Structural Studies of Lanthanide Double Perovskites

by

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All the work presented here is my own unless otherwise stated.

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Abstract

This project focuses on the examination of the structures of lanthanide containing double perovskites of the type $Ba_2LnB'O_{6-\delta}$ (Ln = lanthanide or Y^{3+} and B' = Nb^{5+}, Ta^{5+}, Sb^{5+} and/or Sn^{4+}) using synchrotron X-ray and neutron powder diffraction. The first part of this project examined the relative stability of $R\bar{3}$ rhombohedral and *I*4/*m* tetragonal structures as the intermediate phase adopted by the series $Ba_2LnB'O_6$ (Ln = lanthanide (III) or Y^{3+} and B' = Nb^{5+}, Ta^{5+} or Sb^{5+}). It was found that *I*4/*m* tetragonal symmetry was favoured when B' was a transition metal with a small number of *d*-electrons, such as Nb^{5+} or Ta^{5+}. This is due to the presence of π-bonding in these compounds. In the Ba_2LnNbO_6 and Ba_2LnTaO_6 series $R\bar{3}$ rhombohedral symmetry was, however, favoured over *I*4/*m* tetragonal symmetry when Ln = La^{3+} or Pr^{3+} due to the larger ionic radius of these cations. The incompatibility of the d^0 and d^{10} B'-site cations in this family of compounds was indicated by significant regions of phase segregation in the two series $Ba_2Eu_{1-x}Pr_xNb_{1-x}Sb_xO_6$ and $Ba_2NdNb_{1-x}Sb_xO_6$.

In the second part of this project the compounds in the series $Ba_2LnSn_xB'_{1-x}O_{6-\delta}$ (Ln = Pr, Nd or Tb and B' = Nb^{5+} or Sb^{5+}) were examined to understand the relative stability of oxygen vacancies in these materials compared to the oxidation of the lanthanide cations and to determine if any oxygen vacancy ordering occurred. It was found, using a combination of structural characterisation, X-ray Absorption Near-Edge Structure and Ultra-Violet, Visible and Near-Infrared spectroscopies, that with Ln = Pr or Tb increased Sn^{4+} doping results in a change in the oxidation state of the Ln^{3+} cations to Ln^{4+}. This leads to those series containing little or no oxygen vacancies. A loss of B-site cation ordering was found to accompany this oxidation state change and phase segregation was found to occur in the $Ba_2PrSn_xSb_{1-x}O_{6-\delta}$ series most likely due to the Pr^{3+} and Pr^{4+} cations segregating into different phases. The Nd^{3+} cations in the series $Ba_2NdSn_xSb_{1-x}O_{6-\delta}$, however, can not oxidise to the tetravalent state so the number of oxygen vacancies rises with increasing x. It was found that oxygen vacancies concentrate onto the axial site of the compounds with x = 0.6 and 0.8 at ambient temperature. In $Ba_2Sn_{0.6}Sb_{0.4}O_{5.7}$ the oxygen vacancies were found to change to concentrating on the equatorial site at higher temperatures and it is suggested that this oxygen vacancy ordering plays a role in the adoption of *I*2/*m* monoclinic symmetry.

List of Publications

Parts of the work published in this thesis have been, or are in the process of being, published in several scientific journals. These publications are listed below in the order in which they were published.

1. Saines, Paul J.; Elcombe, Margaret M.; Kennedy, Brendan J.; Structural studies of oxygen deficient lanthanide containing double perovskites. Physica B (2006), 385-386(Pt. 1), 187
2. Saines, Paul J.; Kennedy, Brendan J.; Elcombe, Margaret M.; Structural phase transitions and crystal chemistry of the series $Ba_2LnB'O_6$ (Ln = lanthanide and B' = Nb^{5+} or Sb^{5+}). Journal of Solid State Chemistry (2007), 180, 401
3. Kennedy, Brendan J.; Saines, Paul J.; Kubota, Yoshiki; Minakata, Chiharu; Hano, Hiroko; Kato, Kenichi; Takata, Masaki; Crystal structures and phase transitions in Ba_2HoTaO_6. Materials Research Bulletin (2007), 42, 1875
4. Saines, Paul J.; Spencer, Jarrah R.; Kennedy, Brendan J.; Avdeev, Maxim; Structures and crystal chemistry of the double perovskites $Ba_2LnB'O_6$ (Ln = lanthanide and B' = Nb^{5+} and Ta^{5+}): Part I. Investigation of Ba_2LnTaO_6 using synchrotron X-ray and neutron powder diffraction. Journal of Solid State Chemistry (2007), 180, 2991
5. Saines, Paul J.; Spencer, Jarrah R.; Kennedy, Brendan J.; Kubota, Yoshiki; Minakata, Chiharu; Hano, Hiroko; Kato, Kenichi; Takata, Masaki; Structures and crystal chemistry of the double perovskites $Ba_2LnB'O_6$ (Ln = lanthanide and B' = Nb^{5+}, Ta^{5+}): Part II - Temperature dependence of the structures of $Ba_2LnB'O_6$. Journal of Solid State Chemistry (2007), 180, 3001
6. Saines, Paul J.; Kennedy, Brendan J.; Phase segregation in mixed Nb-Sb double perovskites $Ba_2LnNb_{1-x}Sb_xO_6$. Journal of Solid State Chemistry (2008), 181, 298
7. Saines, Paul J.; Kennedy, Brendan J.; Elcombe, Margaret M.; Harris, Hugh H.; Jang, Ling-Yun; Zhang, Zhaoming; Phase and Valence Transitions in $Ba_2LnSn_xSb_{1-x}O_{6-\delta}$ (Ln = Pr and Tb). Journal of Solid State Chemistry, *In Press*

8. Saines, Paul J.; Kennedy, Brendan J.; Johannessen, Bernt; Poulton, Sarah; Phase and Valence Transitions in $Ba_2LnSn_xNb_{1-x}O_{6-\delta}$. Journal of Solid State Chemistry, *In Press*
9. Saines, Paul J.; Kennedy, Brendan J.; Smith, Ronald I.; Structural Phase Transitions in $BaPrO_3$. Materials Research Bulletin, *In Press*

Outline of Contents

Chapter 1

The ternary and double perovskite structures are introduced with an explanation of the various ways in which perovskites can distort from the ideal cubic structure. The relative stability of perovskites with different octahedral tilt systems is examined and the applications and features of oxygen deficient perovskites detailed.

Chapter 2

The experimental techniques used to study the compounds examined in this thesis are considered. This includes discussion of the basic theory behind the instruments as well as the specific experimental conditions used. The theory involved in determining the structures of the compounds studied in this work, including the use of the Rietveld method, is detailed.

Chapter 3

The synthesis and characterisation of compounds in the series $Ba_2LnB'O_6$ (Ln = lanthanide or Y^{3+} and B' = Nb^{5+}, Ta^{5+} or Sb^{5+}) is discussed. A particular focus is placed on the structural characterisation, carried out at, above and below ambient temperature, using synchrotron X-ray and neutron diffraction. This leads to a discussion about why different compounds in these series adopt different structures.

Chapter 4

A structural study of the two series $Ba_2Eu_{1-x}Pr_xNb_{1-x}Sb_xO_6$ and $Ba_2NdNb_{1-x}Sb_xO_6$ is conducted using synchrotron X-ray diffraction. An understanding of the differences in the structures adopted by compounds containing the d^0 Nb^{5+} and d^{10} Sb^{5+} cations is further developed.

Chapter 5

Compounds in the series $Ba_2LnSn_xB'_{1-x}O_{6-\delta}$ (Ln = Pr or Tb and B' = Sb^{5+} or Nb^{5+}) are examined using a combination of synchrotron X-ray and neutron diffraction, X-ray Absorption Near-Edge Structure and Ultra-Violet, Visible and Near-Infrared spectroscopies. The focus is on examining the relative stability of oxygen vacancies in

the structure of these compounds compared to the oxidation of the Ln^{3+} cations to Ln^{4+}. The effect this has on the structures of these compounds is also examined.

Chapter 6

The structures of compounds in the series $Ba_2NdSn_xSb_{1-x}O_{6-\delta}$ are examined using synchrotron X-ray and neutron diffraction at, above and below ambient temperature. A focus is placed on evidence for these compounds featuring oxygen vacancy ordering and the absorption of water in the crystal structure of compounds in this series.

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List of Abbreviations

Å	Angstrom, 1×10^{-10} m
ΔE/E	Energy resolution expressed as a fraction of the energies being resolved
χ^2	Goodness of fit
δ	The number of oxygen vacancies in a compound
ϕ	Out-of-phase tilt
λ	Wavelength
$A_2BB'O_6$	General formula for a double perovskite where B and B' are the two octahedrally co-ordinated cations
ABX_3	General formula for a ternary perovskite where A is the larger cation that occupies the 12-fold co-ordination site, B the smaller cation that occupies the octahedral site and X is the anion, usually oxygen
AINSE	Australian Institute of Nuclear Science and Engineering
ANBF	Australian National Beamline Facility
ANSTO	Australian Nuclear Science and Technology Organisation
ARC	Australian Research Council
ASRP	Australian Synchrotron Research Program
B'	Second octahedrally co-ordinated cation in a double perovskite structure
BVS	Bond valence sum
CW	Constant wavelength (neutron diffractometer)
DEST	Department of Education, Science and Training
DFT	Density Functional Theory
E/ΔE	Inverse of ΔE/E
EDX	Energy Dispersive X-ray
e_t	Tetragonal spontaneous strain
eV	Electron Volts
EXAFS	Extended X-ray Absorption Fine Structure
FWHM	Full width at half maximum
GGA	Generalized gradient approximation
GSAS	General Structure Analysis Software
HIFAR	High Flux Australian Reactor

HRPD	High Resolution Powder Diffractometer (at HIFAR)
hrs	Hours
ICSD	Inorganic Crystal Structure Database
JCPDS	Joint Committee on Powder Diffraction Standards
Ln	Lanthanide or Y
M	Metal cation
MRPD	Medium Resolution Powder Diffractometer (at HIFAR)
NIST	National Institute of Standards and Technology
NSRRC	National Synchrotron Radiation Research Center
PAW	Projector augmented wave method
PBE	Perdew-Burke-Ernzerhof
PCA	Principle component analysis
PPDA	Python Powder Data Analysis
PTFE	Polytetrafluoroethylene
PZT	$Pb(Zr_{1-x}Ti_x)O_3$
Q	Order parameter of the Landau free energy expansion
r	Ionic radius
RAL	Rutherford Appleton Laboratory
R_p	Profile factor
R_{wp}	Weighted profile factor
SEM	Scanning Electron Microscopy
SOFC	Solid oxide fuel cell
t	Tolerance factor (of a perovskite)
T_c	Critical temperature
TGA	Thermogravimetric Analysis
TOF	Time-of-flight (neutron diffractometer)
UV-Vis-NIR	Ultra-Violet, Visible and Near-Infrared
VASP	Vienna *ab initio* simulation package
XANES	X-ray Absorption Near-Edge Structure
XRF	X-ray Fluorescence