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High-pressure gas hydrates J. S. Loveday, R. J. Nelmes and H. E. Maynard, SUPA, School of Physics and Centre for Science at Extreme Conditions, University of Edinburgh, Mayfield Road, Edinburgh, EH9 3JZ, UK
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Many simple gases that do not interact strongly with water form crystalline hydrates in which the gas molecules or atoms occupy 'cages' formed by a framework of water molecules. These clathrate hydrates are stabilised by hydrophobic gas-water interactions and are model systems for the study of these interactions. Many gas hydrates also occur in nature and their properties provide a basis for modelling of planetary evolution and processes. For example, a destabilisation of methane hydrate in the Earth's oceans is thought to have led to catastrophic global-warming events in the Earth's past.

Gas clathrate hydrates are stabilised by modest pressures in the range 0-0.5 GPa, and the dissociation temperature of methane hydrate rises from ~190 to ~320 K in this pressure range. But there was a general expectation, based on modelling studies, that higher pressures, in the 1-2 GPa range, would render all clathrate hydrates unstable with respect to their parent species. However, over the past seven years, a series of experiments has shown that in a large number of gas-water systems this is not the case. Instead, structural transformations occur to new hydrate structures which remain stable to significantly higher pressures. In this poster we will review this work to identify trends in behaviour and structures and to make suggestions for further work.

MS23 P02

Reservoir Minerals for Immobilization Herbert Pöllmann, *Department of Mineralogy, University of Halle/Saale, Germany.*
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Keywords: mineral reservoir, nuclear waste, substitution

The incorporation of ions in different minerals is known for a long time by the expression of SYNROC [1]. Different mineral phases were proven to be capable to incorporate radioactive elements. The system CMAS was used by [2] for the immobilization in glass-ceramics.

Different crystal structures and their capability for incorporation of large ions will be discussed in this paper. The use of microporous open structures like Hollandite and other manganese oxides is included. The rare minerals like Pyrochlore/ Mikrolithe/Betafite, Zirkonolite and also silicates like Celsian, Pollucite and Nephelin are included. The various diadochic substitutions in these minerals will be discussed and on this basis their potential for incorporation of different ions will be shown.

Reservoir minerals are potentially capable to incorporate different ions in their crystal structure and are rather insoluble. Crystallochemical rules control these capabilities.

The synthesis of these minerals can be performed by a sintering process (ceramic process) but also by hydraulic reactions as they occur in the hydration process of a typical cementitious material.

The minerals formed are called primary mineral reservoirs (formed at elevated temperatures) and secondary mineral

reservoirs (formed at ambient temperatures). Often a comparison to natural occurring minerals and their chemical composition can help to understand formation conditions and stability over long geological time scales.

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[2] Ardizio, G.; Settembre, D; Ceramic Forum international, E21-E23, (2003)

MS23 P03

Structure and property of Hollandite-type $K_xM_xSn_{8-x}O_{16}$ (M; Ga and Fe, $x \sim 2$) single crystal Kenjiro Fujimoto, Kenji Takamori, Shigeru Ito, *Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, Chiba, Japan.*
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Keywords: Hollandite, One-dimensional tunnel structure, Nuclear waste, Ion conductivity, Catalyst

Hollandite-type compounds have a tetragonal symmetry and contain one-dimensional tunnels along the unique axis with a lattice period of about 0.3 nm. The framework of this type of structure consists of double chains of MO_6 (M; metal) octahedral edge shared with adjacent ones. Sn-hollandite compounds are promising materials as fast ion conductor [1], as nuclear waste immobilizer [2], and as NO_x reduction catalysts [3]. Detailed data such as the atomic distance and atomic coordinate will be necessary to characterize these properties.

In this study, Hollandite-type $K_xM_xSn_{8-x}O_{16}$ (M; Ga and Fe, $x \sim 2$) single crystal was grown by flux slow cooling method. We have hitherto succeeded single crystal growth of hollandite-type $K_{1.88}Ga_{1.88}Sn_{6.12}O_{16}$ (KGSO) and $K_{1.98}Fe_{1.98}Sn_{6.02}O_{16}$ (KFSO) by slow-cooling from 1350 °C to 1000 °C under flux melt consisting of a 40 mol% crystal composition of $(K_2O)_{1.0-1.1}(M_2O_3)_1(SnO_2)_1$ and a 60 mol% flux composition of $(K_2O)_2(MoO_3)_1(B_2O_3)_1$. The average size of these single crystals was 2 mm in length and 100 μm in diameter, approximately.

The KGSO and KFSO single crystal was characterized by x-ray diffraction for obtaining crystallographic information such as lattice constant, atomic coordination, bond length and so on. The lattice constant of KGSO and KFSO showed $a_{KGSO} = 1.0389(2)$ nm, $a_{KFSO} = 1.0385(11)$ nm, $c_{KGSO} = 0.3132(2)$ nm, $c_{KFSO} = 0.3135(7)$ nm, $Volume_{KGSO} = 0.3381(2)$ nm³, $Volume_{KFSO} = 0.3380(9)$ nm³, the final reliability factor R_{KGSO} , R_{KFSO} , wR_{KGSO} and wR_{KFSO} converged 0.0325, 0.0298, 0.0513 and 0.0878, respectively.

The electrical property was measured by the AC impedance method in the frequency region from 5 Hz to 13 MHz. The electrical conductivity showed 1.68×10^{-2} S·cm⁻¹ at room temperature and 1.65×10^{-1} S·cm⁻¹ at 200 °C. These values showed higher than the other hollandite-type compounds. The activation energy was 0.18 eV. Electric conduction process was investigated from the electrical conductivity data and electron density distribution map obtained by structure refinement.

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[2] A.E. Ringwood, S.E. Kesson, N.G. Ware, W. Hibberson, A. Major, *Nature* 278 (1979) 219.

[3] M. Watanabe, T. Mori, S. Yamauchi, H. Yamamura, *Solid State Ionics* 79 (1995) 376.