COMPLEX OXIDES WITH OCTAHEDRAL FRAMEWORKS: LEWISITE AND LOPARITE

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P08.09.012 HIGH TEMPERATURE SUPERIONIC PHASES IN THE $(PBF_2)_{1-X}$-$(MF)_X$, SYSTEMS WITH M= K, RB AND CS. P. Berastegui, Inorganic Chemistry, Arrhenius Laboratory, Stockholm University, S-10691 Stockholm, Sweden and S. Hull, ISIS Facility, CLRC Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK.

The crystal structure and ionic conductivity of polycrystalline samples of PbF_2 doped with KF, RbF and CsF have been investigated at temperatures up to ~700K using neutron diffraction and complex impedance measurements. The maximum solubility of KF in β-PbF_2 was found to be about 1 %, while the creation of charge compensating anion vacancies induced an increase in the ionic conductivity at ambient temperature by a factor 5.6×10^3. At higher KF contents of $0.333 \leq x \leq 0.68$, a high temperature superionic phase with a body centred cubic cation sublattice was observed above a transition temperature of T_c ~ 520-590 K, with a related abrupt increase in the ionic conductivity. Within this high temperature modification, the anions are predominantly disordered over the tetrahedral interstices, and its structure can thus be described as an *anti* α-AgI type. In the case of $(PbF_2)_{1-x}$-$(RbF)_x$, an increased tendency towards ordering of the two cation species over the 0,0,0 and ½,½,½ sites was observed as the dopant content increased within the stability range $0.333 \leq x \leq 0.5$. This is accompanied by a change in the preferred anion location towards the octahedral positions as the mean structure tends towards a partially ordered perovskite-type arrangement. A fully ordered perovskite-type structure was observed in the $(PbF_2)_{1-x}$-$(CsF)_x$ system where only a single line phase at x = 0.5 can be observed. This phase shows no evidence of superionic behaviour at elevated temperatures.

P08.09.013 HIGH TEMPERATURE STRUCTURE TRANSITIONS OF $SrHFO_3$. S.L. Cuffini [1], J.A. Guevara, Y.P. Mascarenhas [2], A.N. Fitch[3]. [1] INFIQC, Fac. Ciencias Quimicas. U.N.C. Agencia 4, CP. 61 - Córdoba. Argentina. [2] IFSC-USP, C.P. 369-15690-970. Sao Carlos. Brazil. [3] ESRF, BP 220, F-38043 Grenoble Cedex, France.

Strontium hafniate (SH) is a refractory compound melting at 2730 C, which belongs to the perovskite family. Although this compound has been known for well over 50 years, the crystal structures at high temperature, where phase transitions have been reported, have not been examined thoroughly (1).The purpose of this work is to report the crystal structures of this compound not only at room temperature but also at high temperature in order to determine the nature of the structural phase transitions. The x-ray diffraction patterns collected at beam line BM16 at ESRF were refined using Rietveld Method and the temperature range studied was from room temperature up to 1000C. At room temperature, the structure showed a small deviation from the pattern of a cubic perovskite, however the small superlattice reflections could be refined in space group Pnma with lattice parameters, a=5.7889(2)A, b=8.1716(3)A and c=5.7772(2)A. At higher temperatures, SH showed a phase transition from Pnma to I4/mcm at around 500C and from I4/mcm to Pm-3m around 900C. This behaviour is comparable with other perovskite like SrRuO3 and SrZrO3 which exhibit similar transitions in this temperature range.

(1) V.P. Red'ko, A.V. Shevchenko and L.M. Lopato, Inorganicheskie Materialy, 24, 2027 (1988)

P08.09.015 HIGH PRESSURE STUDIES ON CHALGOGENIDE MISFIT LAYER STRUCTURES, AND THEIR COMPONENT STRUCTURES. Wulf Depmeier, Karsten Knorr and Lars Ehm, Institut für Geowissenschaften, Mineralogie / Kristallographie, Universität Kiel, Olshausenstr. 40, D 24098 Kiel, Germany

In the context of an interdisciplinary research project, comprising theoretical and experimental physicists, inorganic chemists and crystallographers, we have started an investigation into the high pressure behaviour of misfit compounds with the idealised formula $(MX)_{1+x}(TX_2)_m$ with M = Sn, Pb, Bi, Rare Earth; T = Ti, V, Cr, Nb, Ta and X = S, Se. The ultimate goal of the project is to gain a thorough understanding of the detailed geometrical and electronic structure of the compounds, and their associated properties.

The focus is on the interfaces between MX and TX_2 layers, and the van-der-Waals gaps between adjacent TX_2 layers. In order to facilitate the understanding of the complex and usually aperiodic misfit compounds [1], we decided to start high pressure work on the much simpler component structures, such as PbS, 1T-TiS_2, and 2H-NbS_2. Despite their simplicity, very little is known about the high pressure behaviour of these compounds. Experiments use x-ray powder diffraction in diamond anvil cells up to 100 kbars. The high pressure studies on misfit compounds and their component structures are interesting, because the topology of the structures, the electronic configuration of the constituents, and the band structures of the crystals promise to present a rich phenomenology [2]. The experiments are accompanied by theoretical studies on the ab initio level, performed in parallel in our group.

[1] Rouxel, J., Meerschaut, A. & Wiegers, G.A.: Chalcogenide misfit layer compounds. J. Alloys and Compounds 229, 144 - 157 (1995).
[2] Wiegers, G.A.: Charge transfer between layers in misfit layer compounds. J. Alloys and Compounds 219, 152 - 156 (1995).

P08.09.016 COMPLEX OXIDES WITH OCTAHEDRAL FRAMEWORKS: LEWISITE AND LOPARITE. N. V. Zubkova, D. Yu. Pushcharovsky, Geology Department, Moscow State University, 119899 Moscow, Russia, Arakcheeva A. V., Institute of Metallurgy RAN, Leninsky av., 49, 117334 Moscow, Russia, D. Atencio, University of Sao Paolo, Sao Paolo, Brasil

Pyrochlore - like structure of lewisite (general formula - $A_{2-m}B_2[O_6(OH)]$ from Tripui, Ouro Preto, Minas Gerais, Brazil was refined up to R_{hkl} = 0.022 in space group *Fd3m*, a = 10.311(6)Å, V = 1096.23Å^3. The averaged results of the EDS chemical analyses corresponded to the chemical formula: $(Ca_{0.91},Na_{0.12},Fe_{0.22},Al_{0.13},Sb^{3+}_{0.32})(Sb^{5+}_{1.27},Ti_{0.72})O_6(OH)$.

Similarly to pyrochlore [1], the structure of lewisite is based on a defect simple cubic packing of (OH) - groups and O atoms, with A - and B - atoms occupying 1/2 of cubic voids. Large A - cations have cubic coordination and B - atoms - 6 coordination due to the vacancies.

Crystal structure of loparite, $(Ti,Nb)(Na,Ce,Ca,Sr)O_3$ from Lovozero alkaline massive, was refined up to R_{hkl} = 0.041 in space group *Pn3m* with double perovskite parameters of the cubic unit cell a = 7.767(1)A [2]. The lattice dimensions of loparite are doubled because of the ordering of A - and B - cations. Thus loparite can be characterized by general formula $A'A''_3B'_2B''_2O_{12}$.

Both structures comprise the octahedral frameworks. In loparite the voids are filled by ordered Ca,REE and Na,REE cations. In lewisite the voids are filled by (OH) - group surrounded by 4 (Ca,Sb) - cations.

1. Lima-de-Faria, J. (1994), Structural Mineralogy, Kluwer A. P., Dordrecht,1994.
2. Zubkova, N.V., Arakcheeva, A. V., Pushcharovsky, D.Yu., (1998) ECM-18 Abstracts, 1998.

P09.09.001 CHEMICAL PROPERTIES OF TRANSITION METAL CATIONS IN ION EXCHANGED ZEOLITES. AN AB INITIO STUDY. Judit E. Šponer, J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, Prague 8, Czech Republic