangement of the neighbours. The structure of mesoporous materials will be presented and compared to zeolite structures.

[1] H. Klein, C. Kirschhock, H. Fuess J. Chem. Phys., 98, 12345-12360 (1994)

**MS10.10.02 STRUCTURAL DETERMINATION OF MESOPOROUS MATERIALS BY ELECTRON MICROSCOPY.** Osamu Terasaki, Department of Physics, Graduate School of Science, Tohoku University, Sendai 980-77, JAPAN

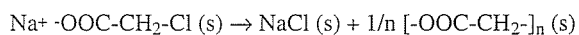
HREM images of zeolites and related materials ("zeolites") give an important clue to solve the structures with diffuse scattering which are difficult to be solved from the averaged structural information that diffraction experiment can normally provide. New "zeolites" have been synthesized and most of them contain many different kind of defects and at the same time a size of synthetic crystal is small. Electron Microscopy (EM) may be the best way to solve their basic structures. Recently EM has also been extended to apply for the study of the surface structures of "zeolites", which give information of crystal growth unit and process. At the symposium, recent studies of the fine structures of "zeolites" will be presented. As a whole, the advantage of electron microscopy for the study will be discussed.

**MS10.10.03 STRUCTURE-PROPERTY STUDIES IN FRAMEWORK MATERIALS.** Brian H. Toby, Reactor Radiation Division, National Institute of Standards and Technology, Gaithersburg MD 20899 USA and John B. Higgins, Air Products and Chemicals, Allentown PA 18195 USA

Zeolites and related molecular sieves are used in a wide variety of commercial applications: as catalysts for production of fine and commodity chemicals, such as the cracking of petroleum to gasoline; as ion exchange media, used in detergent formulations to reduce hardness of water; and as selective adsorbents, with applications such as the industrial separation of gases. This paper will provide an overview to some of the industrial applications of zeolites and will present examples where structural studies can provide a greater understanding of materials properties.

**MS10.10.04 SALT SKELETONS AND POROUS POLYMERS: THE SOLID-STATE REACTIVITY OF HALOGENOACETATES.** Matthias Epple, Institute of Inorganic and Applied Chemistry, University of Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany

By simply heating salts of halogenoacetic acids, a solid-state polymerization takes place, e.g., with sodium chloroacetate:



This pure solid-state reaction leads quantitatively to an intimate mixture of the simplest polyester, called polyglycolide, and sodium chloride. NaCl is deposited in a polymer matrix as cubes with edge lengths of 1-2  $\mu$ m. Upon burning the polymer, a skeleton of NaCl cubes remains. Extracting the sodium chloride with water leaves the water-insoluble polyglycolide matrix as highly porous crystal dotted with "inverse NaCl crystals", i.e. cubic holes with edge lengths of 1-2  $\mu$ m. This porous polyglycolide may be of high interest in pharmaceutical technology, because it is easily biodegradable in the body.

This unusual reaction takes place in a couple of halogenoacetates with different combinations of metal cation and halogen. Unfortunately, it was impossible so far to determine the crystal structure of any halogenoacetate (and none is reported in the literature!). Therefore, the course of the reaction was studied by X-ray diffractometry and X-ray absorption spectroscopy (EXAFS). Both techniques were applied *ex situ* and *in situ*, i.e., at elevated temperature. Beside these structural techniques, thermal analysis and solid-state NMR were applied.

M.Epple, L. Troger, J. Chem. Soc., Dalton Trans., 1996, 11-16.