Journal of Alloys and Compounds, 182 (1992) 355–364
JALCOM 159

Chemical constitution of various Sr–Ir–O phases

B. L. Chamberland
Department of Chemistry, University of Connecticut, Storrs, CT 06269 (USA)

A. R. Philpotts
Department of Geology and Geophysics and the Institute of Materials Science, University of Connecticut, Storrs, CT 06269 (USA)

(Received October 22, 1991; in final form November 4, 1991)

Abstract

The compositions of several phases in the Sr–Ir–O system have been reported in the past thirty years, and the single crystal structures of three of these have now been determined. The formulation for one of these phases, namely the body-centered cubic, has been assigned different ratios of strontium, iridium and oxygen by various workers, which has led to some confusion as to its exact chemical composition. To clarify this situation, a study of the composition of the different Sr–Ir–O phases was carried out by electron microprobe analysis using a Kevex quantum energy dispersive detector, which is readily capable of detecting the K_α X-ray emission from oxygen along with that from heavier elements. Reference standards of pure IrO_2, SiO_2 (quartz), fused $SrCl_2$ and $SrCO_3$ were used for calibration of Ir, O, Cl and Sr contents respectively. In addition, the Sr to Ir ratio was determined by using known standards such as the well-characterized monoclinic and orthorhombic (high-pressure) forms of $SrIrO_3$, and Sr_2IrO_4. The analysis of the body-centered cubic Sr–Ir–O phase indicates a chemical formula of $Sr_{0.79}IrO_{2.8}Cl_{0.07}$. The trace of chlorine may be necessary to stabilize this structural form of the compound.

1. Introduction

The strontium–iridium–oxygen system has been studied by a number of researchers during the past thirty years. The earliest work conducted by J. J. Randall *et al.* [1], who first prepared Sr_2IrO_4 and determined its crystal structure. This compound was found to have the K_2NiF_4 structure and represents an oxide compound that is isostructural to a fluoride compound. The compound with composition Sr_4IrO_6 was then prepared by Randall, but single crystals could not readily be isolated for structural characterization. A small single crystal (of approximately 0.03 mm in its greatest dimension) was obtained from a thermal treatment of the powder at 1510 °C for 16 h. The Laue group was found to be $\bar{3}$m, suggesting the structure to be trigonal. The Sr_4IrO_6 phase was later determined to be isostructural with the compound Sr_4PtO_6, which was prepared in single crystal form and studied by the Weissenberg and precession methods. The results of these studies were

0925-8388/92/$5.00

presented [2] in 1959. In 1971 Longo, Kafalas and Arnott [3] reported the preparation of a monoclinic form of $SrIrO_3$. This phase undergoes a transformation to the orthorhombic perovskite-type structure at 40 kbar and 1000 °C. Further, it was found to reduce readily under hydrogen to metallic iridium and Sr_2IrO_4 at low temperatures. These authors later reported the formation of several Ruddlesden and Popper phases: $SrIrO_3 \cdot (SrO)_n$, where $n = 0$, 0.33 and 0.50, all generated [4] at high pressures. A complete phase study in the Sr–Ir–O system was carried out by McDaniel and Schneider [5], and they reported nine different phases. Three of these phases were stable but the remaining six were considered to be metastable compounds under atmospheric conditions. The stable compounds obtained in this latter study included Sr_4IrO_6, Sr_2IrO_4 and the monoclinic form of $SrIrO_3$. These authors also noted the formation of a mixed product containing a body-centered phase, to which they assigned the formula $Sr_2Ir_3O_8$.

Sleight [6] reported the hydrothermal synthesis of several ternary oxides containing a central precious-metal ion. Several of these compounds possessed the cubic $KSbO_3$-type structure. The compound $Sr_{0.5}IrO_3$ was reported as having a body-centered cubic structure and was believed to be similar in composition to the isostructural barium analog, which also was formed under similar hydrothermal conditions. The formulation assigned to the barium analog was based on the barium chemical analysis, its density and isostructural features to the $KSbO_3$ structure. It is reported as $Ba_{0.5}IrO_3$. These two body-centered cubic compounds are believed to contain pentavalent iridium ions. Recently, the structure of the body-centered cubic phase was reported by Schmalle *et al.* [7] to have the chemical composition $SrIrO_3$.

In this paper we report on the structure and chemical compositions of the stable, structurally known ternary compounds in the Sr–Ir–O phase diagram using a sensitive method of chemical analysis for small crystals of well-characterized materials.

2. Experimental details

Crystals or coarse powders of the Sr–Ir–O phases were prepared by solid-state diffusion methods or by crystal growth in a $SrCl_2$ flux at 1000 °C. These experiments produce crystals suitable for electron microprobe analysis. (Details of the analytical measurements are presented in Section 3.) Reference standards included pure, crystalline IrO_2, quartz (SiO_2), fused $SrCl_2$ and $SrCO_3$. Data were collected on several individual particles or crystals in a given sample to ensure sufficient quality of analysis. The L-lines were used in the iridium and strontium analyses because the K-lines for these elements have too high an energy to show significant excitation under the accelerating voltage (15 kV) used in the analyses. The K-lines were used for oxygen and chlorine.

Powder-diffraction patterns for the different phases were obtained using a Debye–Scherrer camera with Ni-filtered Cu Kα radiation. The indexed powder-diffraction patterns were analyzed with computer programs to generate the least-squares refinement of the unit cell parameters that are reported here. The final results are presented in Table 1.

2.1. *Monoclinic $SrIrO_3$ phase*

$SrIrO_3$ was prepared by the reaction of $Sr(NO_3)_2$ and high surface area IrO_2 at 950 °C in air for 24 h, followed by a regrinding and a second heating in air at 1000 °C for 10 h. The pure, single-phase product was characterized by its monoclinic powder pattern and refinement of the powder-data generated unit cell parameters that are in good agreement with those reported in the literature [3] for this phase.

This monoclinic phase has been reported to possess a distorted, six-layer hexagonal, $BaTiO_3$-type structure, with the possible space group C2/c.

2.2. *Orthorhombic $SrIrO_3$ phase*

The monoclinic $SrIrO_3$ phase was heated to 1000 °C at 60–65 kbar pressure for 2 h, followed by a rapid quench to room temperature and then gradual release of pressure. The black, single-phase product was characterized by an orthorhombic, perovskite-type powder pattern. Refinement of the powder-data generated unit cell parameters that are also in good agreement with those reported in the literature [3] for this high-pressure phase.

This orthorhombic phase is believed to be related to the perovskite structure and is isostructural with the orthorhombic form of $GdFeO_3$ having the space group Pbnm.

2.3. *Tetragonal Sr_2IrO_4 phase*

Sr_2IrO_4 was prepared by the reaction of $Sr(NO_3)_2$ and finely divided IrO_2 (2:1 molar ratio) at 950 °C for 24 h, followed by a regrinding and second heating at 1000 °C for 10 h. The pure, single-phase product was characterized by its tetragonal powder diffraction pattern, and refinement of the powder-data generated unit cell parameters that are in good agreement with those reported in the literature for this K_2NiF_4-type product, which has the $I4/mmm$ space group. Sr_2IrO_4 was found to be isostructural with the K_2NiF_4 structure [1]. The unit cell data are presented in Table 1.

2.4. *Body-centered cubic Sr–Ir–O phase*

In an attempt to grow crystals of $SrIrO_3$ using a powdered sample of the monoclinic phase with a $SrCl_2$ flux at 1000 °C, small crystals of a new phase were produced. Characterization of this new phase by X-ray powder techniques indicated a body-centered cubic product. Its powder diffraction pattern is similar to that reported [5] for the compound $Sr_2Ir_3O_8$. The majority of the product formed in this crystal growth experiment was found to be a body-centered cubic phase.

This body-centered cubic phase was recently determined [7] to be isostructural with $KSbO_3$ having the space group $I2/m\bar{3}$. Two other ternary

TABLE 1

Unit cell parameters for various Sr–Ir–O phases

Reported composition	Crystal class	Unit cell parameters				Reference
		a	*b*	*c* (in Å)[a]	*β* (in °)	
$SrIrO_3$	Monocl.	5.604	9.618	14.174	93.26 (±0.1%)	3
$SrIrO_3$	Monocl.	5.615(3)	9.618(3)	14.167(4)	93.30(2)	Refined data [3]
$SrIrO_3$	Monocl.	5.569(2)	9.668(3)	14.261(7)	93.23(4)	This work
$SrIrO_3$	Monocl.	5.603	9.612	14.16	93.23	8
$SrIrO_3$	Orthorh.	5.60	5.58	7.89		3
$SrIrO_3$	Orthorh.	5.597(1)	5.581(1)	7.752(2)		This work
Sr_2IrO_4	Tetrag.	3.885(1)		12.921(4)		Refined data [1]
Sr_2IrO_4	Tetrag.	3.882(1)		12.920(7)		This work
Sr_2IrO_4	Tetrag.	3.89		12.92		4
Sr_2IrO_4	Tetrag.	3.883		12.89		8
$SrIrO_3$	b.c.c.	9.340(2)				7
$Sr_2Ir_3O_8$	b.c.c.	9.344				5
$Sr_{0.5}IrO_3$	b.c.c.	9.27				6
$Sr_{0.8}IrO_{2.8}Cl_{0.1}$	b.c.c.	9.346(4)				This work
Sr_4IrO_6	Hexag.	9.537(9)		12.45(3)		Refined data [2]
Sr_4IrO_6	Hexag.	9.665(4)		12.25(1)		This work
Sr_4IrO_6	Hexag.	9.736		11.886		5
Sr_4IrO_6 (low)	Hexag.	9.860		18.786		5

[a] The number in parentheses is the experimental standard deviation in the last reported digit.

iridium oxides have been reported with this same structure, and each of these contain some pentavalent iridium ions. These are $KIrO_3$ [9] and $La_3Ir_3O_{11}$ [10] crystallizing in the space group Pn3. The basic framework in this structure is the edge-shared octahedral pairs, that are further linked through vertices (free apical positions) to form an intricate structure containing tunnels which contain the large cations or clusters, such as the La_4O groups in $La_3Ir_3O_{11}$.

2.5. *Trigonal Sr_4IrO_6 phase*

Sr_4IrO_6 was prepared by the reaction of 4 moles $SrCO_3$ and 1 mole of high surface area IrO_2 at 1450 °C for 40 h under a slow stream of oxygen. The product was reground and refired in oxygen at 1200 °C for 10 h. The pure, single-phase product was characterized by its powder-diffraction pattern and refinement of the powder-data generated unit-cell parameters that are in good agreement with those reported in the literature for this particular phase. No excess carbonate was detected in the IR spectrum. This compound was found not to be stable over time and tends to hydrolyze in air to strontium hydroxide/strontium carbonate and a strontium–iridium oxide with a reduced Sr to Ir ratio. This phase was not analyzed in this present study because of the problem with hydrolysis in moist air or in water, which is used in the polishing of samples prior to electron microprobe analysis. It is included here for sake of completeness by listing all known stable phases in the Sr–Ir–O system. The structure of this trigonal phase was determined [2] several years ago to be isostructural with the K_4CdCl_6-type structure, which has the trigonal space group $R\bar{3}c$. The structure of three ternary precious-metal oxides with formulation Sr_4MO_6, where M = Pt, Rh or Ir, were observed to be isostructural with K_4CdCl_6.

3. Analytical results

Determination of the strontium–iridium–oxygen content of these compounds was carried out by electron microprobe analysis using an energy dispersive Kevex detector on an MAC 5 electron microprobe. The analyses were carried out with an electron beam having an accelerating voltage of 15 kV and a beam current of 400 pA; the beam diameter was less than 10 μm and the counting time was 400 s live time for the standards, and 100 s live time for the Sr–Ir–O samples. The elemental X-ray emission was collected with a Kevex thin-windowed quantum energy dispersive detector, which is capable of detecting X-rays from the ions in the crystalline structure. The data were processed with the Kevex QUANTEX program, which corrects for atomic number, absorption effects [11] and fluorescence (ZAF) according to the MAGIC V program first described by Colby [11]. The data were normalized to give atomic percent values of 100%, but the results reported here are the (normalized) weight percent of the different elements analyzed. The precision (as 2 sigma) is based on the counting statistics for each element

TABLE 2

Analysis of small crystals from the body-centered cubic phase[a]

Phase	% strontium	% iridium	% oxygen	% chlorine
Orthorh. $SrIrO_3$	27.70 (0.14)	59.77 (0.29)	12.53 (0.30)	– (–)
Monocl. $SrIrO_3$	28.54, 27.24 (0.14)	57.82, 59.64 (0.28)	13.64, 13.12 (0.32)	– (–)
Sr_2IrO_4	39.92, 40.07 (0.20)	43.66, 44.20 (0.21)	16.41, 15.73 (0.39)	– (–)
b.c.c.	22.83, 22.11 (0.14)	60.13, 61.70 (0.03)	14.66, 14.26 (0.34)	0.96, 0.94 (0.02)
	22.70, 23.29 (0.12)	62.30, 61.25 (0.29)	14.63, 14.23 (0.34)	1.00, 1.13 (0.04)
	21.79, 21.62 (0.08)	63.10, 63.29 (0.20)	[14.48, 14.48]	0.61, 0.62 (0.00)

[a] The numbers in parentheses are the 2 sigma precision values; the numbers in brackets are the oxygen values determined by difference.

TABLE 3

Theoretical compositions of three Sr–Ir–O phases

Phase			
	% Theo.	Obs. (av. data)	
		Orthorh.	Monocl.
$SrIrO_3$	% Sr 26.7	27.0	27.9
	% Ir 58.6	58.3	58.7
	% O 14.6	14.6	13.4
	% Theo.	Obs. (av.)	
Sr_2IrO_4	% Sr 40.6	40.0	
	% Ir 44.6	43.9	
	% O 14.8	16.1	
	% Calc.	Obs. for b.c.c. (av.)	
$Sr_{0.79}IrO_{2.8}Cl_{0.07}$	% Sr 22.4	22.3	
	% Ir 62.3	62.1	
	% O 14.5	14.5	
	% Cl 0.80	0.80	

in the individual analysis. The highest deviations in the analytical data were for the oxygen content. Multiple analyses were carried out on the monoclinic $SrIrO_3$ sample and the Sr_2IrO_4 crystalites. Six individual analyses were performed on small crystals from the body-centered cubic phase. The results of these individual analyses are presented in Table 2.

These data are compared with the theoretical compositions for the three different Sr–Ir–O phases (see Table 3).

The analyses in Table 3 indicate that the standard Sr–Ir–O compounds are in good agreement with the theoretical values for the heavy atoms. The oxygen analyses are not as accurate; they exhibited the lowest precision (2 sigma values between 0.30 to 0.40). The differences may be due to a combination of low weight-percent content, the relative weak-emission peak for oxygen and the low-energy emission of light atoms at the lower limit of the Kevex detector. The background corrections in this low energy region of the spectrum are quite difficult to perform and are somewhat arbitrary from one sample to the other. The use of different standards for oxygen generated different values of weight-percent content. Accurate oxygen analyses can be obtained on single crystals of ternary transition metal oxides using electron probe microanalyses, but several experimental problems must be resolved in order to achieve high accuracy [12]. More consistent data for oxygen were obtained in this work by carrying out a heavy metal analysis and determining oxygen by total difference.

Chlorine, which was detected in all crystals of the body-centered cubic phase analyzed in this study, typically constitutes approximately less than 1 wt.% of the sample. The precision for chlorine in these experiments was of the order of 0.00 to 0.04 (2 sigma). The chlorine standard used in these experiments was a sample of fused $SrCl_2$. The presence of chloride ions was not anticipated at the onset of this research, but was undeniable from its intensity and location. It was at this point that we recognized a major difference with the published compositions of the body-centered phase. This chlorine is believed to be necessary to stabilize the body-centered structure for this Sr–Ir–O phase.

4. Results and discussion

Several different Sr–Ir–O phases were prepared, structurally characterized, then analyzed with the electron microprobe using the Kevex quantum energy dispersive detector. Compounds with known crystal structures and compositions were used as standards for the quantitative analyses. The chemical composition of the body-centered cubic phase was determined to be $Sr_{0.79}IrO_{2.8}Cl_{0.07}$. This formula is quite different from that proposed by McDaniel and Schneider [5], namely $Sr_2Ir_3O_8$ and the $SrIrO_3$ composition assumed by Schmalle *et al.* [7] in their single crystal structure analysis of the body-centered cubic phase. These latter authors also obtained crystals of this phase using a $SrCl_2$ flux at 1000 °C. The other preparation of pure, single-phase material involved the hydrothermal synthesis of the cubic phase using $SrO_2 \cdot 8H_2O$ and iridium dioxide as reactants. This product, however, has a quite different unit cell parameter, which may be the result of Sr content and/or hydroxide ion incorporation in the large tunnels of the structure. The body-centered cubic phase in this Sr–Ir–O phase is most probably stabilized by the chlorine atoms in the large tunnels of the $KSbO_3$-type structure. The deficiency of strontium, which would normally occupy disordered positions within these tunnels, would also generate several vacant sites for the chloride ions, or the water molecules (as in the hydrothermal synthesis). The structure of $SrIrO_3$ reported by Schmalle *et al.* [7] utilizes several sites for the strontium ions *i.e.* 16f, 8c and 2a. These sites, however, are only partially occupied: 0.18, 0.02 and 0.014 respectively. This distribution accounts for three Sr atoms required for the stoichiometric composition, but a calculation of the oxygen content from site symmetry and site occupancy factors yields 15 oxygen atoms instead of the 9 required for the stoichiometric formula. The low site occupancy for Sr in different site positions of the structure indicates that chloride ions could also occupy these positions and give rise to the observed electron density found in these regions. The availability of sites in the large tunnels could easily accommodate the large chloride ions. These same sites could be used to hold hydroxide ions which are possibly present in the case of the hydrothermal body-centered cubic product obtained by Sleight [6]. McDaniel and Schneider were probably not able to isolate this phase in a pure state at high temperature because the halogen was not present and the structure could therefore not be completely stabilized. Our attempts to prepare this phase by direct solid-state methods at high temperature also failed to generate the pure body-centered cubic product when the ratios given by McDaniel and Schneider were used. From the analytical results and the chemical formula of the body-centered cubic phase, we infer the presence of trace amounts of pentavalent iridium ions, which may also be responsible for the stability of this particular structure. These data suggest that the body-centered cubic phase is non-stoichiometric and individual crystals, as studied in this investigation, could also be non-homogeneous in chemical composition. The differences in unit cell parameters for the body-centered cubic phase, as reported by different workers (see Table 1), would also support these conclusions.

5. Conclusions

The body-centered cubic phase obtained in the Sr–Ir–O system during crystal growth attempts of $SrIrO_3$ single crystals were found to have a different composition and formulation from those previously reported in the literature. The structure recently presented for the body-centered cubic $SrIrO_3$ phase actually represents the structure for the phase now analyzed to be $Sr_{0.79}IrO_{2.8}Cl_{0.07}$. The chloride ion is believed to be necessary to stabilize this unusual form of the compound, which crystallizes with the $KSbO_3$-type structure.

Acknowledgments

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The authors also wish to thank Mr. Howard Kanare for the initial studies on these compounds. Mr. Rick Bennett of the Department of Geology and Geophysics is thanked for the sample preparation prior to carrying out the electron microprobe analyses.

References

1 J. J. Randall, Jr., L. Katz and R. Ward, *J. Am. Chem. Soc.*, *79* (1957) 266.
2 J. J. Randall, Jr. and L. Katz, *Acta Crystallogr.*, *12* (1959) 519.
3 J. M. Longo, J. A. Kafalas and R. J. Arnott, *J. Solid State Chem.*, *3* (1971) 174.
4 J. A. Kafalas and J. M. Longo, *J. Solid State Chem.*, *4* (1972) 55.
5 C. L. McDaniel and S. J. Schneider, *J. Res. Nat. Bur. Stand., Sec. A*, *75* (1971) 185.

6 A. W. Sleight, *Mater. Res. Bull.*, *9* (1974) 1177.
7 H. Schmalle, Ch. Gurtner, H. R. Oswald and A. Reller, *Z. Kristallogr.*, *191* (1990) 239.
8 W. D. Komer and D. J. Machin, *J. Less-Common Met.*, *61* (1978) 91.
9 R. Hoppe and K. Claes, *J. Less-Common Met.*, *43* (1975) 129.
10 F. Abraham, J. Trehoux and D. Thomas, *J. Less-Common Met.*, *63* (1979) 57.
11 J. W. Colby, in *Advances in X-Ray Analysis*, Vol. 11, Plenum Press, New York, 1979, p. 287.
12 A. P. Mackenzie, *Physica C*, *178* (1991) 365.