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The Characterization of $Ba_3Re_2O_9$ and $Sr_3Re_2O_9$

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The compounds $Ba_3Re_2O_9$ and $Sr_3Re_2O_9$ were prepared by the solid state reaction of the corresponding alkaline-earth oxide with ReO_3 at 750 to 900°C in sealed, evacuated, fused silica tubes. The two compounds are isostructural, having the nine-layer ABO_3 structure with vacant central octahedra. The unit cell parameters are given. The magnetic susceptibility for $Ba_3Re_2O_9$ indicates Curie–Weiss behavior with a Re^{6+} moment having localized electrons. The magnetic data for $Sr_3Re_2O_9$ suggest delocalized electron behavior from its temperature-independent susceptibility. Both compounds appear to have semiconducting properties, but the strontium analog is a better conductor. Both compounds are unstable when heated in air above 400°C. They are readily decomposed by chemical oxidizing agents.

Introduction

Ternary rhenium oxides are known for a variety of basic cations (alkali metals and alkaline-earth metals). A survey of the chemistry of various derivatives has recently been published (*1*). Lower valent ternary oxides of rhenium, however, are relatively few in number even though several attempts have been made to isolate tetravalent and hexavalent rhenium derivatives.

All attempts to prepare $SrReO_3$ and $BaReO_3$ under a variety of experimental conditions always yielded metallic rhenium and a layer-type perovskite derivative. This study was undertaken to determine the composition, crystallographic and magnetic data, and chemical and physical properties of these new layer-type products.

Experimental Section

Reactants

The alkaline-earth oxides were prepared by heating the carbonates or peroxides at 800 to 1000°C *in vacuo* until the pressure in the system reached a value of 1×10^{-4} Torr. $BaCO_3$ and $SrCO_3$ were obtained from the Johnson Matthey Co., while BaO_2 and SrO_2 were purchased from A. D. Mackay, Inc. Rhenium(VI) oxide was obtained from Alfa Inorganic, Inc.

Preparation

All the solid state reactions were carried out on pellets, prepared from finely divided reactant powders, sealed in fused silica tubes previously evacuated to 2×10^{-5} Torr in a high vacuum system. The reactants and pellets were normally handled in a glove bag under dry nitrogen. The sealed silica tubes were heated in the temperature region 500 to 1000°C for periods of 24 to 56 hr prior to analysis and characterization. The black, microcrystalline products, once prepared, were stable in air over long periods of time but were decomposed readily in acid or basic media.

By varying the alkaline-earth to rhenium oxide ratio, it was found that a homogeneous product could only be obtained with 3 moles of alkaline-earth oxide to 2 moles of rhenium trioxide.

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TABLE I

INDEXED POWDER DIFFRACTION DATA

	$Ba_3Re_2O_9$			$Sr_3Re_2O_9$		
h k l	*I*	d_{obs}	d_{calc}	*I*	d_{obs}	d_{calc}
1 0 1	10	4.813	4.840	10	4.510	4.671
0 1 2				10	4.294	4.334
0 1 5	100	3.165	3.176	100	3.044	3.084
1 1 0	100	2.863	2.875	90	2.768	2.773
0 0 9	15	2.293	2.291			
0 2 1				20	2.390	2.384
1 1 6				20	2.142	2.137
2 0 5	90	2.129	2.131	70	2.063	2.062
1 0 10	10	1.908	1.905	10	1.868	1.856
0 2 7				50	1.833	1.843
2 0 8	30	1.789	1.790			
1 1 9				20	1.746	1.740
1 2 5	80	1.711	1.712	80	1.653	1.655
3 0 0	70	1.660	1.660	20	1.596	1.601
0 2 10	60	1.590	1.588			
1 2 8	20	1.519	1.520			
2 2 0	70	1.439	1.437	20	1.388	1.386
2 1 10	65	1.394	1.390	20	1.346	1.348
3 1 5	60	1.310	1.310	10	1.259	1.264
1 0 16	25	1.246	1.247			
2 2 9	20	1.218	1.218			
3 0 12	30	1.194	1.194	20	1.155	1.158
1 3 10	40	1.151	1.147	20	1.111	1.111
2 2 12	20	1.103	1.102	10	1.066	1.068

The reaction can therefore be written as

$$3\,BaO + 2\,ReO_3 \rightarrow Ba_3Re_2O_9$$

and

$$3\,SrO + 2\,ReO_3 \rightarrow Sr_3Re_2O_9.$$

X-ray Properties

Powder diffraction patterns were obtained with a Debye–Scherrer camera (114.6 mm diam) utilizing Ni-filtered, Cu$K\alpha$ radiation. The powder data were indexed and the cell parameters were refined using a computerized, least-squares program. The powder data with intensities (visual estimates) are given in Table I. All the diffraction lines were indexed according to the rhombohedral conditions $-h + k + l = 3n$. The refined unit cell parameters are:

Compound	Hexagonal cell	Volume (Å^3)	Rhombohedral cell
$Ba_3Re_2O_9$	$a = 5.749 \pm 1, c = 20.614 \pm 4$ (Å)	590.1 ± 3	$a = 7.631$ (Å), $\alpha = 44.26°$
$Sr_3Re_2O_9$	$a = 5.545 \pm 2, c = 20.12 \pm 2$ (Å)	535.7 ± 4	$a = 7.430$ (Å), $\alpha = 43.82°$

The space group for $Ba_3Re_2O_9$ is $R\bar{3}m$ and from the similarity of the two powder diffraction patterns, the two derivatives are believed to be isostructural.

Magnetic Data

Susceptibility measurements were made with a Faraday magnetic balance in the temperature region 80 to 300°K. The diagmagnetic corrections for the ions were taken from Selwood's data (*2*).

For $Ba_3Re_2O_9$ the magnetic data suggested Curie–Weiss behavior in the region 80 to 230°K. No field dependence was noted at 80°K and at room temperature. The paramagnetic Curie constant is −254°K and the magnetic moment (per rhenium) is 1.55 μ_B. At higher temperature the magnetic properties deviate from ideal Curie–Weiss behavior.

$Sr_3Re_2O_9$ shows different magnetic behavior. The susceptibility data suggest temperature-independent paramagnetism between 80 and 300°K. The molar susceptibility is 450×10^{-6} cgs (per Re atom). A slight field dependence was noted at 80°K and at room temperature, indicating some slight ferromagnetic impurity in the sample.

Resistivity Data

Electrical resistivity measurements were made on pellets of $Ba_3Re_2O_9$ and $Sr_3Re_2O_9$ which had been prepared at 800°C in sealed, evacuated silica tubes. A two-probe method was used and the results obtained are only qualitative in nature. The resistivity data were obtained between liquid nitrogen temperature and 250°C. The data obtained on both samples showed semiconducting behavior with rapidly decreasing resistivity with increasing temperature. The calculated activation energy (from a log plot of the resistance as a function of reciprocal temperature) was 2.22 eV for $Ba_3Re_2O_9$ and 1.82 eV for $Sr_3Re_2O_9$.

Infrared Spectra

Infrared data were obtained in KBr disks with a Perkin–Elmer Model 283 spectrometer in the region 200 to 4000 cm^{-1}. The spectra confirmed the absence of hydroxide groups and water. $Ba_3Re_2O_9$ showed a strong doublet at 908 and 922 cm^{-1}. $Sr_3Re_2O_9$ showed an even stronger doublet at 912 and 922 cm^{-1}.

Thermal Analysis

Thermo-analytical data were obtained on a duPont Model 990 thermal analyzer with DTA and TGA modules. The DTA experiments were conducted in a gettered argon atmosphere, whereas the weight gain experiments were carried out in the TGA unit using oxygen as the oxidizing medium.

$Ba_3Re_2O_9$ and $Sr_3Re_2O_9$ were found to be stable in an inert atmosphere to 1100°C.

$Ba_3Re_2O_9$ gains 1.6% on heating in oxygen, the maximum weight gain occurring in the 400°C range. A 1.7% weight gain is expected for the oxidation reaction

$$Ba_3Re_2O_9 + \tfrac{1}{2}O_2 \rightarrow Ba_3Re_2O_{10}.$$

The powder diffraction pattern of the yellow TGA product indicated the formation and crystallization of α-$Ba_3Re_2O_{10}$ (*3*).

$Sr_3Re_2O_9$ showed a 2.1% increase in weight on oxidation at 400°C. The theoretical weight gain is 2.08% according to a reaction similar to that given above for the barium analog. The X-ray diffraction pattern of the yellow oxidation product indicated the formation of $Sr_3Re_2O_{10}$.

Discussion

The preparation of two new alkaline-earth rhenium(VI) oxides is of interest in that this oxidation state for rhenium has been claimed to be very uncommon for the element (*1*). However, the attempted preparations of alkaline-earth $ARe^{4+}O_3$ and $A_2Re_2^{5+}O_7$ derivatives yielded only $A_3Re_2^{6+}O_9$ as the stable ternary products.

The binary oxide ReO_3 is well known and several rhenium bronzes M_xReO_3 (M = Na, K, H) have been reported (*4*, *5*). Several ordered perovskite-type materials of composition $A_2M^{2+}Re^{6+}O_6$ have also been synthesized (*6*). The rhenium ions in all of these examples occupy octahedral sites in cubic or hexagonal structures. The single crystal structure of $Ba_3Re_2O_9$ has recently been reported (*7*). The perovskite-related structure is a metal-deficient layer structure based on the nine-layer sequence (*chhchhchh*) in which the central face-shared octahedron is vacant. This is to be expected in order to minimize the Re^{6+}–Re^{6+} repulsive forces which would exist in the filled nine-layer structure.

Octahedral coordination for the Re^{6+} ions is also observed in the $Ba_3Re_2O_9$ derivative. The isostructural nature of $Sr_3Re_2O_9$ is based on the similarity of the powder diffraction patterns, indexing, and cell parameters to those of $Ba_3Re_2O_9$. Attempts are being made to determine the structure of $Sr_3Re_2O_9$ to verify this assumption (*8*).

The magnetic data on $Ba_3Re_2O_9$ are consistent with Re(VI), in that the observed magnetic moment of 1.55 μ_B is in agreement with the theoretical moment of 1.55 μ_B for Re(VI), allowing for some orbital quenching (*9*).

The temperature-independent susceptibility observed for $Sr_3Re_2O_9$ is consistent with delocalized electron description for the $5d^1$ electron in rhenium(VI). The overlap integrals for the orbitals in adjacent vertex-shared octahedra would be enhanced by the smaller strontium cation (smaller unit cell volume). In ReO_3, where there are no interfering cations, complete delocalization occurs to yield a metallic conductor. Good conductivity is also observed in the rhenium bronzes M_xReO_3. The semiconductivity behavior for $Sr_3Re_2O_9$ is consistent with the two-dimensional interactions of vertex-connected octahedra in the structure. Conductivity in the third dimension (along the c-axis of the hexagonal structure) is destroyed by the vacant octahedra. The conduction in $Sr_3Re_2O_9$ was enhanced in comparison to that observed for the (localized) $Ba_3Re_2O_9$ system.

The infrared data indicate a strong Re–O absorption band in the same region as that observed in other compounds containing ReO_6 octahedral groups. The splitting may originate from some irregularity in the octahedral polyhedron (3 Re–O at 2.06 Å and 3Re–O at 1.86 Å observed (7) in $Ba_3Re_2O_9$).

Both derivatives are unstable to air oxidation or to oxidizing agents (such as the halogens) and to oxidizing acids.

A study of the mixed system $Ba_{3-x}Sr_xRe_2O_9$ is planned in order to determine the composition in which conduction is primarily dependent upon the temperature parameter.

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