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High oxygen pressures and the stabilization of the highest oxidation states of transition elements

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Abstract

The stabilization of the highest oxidation states $n+$ of transition elements M^{n+} is an important way of evaluating the role of the covalency of the (M^{n+}–O) bond in the physico-chemical properties of corresponding oxygen lattices. Recently, using high oxygen pressures, Ir(VI) has been stabilized in $A_2BIr(VI)O_6$ oxides with the perovskite-type structure (A = La,Ba,Sr; B = Ca,Sr,Mg,Zn,Li). Through XRD and XANES analyses, the M^{n+}–O distance and the splitting energy between t_{2g} and e_g levels at the Ir(VI) site have been evaluated. The magnetic properties of such ordered $A_2BIr^{n+}O_6$ perovskites (n = IV,V,VI) have been discussed as a function of the covalency of the Ir^{n+}–O bond and the Ir^{n+}–O distance.

Keywords: High oxygen pressures; High oxidation states; Ir(VI) oxides

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1. Introduction

When the formal oxidation state $n+$ of a transition element M increases, its ionic radius is consequently decreased, the local crystal field energy is enhanced and the covalency of the M^{n+}–O bond is significantly increased. These different local phenomena drastically modify the physico-chemical properties of the host lattice and result in effects comparable to the influence of very high pressures on an oxygen lattice containing M^{n+} cations with a constant $n+$ value.

2. High oxygen pressures

Three main routes can be used to generate oxygen pressures [1]:

- compressed gas ($P_{max} \approx 500$ MPa, $T_{max} \approx 850°C$);
- oxidizing solutions ($P_{max} \approx 500$ MPa, $T_{max} \approx 850°C$);
- in situ thermal decomposition of $KClO_3$ or unstable oxides in the reaction cell of a belt-type apparatus ($P_{max} \approx 7$ GPa, $T_{max} \approx 2000°C$).

During the last 25 years, the development of high oxygen pressures in Bordeaux has led to a great improvement in the preparation methods of new oxides with unusual oxidation states of transition metals (Table 1).

In addition, different electronic phenomena can be associated with the stabilization of high oxidation states of d elements. For example, the transition from one electronic configuration to another (for example low-spin → high spin) as a function of temperature has been studied, particularly in the case of Co(III) in

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Table 1
Some unusual oxidation states of 3d elements stabilized under oxygen pressures

Element	Oxidation state	Host lattice	Reference
Fe	Fe(IV)	$A_{0.50}La_{1.50}Li_{0.50}Fe_{0.50}O_4$ (A = Ca,Sr,Ba)	[4]
	Fe(V)	La_2LiFeO_6	[5]
Co	Co(III)	$LnCoO_3$	[6]
		$SrLnCoO_4$	[7]
		$(A_{0.50}La_{1.50})M_{0.50}Co_{0.50}O_4$ (A = Ca,Sr,Ba; M = Mg,Zn)	[8]
	Co(IV)	$(Sr_{0.50}La_{1.50})Li_{0.50}Co_{0.50}O_4$	[9]
Ni	Ni(III)	$LnNiO_3$	[10]
		$SrLnNiO_4$	[11]
		$(A_{0.50}La_{1.50})M_{0.50}Ni_{0.50}O_4$	[12]
Cu	Cu(III)	$LaCuO_3$	[13,14]
		$La_2Li_{0.50}Cu_{0.50}O_4$	
		$SrLaCuO_4$	[15]

Table 2
Evolution of the average Ir oxidation state as a function of the experimental conditions for the A_2MIrO_6 (A = Sr,Ba; M = Ca,Sr,Zn,Mg) perovskites

Theoretical composition	Oxygen pressure treatment	Average Ir oxidation state
Ba_2CaIrO_6	880°C, 60 MPa, 48 h	5.99
Ba_2CaIrO_6	900°C, 6 GPa, 10 min	6.00
Ba_2SrIrO_6	880°C, 60 MPa, 48 h	5.88
Ba_2ZnIrO_6	880°C, 60 MPa, 48 h	5.75
Ba_2ZnIrO_6	1000°C, 7 GPa, 15 min	5.96
Sr_2CaIrO_6	880°C, 60 MPa, 48 h	5.98
Sr_2CaIrO_6	900°C, 6 GPa, 5 min	5.99
Sr_2MgIrO_6	880°C, 60 MPa, 48 h	5.75
Sr_2MgIrO_6	900°C, 6 GPa, 5 min	5.81
Sr_2ZnIrO_6	880°C, 60 MPa, 48 h	5.54
Sr_2ZnIrO_6	1000°C, 7 GPa, 15 min	5.72

Table 3
Evolution of the Ir^{n+}–O bond distance vs. the oxidation state n

Oxide	$n+$	$d(Ir^{n+}–O)$ (± 0.005 Å)
$SrIrO_3$	IV	2.005
La_2MgIrO_6	IV	2.004
La_2ZnIrO_6	IV	1.998
La_2LiIrO_6	V	1.959
Ba_2YIrO_6	V	1.962
Ba_2CaIrO_6	VI	1.926
Ba_2SrIrO_6	VI	1.928
Sr_2CaIrO_6	VI	1.922

Table 4
Variation of the energy splitting ΔE (eV) between t_{2g} and e_g states for different Ir^{n+} oxides

Oxide	$n+$	ΔE (± 0.01 eV)
La_2MgIrO_6	IV	3.18
La_2ZnIrO_6	IV	3.05
La_2LiIrO_6	V	3.67
Ba_2YIrO_6	V	3.26
Ba_2CaIrO_6	VI	3.89
Ba_2SrIrO_6	VI	3.88
Sr_2CaIrO_6	VI	3.90

oxygen lattices derived from the perovskite structure [2]. Another example is the disproportionation $2M^{n+} \rightarrow M^{(n+1)+} + M^{(n-1)+}$ which has been investigated for Fe(IV) in the $AFeO_3$ oxides as a function of the steric effect of the cation A (Ca,Sr) using ^{119}Sn Mössbauer spectroscopy [3].

Due to the large increase in the local crystal field energy on going from the 3d to the 5d series, the highest oxidation states can be obtained for the third row of transition elements. Recently, Ir(VI) has been stabilized in different oxides with the perovskite structure.

3. Preparation and characterization of the A2MIr(VI)O_6 perovskites (A = Sr, Ba; M = Ca, Sr, Zn, Mg)

These materials were prepared through solid state reactions in three or four steps.

A stoichiometric mixture of the reactants was calcinated at approximately 850°C for 24 h, and then heated at approximately 950°C in an oxygen atmosphere for two days. The third step consisted of treatment under oxygen pressure (compressed gas) at 880°C and 60 MPa for 2 days. The last one was treatment under very high oxygen pressures (5–7 GPa) at 900°C using the in situ decomposition of $KClO_3$ [16].

The experimental conditions and the resulting value of the oxidation state of iridium are reported in Table 2 for the various A_2MIrO_6 compounds.

In order to study the evolution of the Ir^{n+}–O distance and of the local crystal field energy vs. the oxidation state $n+$, several iridium perovskites have been investigated using XANES (X-ray absorption near edge structure) and Ir-L_{III}-edge EXAFS (Extended X-ray absorption fine structure) [17].

Table 3 gives the variation of the Ir^{n+}–O distance vs. the n value in different perovskite-type lattices [17].

The values of the energy splitting between the t_{2g} and e_g states is reported in Table 4 for different Ir^{n+} oxides [17].

The ΔE value increases with increasing $n+$ value but the influence of the competing M—O bond to the Ir^{n+}-O ones also plays an important role. A weak competing bond, such as Li-O in $La_2LiIr(V)O_6$ leads to a strong splitting.

4. Conclusion

The use of oxygen pressure appears to be an important tool for the stabilization of unusual oxidation states of transition elements. The selection of the competing bond and the local symmetry is of great help in optimizing the local crystal field energy and consequently improving the stabilization of unknown or uncommon valencies leading to a highly covalent M—O bond.

References

[1] G. Demazeau, Thesis, University Bordeaux I, 1973.

[2] G. Demazeau, S.H. Byeon, J.M. Dance, J.H. Choy, M. Pouchard, P. Hagenmuller, Eur. J. Solid State Inorg. Chem. 29 (1992) 283-300.

[3] G. Demazeau, P. Fabritchnyi, L. Fournes, S. Darracq, I.A. Presniakov, K.V. Pokholok, V.P. Gorkov, J. Etourneau, J. Mater. Chem. 5 (1995) 553-556.

[4] G. Demazeau, M. Pouchard, N. Chevreau, J.F. Colombet, M. Thomas, F. Menil, P. Hagenmuller, J. Less Common Met. 76 (1980) 279.

[5] G. Demazeau, B. Buffat, F. Menil, L. Fournes, M. Pouchard, J.M. Dance, P. Fabritchnyi, P. Hagenmuller, Mat. Res. Bull. 16 (1981) 1465.

[6] G. Demazeau, M. Pouchard, P. Hagenmuller, J. Sol. State Chem. 9 (1974) 202.

[7] G. Demazeau, Ph. Courbin, I.G. Main, G. Le Flem, C.R. Acad. Sc. 283 (1976) 61.

[8] G. Demazeau, M. Pouchard, L.M. Zhu, P. Hagenmuller, Z. Anorg. Allg. Chem. 555 (1987) 64.

[9] B. Buffat, G. Demazeau, R. Black, Y. Takeda, M. Pouchard, P. Hagenmuller, C. R. Acad. Sc. 295 (1982) 557.

[10] G. Demazeau, A. Marbeuf, M. Pouchard, P. Hagenmuller, J. Sol. State Chem. 3 (1971) 582.

[11] G. Demazeau, M. Pouchard, P. Hagenmuller, J. Sol. State Chem. 18 (1976) 159.

[12] L.M. Zhu, G. Demazeau, M. Pouchard, J.M. Dance, P. Hagenmuller, J. Sol. State Chem. 78 (1989) 46.

[13] G. Demazeau, C. Parent, M. Pouchard, P. Hagenmuller, Mat. Res. Bull. 7 (1972) 913.

[14] J.B. Goodenough, N.F. Mott, M. Pouchard, G. Demazeau, P. Hagenmuller, Mat. Res. Bull. 8 (1973) 647.

[15] J.B. Goodenough, G. Demazeau, M. Pouchard, P. Hagenmuller, J. Sol. State Chem. 8 (1973) 325.

[16] D.Y. Jung, Thesis, University Bordeaux I, 1313, 1995

[17] J.H. Choy, D.K. Kim, S.H. Hwang, G. Demazeau, D.Y. Jung, J. Am. Chem. Soc. 117 (1995) 8557.