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STUDIES OF THE EFFECT OF AGE ON THE STRUCTURE OF POLYCRYSTALLINE ReO_3 *

C.A. Majid **
International Centre for Theoretical Physics, Trieste, Italy.

ABSTRACT

Structural studies of polycrystalline $H_{0.57}ReO_3$ grown with age of ReO_3 placed in air for $2\frac{1}{2}$ years, at normal room temperature conditions, are reported. $H_{0.57}ReO_3$ phase was found to be orthorhombic with space group P_{mm2} and lattice parameters as follows:

$$a_0 = 5.888 \pm 0.003\ \mathring{A};\quad b = 12.996 \pm 0.002\ \mathring{A}$$
$$c_0 = 5.884 \pm 0.005\ \mathring{A};\quad \alpha = \beta = \gamma = 90.00$$
$$v = 450.25\ \mathring{A}^3;\ Z = 6$$
$$D_m = 4.974 \pm 0.032\,\mathrm{gm\cdot cm^{-3}};\quad D_x = 5.196\,\mathrm{gm\cdot cm^{-3}}$$

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** Permanent address: Nuclear Materials Division, Pakistan Institute of Nuclear Science and Technology, P.O. Nilore, Rawalpindi, Pakistan.

INTRODUCTION

Rhenium trioxide, ReO_3, has been thought to be chemically stable compound in air at normal room temperature conditions (1). However, with ReO_3 single crystal left in the air, a gradual change in the diffraction pattern has been observed and growth of an hydrogen rhenium bronze, H_xReO_3, has been suggested (2,3). The hydrogen rhenium bronzes are ternary oxide phases which are derived from ReO_3 by the insertion of the atomic hydrogen. For this purpose various techniques like the cathodic reduction of ReO_3 in aqueous H_2SO_4 (4), the hydrogen spillover methods (5,6), and boiling of ReO_3 single crystal in water (2,3) etc. have been tried. The structure of the resultant phase seems to be strongly dependent on the amount of hydrogen content present in the ReO_3 matrix and/or on the method of preparation of the sample. In terms of crystal structure, Dickens and Weller (6) have reported three regions of phase growth as a function of hydrogen content in the H_xReO_3 system. With the hydrogen content increasing, the unit cell symmetry of the resultant compound increased from orthorhombic through tetragonal to cubic (6). Also the amount of the hydrogen intaken by ReO_3 varies with the method of sample preparation (4,5,6). Such samples have shown contradictory results on other investigations (7,8,9). To the author's knowledge, there is little or no information available about the effect of age and phases etc. thus grown, of polycrystalline ReO_3. The present investigations are the first of this kind.

EXPERIMENTAL

Polycrystalline ReO_3 was obtained from m/s Alpha Ventron Corp., USA. It was completely crystalline and was at least 99 at% ReO_3 phase. This was examined using the X-ray diffraction method. The experimental samples were left in air at normal room temperature (298 K) conditions, in a dust free environment, and their X-ray diffraction patterns recorded after regular intervals of time (approximately 2-3 months). The humidity level in the room was recorded. It ranged from 40-60 at%. The X-ray diffraction data were recorded using a computer controlled powder diffractometer model DMAX-IIIA of M/S Rigaku Corporation, Japan. Cu-K_α radiation (λ=1.54056 Å), monochromatized by a graphite crystal placed in the diffracted beam, was used and intensities were recorded at 0.02 2θ steps using a NaI detector. The number of counts were large enough to ensure that the statistical error was less than 1.0 at%. The experimental intensities were corrected for air scattering, polarization of the X-rays, absorption in the specimen and preferred orientation etc. according to the procedures described in Klug and Alexander (10) and Lipson and Steeple (13). The powder X-ray data was indexed using the computer programme ITO (11). The hydrogen content in the samples was determined using the thermogravimethic analysis (TGA) and their density was measured by the Archimede's principle.

RESULTS AND DISCUSSION

The X-ray diffraction pattern of polycrystalline ReO_3, when left in air was found to change gradually with age. The diffraction lines characteristic of cubic ReO_3 gradually decreased in intensity and several new peaks which were sharp and well separated from those of the mother phase, made their appearance. These peaks grew stronger with the age of the sample. This clearly suggested the growth of a new phase/phases at the expense of the original ReO_3 phase. Initially these changes were found to be quite rapid but became slow with an age of the sample. In a period of two and half years, the sample was found to contain the ReO_3 phase to the extent of about 3.5 at% while the remaining had undergone a phase transformation to some new phase/phases. The position of the above mentioned new diffraction peaks did not correspond to any of the compositions in the system hydrogen-ReO_3 and/or waster-ReO_3 etc., reported in the literature; suggesting the growth of some new composition. Nevertheless, all these peaks could be indexed on the unit cell in the orthorhombic system. The merit (11,12,13) being 43.5. The X-ray powder data for this new phase/composition is shown in Table I. The unit cell parameters computed here are as follows.

$a_o = 5.888 \pm 0.003$ Å
$b_o = 12.996 \pm 0.002$ Å
$c_o = 5.884 \pm 0.005$ Å
$\alpha = \beta = \gamma = 90.0^o$

Unit cell volume:
$V = 450.25$ Å^3

No. of chemical formula in the unit cell:
$Z = 6$

Measured density:
$D_m = 4.974 \pm 0.032\ gm\cdot cm^{-3}$

X-ray density:
$D_x = 5.196\ gm\cdot cm^{-2}$

No extinction was observed for the reflections. The space group was determined to be P_{mm2} (X-ray data also satisfy the conditions of the space group No. 18, $P_{2_1 2_1 2}$).

On the basis of the above results and the information obtained from the thermogravimetric analysis (TGA), we could determine the new phase as $H_{0.57}ReO_3$, a composition in the H_xReO_3 system. The formation of an hydrogen rhenium bronze in the present case under the effect of water vapor in the air over a length of time is in agreement with the observation of other authors for the single crystal of ReO_3(2,3). After 2 1/2 years, $H_{0.75}ReO_3$ was found to be present in the sample to the extent of about 94 at% .

The powder X-ray diffraction pattern did not reveal any evidence for the presence of any diffraction line below the diffraction angle $2\theta=16^o$. There were, however, some very weak lines present in the diffraction pattern which could not be indexed on the unit cell parameters of the composition $H_{0.57}ReO_3$. But these reflections could be indexed on the unit cell constants reported in Kimizuka et al. (2) and/or Weller and Dickens (5), for a low hydrogen

content phase (H_xReO_3; x=0.25 or so: a_o=3.77;b_o=3.74 and c_o=3.71) The concentration of such a phase was small; being around 1.5 at% or so). Also no evidence for the formation of a superlattice having double the lattice constant of cubic ReO_3 (a_o=7.50 Å) was found.

To the author's knowledge as there was no information available in the literature on the unit cell parameters of the composition under present study, therefore, no comparison could be made. Nevertheless, the p-type unit cell observed in the present study for $H_{0.57}ReO_3$ crystal is in agreement for other compositions in the system H_xReO_3, having low hydrogen content, reported in Kimizuka et al. (2) and Horiuchi et al. (3).

Also there was no information available on the density of any of the composition in the system H_xReO_3; therefore, no comparison could be made.

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TABLE I

Powder X-ray data for $H_{0.57}ReO_3$

$\Delta\theta° = 2\theta_{exp} - 2\theta_{calc}$

SR. NO.	$2\theta_{EXP}$ (DEGREES)	I/I_o	d_{EXP} (Å)	HKL	$\Delta\theta°$ (DEGREES)
1.	16.506	100	5.3660	110	+0.011
2.	25.380	88	3.5064	121	-0.012
3.	25.512	20	3.4884	031	-0.007
4.	27.401	19	3.2522	040	-0.028
5.	30.323	24	2.9452	200	+0.012
6.	31.110	2	2.8723	012	-0.034
7.	33.370	2	2.6829	220	-0.016
8.	34.728	38	2.5809	211	-0.007
9.	34.788	64	2.5767	112	+0.035
10.	35.000	25	2.5616	141	-0.007
11.	37.795	4	2.3783	150	-0.008
12.	40.038	21	2.2501	231	-0.004
13.	41.350	32	2.1817	240	+0.002
14.	43.442	12	2.0813	202	-0.007
15.	46.757	8	1.9412	310	-0.014
16.	47.257	25	1.9218	161	+0.012
17.	49.206	23	1.8502	251	-0.014
18.	51.005	33	1.7891	123;330	-0.005
19.	51.560	5	1.7711	170	-0.014
20.	52.139	18	1.7528	242	-0.013
21.	56.287	5	1.6331	302;203	-0.013
22.	56.589	1	1.6251	080;252	-0.021
23.	56.765	14	1.6204	312;213	-0.018
24.	58.914	6	1.5663	350;081	-0.002
25.	60.537	11	1.5282	332	-0.02
26.	61.001	11	1.5177	271	-0.017
27.	63.136	4	1.4714	004	-0.018
28.	65.565	10.5	1.4226	280;082	-0.015
29.	65.740	5	1.4193	411	+0.01
30.	66.122	10	1.4122	361;163	-0.004
31.	66.628	1.5	1.4025	190	-0.002
32.	67.726	5	1.3824	352;253;182;281	+0.010
33.	69.205	15	1.3564	431;134;323	-0.012
34.	69.643	3	1.3489	370;073	-0.012
35.	70.138	8.5	1.3406	440;044	+0.010
36.	71.631	9.6	1.3163	402;204	+0.006
37.	73.965	7	1.2804	282;054	+0.006
38.	74.946	6.4	1.2661	291;192	+0.002
39.	76.020	5.5	1.2509	154;083	+0.008
40.	76.784	6.3	1.2403	1 10 1	+0.016
41.	77.860	4.3	1.2258	273;372	+0.007
42.	78.322	12	1.2198	244;442	-0.008
43.	81.800	6.7	1.1765	005;304	+0.028
44.	82.500	2	1.1683	363	+0.001
45.	82.725	1	1.1656	2 10 1;1 10 2	-0.024
46.	82.950	1	1.1630	390	+0.006
47.	83.388	1.4	1.1580	025;324	-0.008
49.	85.365	12.6	1.1362	125	-0.001
50.	89.895	5.8	1.0903	084;480	+0.005
52.	91.191	1	1.0782	522;1 11 2	+0.008
53.	91.240	1.5	1.0777	1 11 2;225	+0.01
54.	91.86	6	1.0721	055;154	-0.005
55.	92.632	7	1.0652	0 12 1;1 12 0	-0.003
56.	93.247	3	1.0597	235;532	-0.022
57.	95.521	2	1.0404	404	+0.009
58.	97.802	7.8	1.0222	284	+0.044
59.	98.316	6.4	1.0182	165	+0.033
60.	98.626	6.4	1.0158	491;0 12 2	-0.06
61.	99.179	1	1.0116	434;0 11 3	+0.012
62.	101.152	5.7	0.9972	325;1 11 3	+0.021
63.	101.592	3.5	0.9940	374;075;473;570	+0.012
64.	102.018	3	0.9910	444	-0.016
65.	102.797	2	0.9856	1 13 0;0 13 1	-0.007
66.	105.993	1.5	0.9645	116	+0.021
67.	108.699	2	0.9479	0 12 3	+0.023
68.	109.782	2	0.9416	275	+0.022
69.	110.290	4	0.9387	046	+0.027
71.	111.790	2	0.9303	206	+0.024
72.	114.312	1	0.9168	0 14 1	+0.020
72.	114.735	2.5	0.9147	365	+0.035
73.	115.235	2	0.9121	095	+0.021
74.	116.357	1	0.9065	156	+0.010
75.	117.915	1.5	0.8990	435	+0.024
76.	118.901	2.8	0.8944	246	-0.003
77.	123.208	1.7	0.8756	613;2 14 1	-0.004
78.	124.164	1	0.8717	592	+0.026
79.	126.516	5.4	0.8625	1 12 4;1 10 5	+0.049
80.	127.249	1.5	0.8596	336	+0.005
81.	127.811	1	0.8576	583	-0.040
82.	133.193	1	0.8393	710	+1.018
84.	139.955	6.2	0.8252	017	-0.009