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The Characterization of Calcium Iridium Oxides

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Several calcium iridium oxides were prepared by solid state reactions and by a hydroxide precipitation technique. These phases were characterized by X-ray powder diffraction data, electrical and magnetic properties. The calcium-rich phase, Ca_4IrO_6, was an insulator exhibiting Curie–Weiss behavior above 77°K with a Weiss constant of −47°K and a magnetic moment of 1.76 μ_B.

Ca_2IrO_4 is a semiconductor and the temperature-dependent susceptibility above 77°K was analyzed in terms of one-dimensional linear chains of octahedrally coordinated Ir^{4+} ions.

Two $CaIrO_3$ phases were isolated, but only the orthorhombic perovskite modification was sufficiently pure for magnetic studies. It was Pauli paramagnetic with metallic conductivity.

Introduction

In the past decade three publications have appeared concerning the preparation and crystal structure of several calcium iridium oxides. Rodi and Babel (*1*) first studied the crystal structure of an orthorhombic $CaIrO_3$ phase and shortly thereafter Babel, Rüdorff, and Tschopp (*2*) reported the structure of Ca_2IrO_4. Recently McDaniel and Schneider (*3*) published the phase diagram of the CaO–IrO_2–Ir system in air. These authors identified three stable phases, Ca_4IrO_6, Ca_2IrO_4, and $CaIrO_3$ (layer-type orthorhombic structure), and one metastable phase, $CaIrO_3$ (orthorhombic perovskite). The metastable phase could only be prepared at relatively low temperatures (900–1100°C), and could not be isolated as a single-phase product.

In our general study of ternary transition metal oxides, we attempted to prepare all these phases for magnetic and electrical characterization. A precipitation technique was used (for the first time in conjunction with a platinum-group metal) to isolate $CaIrO_3$ (perovskite-type derivative) as a single-phase product.

Experimental

Reactants

Ir, IrO_2, and K_2IrCl_6 were obtained from the Matthey-Bishop Company and used directly as received. Reagent grade $CaCl_2$, $CaCO_3$ and KOH were obtained from Baker and Adamson, Merck, and Mallinckrodt, respectively.

Apparatus

High-temperature muffle furnaces were used in the solid-state preparations. Temperatures were monitored with Pt/Pt-13% Rh thermocouples to ±10°C. The reaction mixtures were ground with agate mortar and pestles and pressed into pellets prior to firing.

The X-ray data were obtained at room temperature with a 114 mm Debye-Scherrer camera with Ni-filtered Cu$K\alpha$ radiation. Cell dimensions were refined by a least-squares procedure.

The approximate resistances of cold-pressed pellets were measured with a Heathkit vacuum-tube voltmeter at various temperatures.

Magnetic susceptibilities were determined from powders by the Faraday method, using a Cahn microbalance with the samples suspended in a helium atmosphere. The system was calibrated with $HgCo(SCN)_4$, and measurements were taken from liquid nitrogen to room temperature. Diamagnetic corrections used in the calculations were obtained from Selwood (*4*).

Preparations

Ca_4IrO_6

A stoichiometric mixture of Ir metal and $CaCO_3$ was repeatedly ground, pelleted and

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heated at approximately 1100°C for 72 hr to yield pure Ca_4IrO_6.

Ca_2IrO_4

Heating a pelleted, stoichiometric mixture of Ir metal and $CaCO_3$ at 800°C for 4 h, followed by re-pelleting and re-firing at 800°C for 3 hr, with a final heating at 1050°C for 20 hr resulted in pure Ca_2IrO_4.

$CaIrO_3$—Orthorhombic Perovskite

All attempts to prepare a pure orthorhombic perovskite form of $CaIrO_3$ by a solid-state reaction failed. The pure phase was prepared through a complex hydroxide intermediate, in accord with the general reaction scheme indicated below

$$K_2IrCl_6 \xrightarrow{H_2O} IrCl_6^{2-} \xrightarrow[24\text{ hr}]{\text{pH10–12(KOH)}} Ir(OH)_6^{2-}$$

$$\xrightarrow{Ca^{2+}} CaIr(OH)_6 \downarrow$$

Thermal analysis of the $CaIr(OH)_6$ precipitate revealed crystallization of orthorhombic perovskite $CaIrO_3$ at 650–700°C, with decomposition occurring at 1050°C. No Cl^- could be detected in the acid-soluble precursor, $CaIr(OH)_6$, when qualitatively tested with silver nitrate solution.

$CaIrO_3$—Orthorhombic Layer Structure

All attempts to prepare the layer form of $CaIrO_3$ in a pure state were unsuccessful. Ultimately, a small amount was obtained by a manual separation under a microscope from a mixture of Ca_2IrO_4 and $CaIrO_3$ single crystals grown from fused $CaCl_2$. The identities of the phases were confirmed by crystallographic methods.

Results and Discussions

Ca_4IrO_6

The refined hexagonal cell parameters for Ca_4IrO_6 are compared in Table I with those of other workers.

A plot of $1/X_M'$ versus T, where X_M' is the molar susceptibility corrected for diamagnetism only, indicates Curie–Weiss behavior from 79° to 297°K (Fig. 1). No field dependence of the susceptibility is observed throughout this region. A least-squares best fit gave a Weiss constant of −47.2°K. The mean effective moment, calculated for each data point as $\mu_{\text{eff}} = 2.83[X_M'(T-\theta)]^{1/2}$, was 1.76 μ_B.

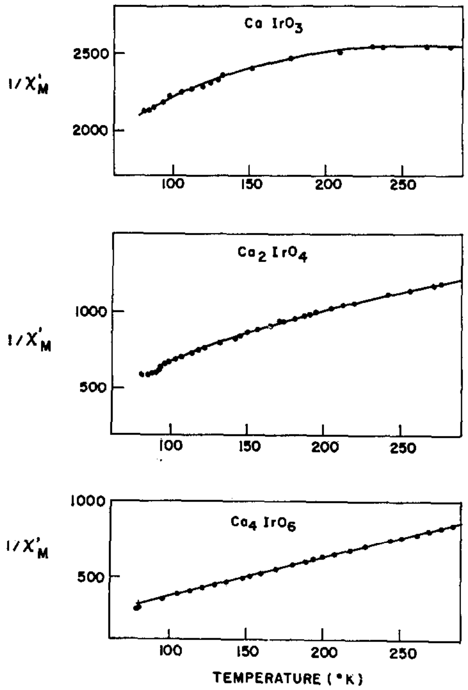

FIG. 1. Corrected reciprocal molar susceptibility *vs.* temperature (°K) for three calcium iridium oxides. Top: $CaIrO_3$ (orthorhombic perovskite). Center: Ca_2IrO_4. Bottom: Ca_4IrO_6.

The relatively small Weiss constant is in accord with the crystal structure (*3*, *5*, *6*) which contains isolated IrO_6^{8-} octahedra sufficiently separated (5.6 Å) to allow only long-range dipole–dipole or feeble direct overlap interactions. The effective moment of 1.76 μ_B at $T > 79$°K agrees well the expected 1.78 μ_B for a $5d^5$ system in a strong octahedral ligand field and with the value determined in the compound $Ba_3IrTi_2O_9$ (*7*), which has the hexagonal $BaTiO_3$ structure.

Electrical measurements indicate that Ca_4IrO_6 is an insulator (33×10^6 Ω at 300°K and 4×10^4 Ω at 400°K), which is consistent with the structure and magnetic data.

Ca_2IrO_4

The refined hexagonal cell parameters for Ca_2IrO_4 agree well with literature values (Table I).

Figure 1 shows a plot of $1/X_M'$ versus T. The discontinuity at 90°K probably indicates the onset of antiferromagnetic order. Attempts to make the data linear by T.I.P. or additional diamagnetic corrections were unsuccessful. Thus the observed susceptibility data could not be treated in terms of Curie–Weiss behavior. Since the structure of Ca_2IrO_4 consists of parallel

TABLE I

REFINED CELL PARAMETERS

Compound	Structure	Space group	Crystal system	Lattice parameters			(Ref.)	Magnetic behavior (liq. N_2 to room temp.)	Electrical behavior (liq. N_2 to 200°C)
				a	*b*	*c*			
Ca_4IrO_6	Rhombohedral K_4CdCl_6	$R\bar{3}c$	Hexagonal	9.314	—	11.204	This work	Antiferromagnetic Weiss const. = −47.2°K	Insulator
				9.330	—	11.228	(*3*)		
Ca_2IrO_4	Sr_2PbO_4	$P\bar{6}2m$	Hexagonal	9.416	—	3.189	This work	Follows theoretical curve for infinite one-dimensional chains.	Semi-conductor
				9.42	—	3.19	(*2*)		
				9.421	—	3.195	(*3*)	Néel temp. = 83.5°K	
$CaIrO_3$	$GdFeO_3$ (orthorhombic Perovskite)	*Pbnm*	Orthorhombic	5.339	7.658	5.575	This work	Pauli-paramagnetic $X_M' = 395 \times 10^{-6}$ c.g.s. units	Metallic conductor
				5.346	7.672	5.587	(*3*)		

chains of edge-shared octahedra (*2*) (as in the rutile structure, but with no cross-linking between neighboring chains), the magnetic data were treated in terms of infinite one-dimensional chains of Ir atoms. This is similar to the interpretation used (*8*) for $CuCl_2$ and $CuBr_2$, where the intra-chain distances (3.31 Å) between paramagnetic Cu atoms are small relative to the interchain distances (3.80 Å). For Ca_2IrO_4, the intra-chain metal–metal distances are 3.19 Å, and the shortest inter-chain distances are 5.44 Å. The appropriate expression for the molar susceptibility, derived (*8*) from the one-dimensional Ising model (*9*), is shown below. The term $(T-\theta)$ has been substituted for T to allow for the possibility of slight inter-chain interactions caused by the large and diffuse nature of the 5*d* orbitals of Ir, compared to the relatively small 3*d* orbitals of Cu.

$$X_M = \frac{Ng^2\beta^2}{4k(T-\theta)}\exp\left(\frac{2J}{kT}\right) \qquad (1)$$

Various combinations of g, J and θ were used to calculate the theoretical susceptibility which matched the experimental data. The best fit was obtained when $(T-\theta)$ was used in the exponential term as well. The final results are shown in Fig. 2, where $2J = -58\ \text{cm}^{-1}$, $g = 2.0$ and theta = −70°K. With these values, the calculated Néel temperature is 83.5°K.

When one considers the simplifications (*8*) introduced in obtaining Eq. (1), and the fact that Ir^{4+} in a strong octahedral field has a T ground term with the possibility for strong orbital coupling, the agreement between theory and experiment is reasonably good. The T ground term for Ir^{4+} can be assumed to be partially removed because of the highly distorted IrO_6 octahedron (*2*); the resulting removal of the degeneracy of the *d* orbitals of Ir would cause an approach to A or E ground-term behavior.

The deviation from theoretical values around the 90°K region is probably due to a combination of factors:

(1). At temperatures approaching that of liquid nitrogen, the energy associated with interchain interactions is of the same order of magnitude as the thermal energy, so the approximations implied by the equation are less valid.

(2). A small amount of paramagnetic impurity may be present in the sample, causing the measured susceptibility to increase abnormally in the low temperature region.

As expected for the chain-type structure, electrical measurements indicated that Ca_2IrO_4 is a semiconductor ($1.9 \times 10^2\ \Omega$ at 300°K and 20 Ω at 500°K).

$CaIrO_3$—Orthorhombic Perovskite

The O′ orthorhombic (O′ nomenclature (*11*) since $c/\sqrt{2}$ is less than a for $a < b < c$) cell constants for $CaIrO_3$ are in good agreement with those reported by McDaniel and Schneider (Table I).

Magnetic-susceptibility measurements show that this form of $CaIrO_3$ is Pauli-paramagnetic, with a molar susceptibility of 395×10^{-6} c.g.s. units/mole (Fig. 1). This is the same order of magnitude as that found for the orthorhombic

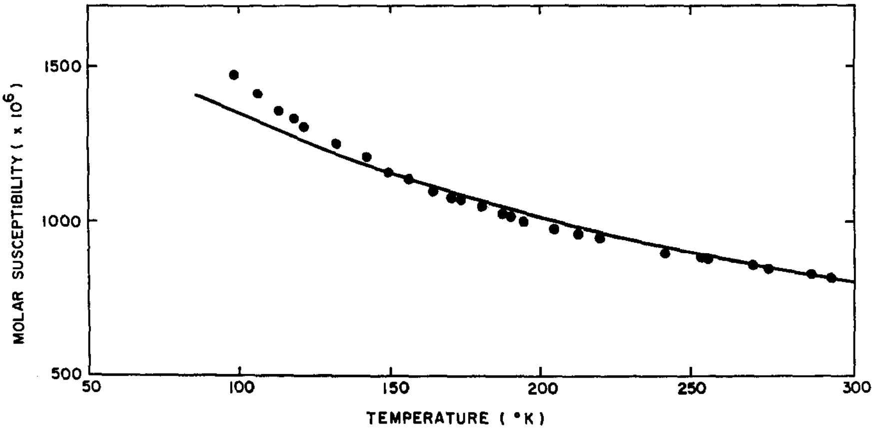

FIG. 2. Molar susceptibility data *vs.* absolute temperature for Ca_2IrO_4. The theoretical curve was derived from Eq. (1) (see text).

perovskite $SrIrO_3$ (high-pressure modification) *(12)*.

As expected for a Pauli-paramagnetic compound, electrical measurements indicate that the orthorhombic perovskite form of $CaIrO_3$ has metallic conductivity (resistance $< 1\ \Omega$ over the temperature range of liquid nitrogen to room temperature).

The increase in X_M' at low temperatures is attributed to a small amount of paramagnetic impurity. An impurity with one unpaired *d* electron of less than 2% is sufficient to produce the observed deviation from linearity.

$CaIrO_3$—Orthorhomibc Layer Structure

Due to the small sample size, the experimental error involved in the susceptibility measurements was so high that no conclusions could be drawn.

Acknowledgments

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