04.4-14 STUDIES OF STRUCTURES AND REACTION RATES IN THE SYSTEM Y_2O_3-$YFeO_3$-$Y_3Fe_5O_{12}$-Fe_2O_3.

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Formation of yttrium iron garnet and yttrium perowskite from yttrium and iron oxides has been studied in sandwich-type diffusion couples. We have been investigating reation rates and reaction mechanisms as well as magnetic structures of the product phases and the microwave properties of the materials. The reaction proceeds by one-way diffusion of cations and anions. Thermally decomposed hydroxides have also been used as starting materials. In this case analysis was made by EPR. In addition to $YFeO_3$ and $Y_3Fe_5O_{12}$, YFe_2O_4 (stable only at reduced oxygen pressure) occurs in the phase diagram.

Garnet formation and phase transitions were observed in a special high temperature ESR cavity at temperatures above 850 K.

Our results on reaction rates may be interpreted in terms of a reaction model developed by Schmalzried (Z.Phys.Chem.N.F. (1962, 33,111).

04.4-15 SOLID STATE REACTIONS - OBSERVATION AND RECORDING IN REAL TIME.

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The author has, for some years, been concerned with the direct observation in the electron microscope of molecularly clean crystal surfaces, both in "static" and "dynamic" conditions. Main references are contained in a paper by A.F. Moodie and C.E. Warble (Phil. Mag. (1977), 35, 201). The ability to record in real time such "dynamic" processes as materials interaction and dissolution at appropriate temperatures allows one the luxury of studying such phenomena at leisure.

A brief description of the low light level image-intensification system now used (J.D. Patterson & C.E. Warble, this Conference) will be given. This system, based upon a Silicon Intensified Target (SIT) tube, in combination with an Arlunya TF4000 Temporal Filter and TV Frame Store, allows electronically integrated specimen images to be recorded either on video tape or directly onto 16 mm movie film.

A 16 mm movie will be shown in real time of (1) metal/oxide interaction and (2) oxide dissolution by water vapour in situ in the electron microscope. Palladium metal is seen to react with magnesium oxide via a liquid-like phase. The reaction is a surface reaction in the sense that it is limited to a few tens of Ångstroms in depth and does not introduce strain into the oxide lattice. Eventually the oxide is entirely "eaten".

Aluminium oxide spheres are observed in dissolution to change from spheres to rather grotesque, intergrown single crystals. Cubic crystals of magnesium oxide can be seen to be attacked primarily on the main (100) faces rather than the cube edges or corners.

04.5-01 STRUCTURES OF THE 1:1 COMPLEXES OF 18-CROWN-6 WITH HYDRAZINIUM PERCHLORATE, HYDROXYLAMMONIUM PERCHLORATE AND METHYLAMMONIUM PERCHLORATE.

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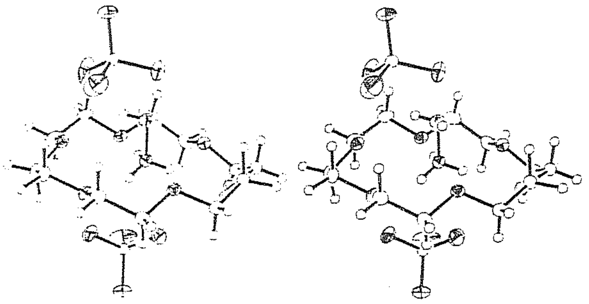
Formula	$C_{12}H_{24}O_6\cdot$ $N_2H_5ClO_4$	$C_{12}H_{24}O_6\cdot$ $HONH_3ClO_4\cdot\frac{1}{2}H_2O$	$C_{12}H_{24}O_6\cdot$ $CH_3NH_3ClO_4$
T/K	115	115	296
Space Group	$Pn2_1a$	$C2/c$	$C2/c$
Z	4	8	8
a/Å	14.567(3)	19.410(5)	24.518(4)
b	13.652(2)	10.231(3)	8.594(2)
c	9.244(2)	21.321(5)	21.447(4)
β/°	(90.0)	116.71(2)	117.04(1)
Radiation	MoKα	MoKα	CuKα
Unique refl.	4198	6898	3590
Max. Sinθ/λ	0.81	0.76	0.63
Current R	0.057	0.066	0.086

All structures were solved by direct methods and refined by full-matrix least squares. Each ring is in the ideal crown conformation, with all C-C bonds gauche and all C-O bonds trans. The hydrazinium complex is unique among complexes of crowns with ammonium and substituted ammonium ions in that the $-NH_3^+$ nitrogen atom lies close to the median plane of the six oxygen atoms of the crown ring in a nesting postion, just 0.11Å from this plane. It is hydrogen bonded to the lower triangle of oxygen atoms; the $-NH_2$ group is hydrogen bonded in turn to two oxygen atoms of the upper triangle in the host, one of these bonds being bifurcated, involving a perchlorate oxygen atom as well:



The assertion that the diameter of NH_4^+ is too large to permit this ion to be in a nesting position in a complex is clearly incorrect. In the hydroxylammonium complex, the nitrogen atom of the $-NH_3^+$ group lies about 0.68Å from the median plane of the crown ring. The $-NH_3^+$ group appears disordered about the O-N bond, with equal weight for two sets of hydrogen positions, hydrogen bonded to the upper and lower triangles of oxygens respectively. The -OH group is hydrogen bonded to the water molecule (which lies on a 2-fold axis); the water molecule is in turn hydrogen bonded to perchlorate ions. The N atom in the methylammonium structure lies 0.83 Å above the mean plane of the crown ring, with the $-NH_3^+$ group perching on the upper triangle of oxygens.