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Surface and bulk phases in substituted cobalt oxide spinels

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Samples of cobalt oxide spinel doped with a range of cations (Li, Ni, Zn, Cu, Al, Ga, Mn, Ti, Sn, Ge) have been prepared and examined by X-ray diffraction and X-ray photoelectron spectroscopy. Surface enrichment in the dopant species is frequently observed. Determination of the ratio of the two cobalt oxidation states in the surface layers is found to be useful in distinguishing between solid solution behaviour and the nucleation of surface phases. This ratio may also be helpful in characterising the preferred occupancy of octahedral and tetrahedral sites in the near surface regions.

Introduction

Materials based on cobalt oxide spinel and prepared as powders or thin films have been of interest because of their potential application in oxidation catalysis, electrode coatings and magnetic devices. The spinel structure is versatile in being able to accommodate a wide range of metal cations and oxidation states and is therefore a suitable candidate as a model system for fundamental studies or for attempting to optimise performance in some particular application. Methods for the preparation of cobaltites have recently been reviewed[1] and it is apparent that there may be difficulty in preparing homogenous, single phase materials. There is a growing body of evidence that certain cobaltites can be prepared which are metastable. Co_2TiO_4 for example is found[2] to disproportionate into Co_3O_4 and Co_2TiO_4 below 827 °C, while for some substituted cobalt spinels $Co_{3-x}M_xO_4$ containing divalent substituents decomposition can occur to liberate oxygen, free MO and a spinel containing less substituent.[3] Furthermore, work on the surface composition of copper substituted cobalt spinel showed a significant enrichment in copper and this was associated with the formation[4] of a surface phase of Cu_2CoO_3. The nature of the cations exposed at the surface of spinel powders has been the subject of some discussion, since certain surface planes do not expose tetrahedral sites.[5] Certain spinels (AB_2O_4 where A = Mn, Zn, Co and B = Mn, Al, Co) have been investigated by Jacobs *et al.* They conclude[5] on the basis of catalytic properties and low-energy ion scattering that the surfaces of these spinels expose only occupied octahedral rather than tetrahedral sites.

The surface cation composition of mixed oxides as determined by techniques such as X-ray photoelectron spectroscopy (XPS) and low-energy ion scattering is commonly found to differ from the anticipated bulk value. Determination of whether this is an experimental artefact, a fundamental thermodynamic property of the system or due to the formation of a distinct surface phase requires careful systematic investigation. Doped spinels can be difficult to investigate at low dopant concentrations. Powder X-ray diffraction (XRD) is commonly used to determine phase purity and the limits of solid solution but it is rather insensitive and unable in isolation to distinguish surface phase formation at low concentrations. The valence state of the dopant and its lattice site preference can frequently be predicted on the basis of background crystallographic knowledge, but this is not always the case. Experimental investigations have employed NMR, Mössbauer spectroscopy, magnetic and diffraction methods. In principle, XPS should be a useful method for the investigation of doped cobalt oxide spinel since it can identify the valence state and give quantitative information. However, in practice the identification of the oxidation state is frequently ambiguous because charging effects cause binding energy shifts which are irreproducible from sample to sample. The commonly used technique of referencing binding energy to adventitious carbon formed on the surface of the sample is often invalid because of the formation of different types of carbon containing compounds on surfaces with different chemical activity. The oxidation state of cations found in the surface layers can be very difficult to explain because of variations in the sample histories before or during analysis. Electron diffraction and WAXS (wide angle X-ray scattering) analysis have been proposed as suitable methods for investigation.[6] Rather than concentrate on the dopant, we have found it useful to investigate the Co^{2+}/Co^{3+} ratio in doped cobalt oxide spinels by XPS. This ratio is expected to vary with the oxidation state and concentration of the dopant. In practice, the ratio can be determined reliably and is found to vary with the nature and concentration of the dopant ion. We have therefore investigated the substitution in cobalt oxide spinel of a range of metal ions with formal oxidation states between 1 and 4 and with known and unknown site preferences, by a combination of XPS and XRD. Our results are discussed with respect to the chemical environment of the substituent, the composition of the surface layers and the composition limit for the onset of surface phase nucleation.

Experimental

Substituted cobalt oxide spinels of composition $Co_{3-x}M_xO_4$ were prepared for the whole range of selected substituents at a value of $x = 0.1$. In addition selected substituents were prepared at compositions in the range $0.025 \leqslant x \leqslant 0.4$. Preparation was carried out by solid state reaction of intimate mixtures of the weighed components. The nitrates were normally used as the starting material, except for the dioxides for titanium and germanium and the dichloride for tin. The precursor starting materials were carefully heated to 500 °C for 1 h to decompose the nitrates, heated to 600 °C with intermittent grinding to achieve homogeneity and then finally heated to 800 °C for 6 h. Completion of reaction and phase analyses were determined by powder XRD using a Philips diffractometer (Model PW 1830), Cu-Kα radiation and the Philips APD 1700 software analysis package. Lattice parameters were determined with respect to silicon as a standard. XPS spectra were obtained on a Kratos XSAM 800 spectrometer fitted with a multichannel detector. Al-Kα radiation was the excitation source and spectra were collected at high resolution (1.2 eV) and in the fixed analyser transmission mode, which gives uniform resolution across the energy range. The samples were mechanically mounted to ensure good electrical contact and data analysis was carried out using the Kratos DS800 software. Spectra were recorded for the O 1s, C 1s, Co 2p and Mn 2p peaks. Quantitative analysis was carried out for the metallic components from the peak areas without correction for matrix effects and the results expressed as a percentage of the cationic components in the analysed volume. Where the two 2p peaks could each be resolved into two components, the proportions were determined by curve fitting and the mean of the ratio of the two chemical states reported (Co, Cu, Mn, Ni). Typical spectra for the cobalt and manganese 2p regions are given in Fig. 1 for manganese doped samples at compositions $x=0.025$ and 0.2.

Results

The powder XRD results in general confirmed that the preparation conditions produced single phase spinel materials. The lattice parameter values are reported in Table 1 and confirm that substitution had occurred to give solid solutions. Lattice expansion was observed with Mn, Ni, Cu, Al, Ga, Ti, and Sn. Contraction was observed with Li, while Zn and Ge produced little change. In the germanium doped materials the amount of dopant entering the lattice was found to increase with dopant concentration, but some residual starting material remained despite varying the reaction conditions. Similarly, with manganese it was found to be necessary to increase the reaction time at $x=0.2$ to obtain single phase material. With nickel, XRD indicated single phase material at $x=0.2$, but not at $x=0.4$. All other compositions were found to be single phase spinel.

The Co^{2+}/Co^{3+} ratio for the pure cobalt oxide spinel was found to be 0.56. Values for this ratio found for the doped samples are summarised in Table 1 and vary between 0.45 and 1.07. Quantitative analysis of the substituent components is also given in Table 1, expressed as a multiple of the value anticipated from the bulk concentration. A wide range of behaviour is observed. Significant enrichment in the substituent component in the analysed surface regions is observed with Ga, Cu, Mn, and Sn. Concentrations closer to the anticipated bulk values are found with Ni, Al, Ti, Ge and Zn. Li and Al could not be detected at the lower concentrations, but changes in the lattice parameter verified that substitution had in fact occurred with these components. For Cu, Mn and Ga where there is significant surface enrichment, the degree of enrichment is found to decrease rapidly with increasing dopant concentration. For Mn and Ga this is accompanied by a regular increase in the Co^{2+}/Co^{3+} ratio. Nickel however shows a concurrent decrease in the enrichment factor and the Co^{2+}/Co^{3+} ratio between $x=0.025$ and 0.1 but increasing values between 0.2 and 0.4.

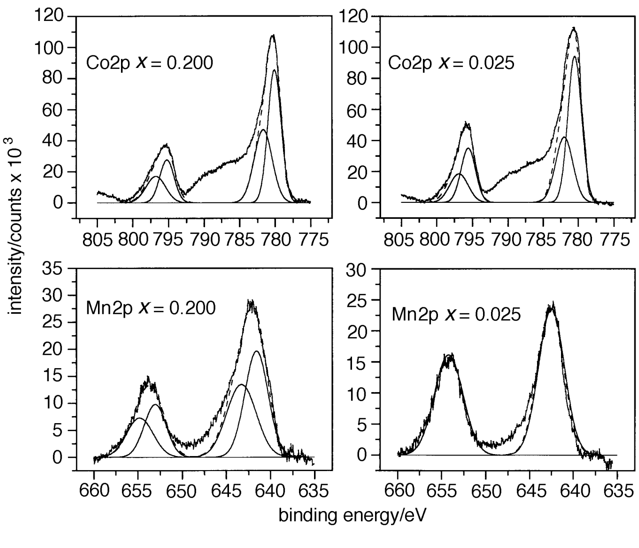

Fig. 1 XPS spectra of the 2p regions of cobalt and manganese in $Co_{3-x}M_xO_4$ (dashed line represents the resultant of the deconvoluted solid lines, overlayed on raw data plot)

Discussion

Cobalt oxide adopts the normal spinel structure with one eighth of the tetrahedral sites occupied by Co^{2+} ions and half the octahedral sites by Co^{3+} ions. Whether any particular composition adopts the normal, inverse or partially inverted spinel structure depends upon lattice energy, crystal field stabilisation and covalency effects. Similarly the site preference for any particular dopant will arise from the balance of energy considerations. Much work has been published on cationic distribution in spinels so that it is possible to predict bulk distributions from lattice parameter data.[7,8] Similarly, thermodynamic data may be used to calculate site preference energies for particular cations.[9] The geometry and bonding at the surface of a spinel will not necessarily be the same as in the bulk of the structure and so the energy balance may be different, resulting in differences in the preferred occupancy of cation sites at the surface. The relative proportions of the exposed surface planes may also vary and thus influence the proportion of exposed octahedral and tetrahedral sites.[5] The experimentally determined Co^{2+}/Co^{3+} ratio (0.56) for the pure oxide is somewhat in excess of the theoretical value (0.50), but this is perhaps to be expected since the oxide surface is analysed in vacuum. The theoretical values of this ratio expected after substitution in the bulk of the oxide by ions of various valencies and at various concentrations are given in Table 2. Comparison of these values with those obtained experimentally (Table 1) shows diverse patterns of behaviour which need to be explained.

Preferred substitution of the dopant for Co^{2+} or Co^{3+} in the analysed volume will directly affect the measured ratio. However, in addition, any surface segregation processes will have an overlying effect. Such effects are well known in oxides and can arise by various mechanisms.[10] If the system is a true solid solution, thermodynamic effects may result in the preferential concentration of the dopant at the surface. When this is the case, the degree of enrichment of the segregating species observed at the surface is found to increase regularly with temperature (at fixed bulk composition) as the system approaches thermodynamic equilibrium. Similarly, for a true solid solution, when the bulk composition of the segregating species is varied, at equilibrium the degree of enrichment at any particular temperature is found to decrease regularly as the bulk concentration of the segregating species is increased. These effects will result in a quantitative change in the concentration of the two cobalt oxidation states if the dopant has preferred site occupancy. Alternatively, the nucleation of a separate, second phase or ‘surface phase’ will result in a complex system which is difficult to analyse quantitatively by XPS. If the second phase contains only one cobalt oxidation state, the observed Co^{2+}/Co^{3+} ratio will be affected. Similarly, any amorphous or quasicrystalline material present as a result of the reaction conditions or thermal history will influence the measured ratio if there is preferred co-ordination of the dopant ion. The experimental results demonstrate most of these possibilities.

Let us first consider substitution in Co_3O_4 by trivalent ions. For manganese at increasing dopant concentration, there is a regular lattice expansion, a regular increase in the Co^{2+}/Co^{3+} ratio and a regular decrease in the degree of enrichment in manganese at the surface (Table 1). This is consistent with a true solid solution. Trivalent manganese is known to preferentially occupy octahedral sites in spinels.[11] However, the observed Co^{2+}/Co^{3+} values are much closer to the expected bulk values (Table 2) than anticipated from the observed

Table 1 XPS and XRD data for substituted cobalt oxide spinels

$Co_{3-x}M_xO_4$	x	Co^{2+}/Co^{3+}	$[M]_{XPS}/[M]_{BULK}$	$[M]_{high}/[M]_{low}$	lattice parameter/Å
Co_3O_4	0	0.56	—	—	8.081(6)
Li^+	0.1	0.67	—	—	8.077(8)
Ni^{2+}	0.025	0.55	8.7	not resolved	8.084(5)
	0.1	0.47	1.6	not resolved	8.086(4)
	0.2	0.45	2.5	not resolved	8.088(8)
	0.4	0.68	3.1	0.7	8.088(9)
Zn^{2+}	0.025	0.9	1.0	—	8.081(0)
	0.1	0.64	1.5	—	8.081(3)
	0.2	0.88	1.2	—	8.081(6)
Cu^{2+}	0.025	0.76	17.8	3.0	8.079(3)
	0.1	0.58	8.1	0.5	8.079(5)
	0.2	0.72	3.2	4.3	8.081(0)
Al^{3+}	0.1	0.52	not determined	—	8.083(6)
	0.3	0.84	1.0	—	8.084(1)
Ga^{3+}	0.025	0.72	42.4	—	8.086(9)
	0.1	0.87	16.8	—	8.092(1)
	0.2	1.04	7.9	—	8.102(4)
Mn^{3+}	0.025	0.46	32.2	not resolved	8.088(5)
	0.1	0.59	9.2	not resolved	8.094(5)
	0.2	0.65	6.2	0.9	8.110(0)
Ti^{4+}	0.025	0.6	3.7	—	8.082(1)
	0.2	0.84	0.7	—	8.091(5)
Sn^{4+}	0.1	0.77	8.7	—	8.083(3)
Ge^{4+}	0.025	0.81	3.7	—	8.080(0)
	0.1	1.07	3.4	—	8.080(3)
	0.2	0.9	1.3	—	8.080(6)

Table 2 Theoretical Co^{2+}/Co^{3+} ratio in the bulk as a function of dopant concentration and dopant valency

valency	$x=0.025$	$x=0.1$	$x=0.2$	$x=0.3$
I	0.47	0.38	0.27	0.17
II	0.49	0.45	0.4	0.35
III	0.51	0.53	0.56	0.59
IV	0.53	0.61	0.75	0.93

degree of enrichment in manganese (at $x=0.1$, a concentration of 0.92 in the surface region would give a Co^{2+}/Co^{3+} ratio of 0.9, whereas a value of 0.59 is observed). Since the binding energies for the analysed manganese and cobalt peaks are fairly close, there is little difference in the relative escape depths and so similar regions of the sample are analysed for each component. At $x=0.2$, two binding states may be distinguished for manganese. One may conclude, therefore, that in the surface regions where manganese is concentrated, manganese can occupy both octahedral (as Mn^{3+}) and tetrahedral sites (as Mn^{2+}) in contrast to the preferred octahedral occupancy in the bulk. Gallium is expected to substitute in octahedral sites in spinels and considerable surface segregation is observed. Again the consistent trends in the increasing Co^{2+}/Co^{3+} ratio and decreasing degree of enrichment with increasing dopant concentration suggest solid solution behaviour. This time however, the ratio of the two cobalt oxidation states is higher than calculated for the bulk in the absence of segregation effects but lower than that calculated by assuming direct substitution of Ga^{3+} for Co^{3+} at the observed degree of enrichment (3.1 at $x=0.1$ rather than the observed 0.87; 1.0 at $x=0.025$ rather than the observed 0.72). The binding energy of the analysed gallium peaks is significantly greater than the cobalt value so that the apparent degree of enrichment is expected to be somewhat overemphasised. However any tendency for gallium to occupy surface tetrahedral sites is much less apparent than with manganese. No surface segregation is apparent with aluminium substitution. At the $x=0.1$ level of substitution, the Co^{2+}/Co^{3+} value is found to be close to the expected bulk value of 0.53. However, with $x=0.3$ the value of 0.8 suggests a higher concentration of Co^{2+} than expected for a solid solution (0.59). This is consistent with the presence of a separate phase such as $Co^{2+}Al^{3+}{}_2O_4$, distinguishable by XPS but not by XRD.

Nickel is known to occupy octahedral sites in doped Co_3O_4 and the end member $NiCo_2O_4$.[12] However, there has been some ambiguity[13] as to whether the formal oxidation state is 2 or 3. A mixture of the two states of nickel in octahedral sites has been proposed for doped Co_3O_4[14] and $NiCo_2O_4$.[15] At values up to $x=0.1$, the XPS results indicate solid solution behaviour as the degree of enrichment in nickel and the value of the Co^{2+}/Co^{3+} ratio decrease steadily with concentration. Above $x=0.2$ phase separation is indicated by increases in these values, while at $x=0.4$ the nickel peaks can be resolved into two components. However, XRD shows a single phase at $x=0.2$, but the presence of additional NiO at $x=0.4$. The increase in the proportion of Co^{2+} at $x=0.4$ is very clear and might result from the presence of $Ni^{3+}Co^{2+}Co^{3+}O_4$. However, this phase is thermally unstable above 400 °C. Unfortunately the XRD pattern of this phase would be obscured by the doped solid solution. Alternatively, the high concentration of Co^{2+} may arise from the transformation.[16,17]

$$Ni_yCo_{3-x}O_4\text{ (spinel)}\rightarrow Ni_zCo_{3-z}O_4\text{ (spinel)}$$

$$+NiO+(Ni,Co^{2+})O\text{ (rock salt)}+O_2$$

The observations cannot simply be explained as the consequence of incomplete reaction or attempting reaction beyond the solid solution limit because that would result in values of Co^{2+}/Co^{3+} closer to 0.56. At low values of x, the Co^{2+}/Co^{3+} ratio is higher than anticipated for solid solution of Ni^{2+}, but lower than anticipated for solid solution of Ni^{3+} and may therefore indicate a mixture of the two states.

With divalent zinc, there is no XPS evidence of surface segregation or XRD evidence of incomplete reaction or phase separation. The Co^{2+}/Co^{3+} value is a little erratic but always high, consistent with the similar transformation.

$$Zn_xCo_{3-x}O_4\ (\text{spinel}) = Zn_yCo_{3-y}O_4\ (\text{spinel}) + ZnO + (Zn,Co^{2+})O\ (\text{rock salt}) + O_2$$

Surface segregation is consistently observed with copper doping. Substitution of Cu^{2+} at tetrahedral sites in Co_3O_4 is well established[16] but the observed Co^{2+}/Co^{3+} value is too high for solid solution behaviour. In addition the copper peaks may be resolved into two components indicating two types of environment (Table 1). These observations are consistent with the presence of the substituted spinel and a surface $Cu_2Co^{2+}O_3$ phase as reported by Bontchev,[4] although this phase is only reported in the phase diagram[18] at temperatures above 915 °C and at high concentrations of copper. Univalent lithium is known[19] to substitute in tetrahedral sites in Co_3O_4. No distinct lithium signal was detected by XPS and so any possible surface segregation can not be characterised. The Co^{2+}/Co^{3+} ratio is, however, found to be considerably in excess of the anticipated value. The presence of a separate phase containing Co^{2+} such as $Li_6Co^{2+}O_4$ is therefore indicated.

All of the tetravalent substituents were found to behave as solid solutions, but with some individual peculiarities. Titanium shows some surface enrichment at low concentration, but a small depletion at $x = 0.2$. Substituting the observed factors gives Co^{2+}/Co^{3+} values close to the observed ones (0.6, 0.6; 0.75, 0.84). This suggests that the preferred occupation of octahedral Co^{3+} sites is maintained right up to the surface regions. Similarly, with germanium, the small observed enrichment factors may be used to adjust the calculated Co^{2+}/Co^{3+} values to approach the observed values (0.6, 0.8; 0.98, 1.07; 0.85, 0.9), again indicating solid solution. For tin however, the significant enrichment at $x = 0.1$ predicts a much higher ratio than is observed in practice (1.1, 0.77). This might indicate either a tendency for tin to occupy tetrahedral Co^{2+} sites in the surface regions, or simply the presence of excess tin oxide undetected by XRD.

Conclusion

Determination of the Co^{2+}/Co^{3+} ratio in the surface regions of doped Co_3O_4 by XPS has been found to be useful in characterising the chemical environment in the surface and near surface regions. In particular, distinctions may be drawn between solid solution behaviour which is influenced by surface segregation effects, and the nucleation of separate surface phases. Phase separation may be detected at lower concentrations than is possible by conventional powder XRD. The results are summarised in Table 3. To further explore the idea that doped spinel cobaltite powders may exhibit preferred site occupancy at the surface in catalytic situations[5] will require careful selection of the dopant, its concentration and the reaction conditions and correlation of the surface analytical and catalytic properties.

Table 3 Bulk and surface phase analysis of substituted cobalt oxides

dopant	solid solution	change in site preference	phase separation	possible surface phase
Li	yes	—	—	Li_6CoO_4
Cu	yes	—	—	$CuCoO_2$
Zn	yes	—	yes	
Ni	yes	—	$x > 0.2$	
Al	yes	—	—	$CoAl_2O_4$
Mn	yes	yes	—	
Ga	yes	yes	—	
Ti	yes	—	—	
Sn	yes	yes?	yes?	
Ge	yes	—	—	

References

1 D. Klissurski and E. Uzunova, *J. Mater. Sci.*, 1992, 285.
2 M. Inagaki and S. Naka, *J. Solid State Chem.*, 1975, **13**, 365.
3 F. Driessens, G. Rieck and H. Coenen, *J. Inorg. Nucl. Chem.*, 1968, **30**, 747.
4 R. Bontchev, PhD thesis, Sofia, 1990.
5 J. P. Jacobs, A. Maltha, J. G. H. Reintjes, V. Ponek and H. H. Brongersma, *J. Catal.*, 1994, **147**, 294.
6 C. Laberty, M. Verelst, P. Lecante, P. Alphonse, A. Mosset and A. Rousset, *J. Solid State Chem.*, 1997, **129**, 271.
7 P. Poix, *Soc. Chim.*, 1965, **5**, 1085.
8 P. Poix, *CR Acad. Sci.*, 1969, **268**, 1139.
9 A. Navrotsky and O. J. Kleppa, *J. Inorg Chem.*, 1967, **29**, 2701.
10 J. Nowotny, in *Science of Ceramic Interfaces*, ed. J. Nowotny, Elsevier, B.V., Amsterdam, 1991, p. 79.
11 B. Boucher, R. Buhl, R. di Bella and M. Perrin, *J. Phys.* (*Paris*), 1970, **31**, 113.
12 G. Blasse, *Phillips Res. Rep.*, 1963, **18**, 383.
13 O. Knop, K. I. G. Reid, Sutarno and Y. Nakagaura, *Can. J. Chem.*, 1968, **46**, 3463.
14 J. A. K. Tareen, A. Malecki, J. P. Doumerc, J. C. Launay, P. Dordor, M. Pouchard and P. Hagenmuller, *Mater. Res. Bull.*, 1984, **19**, 989.
15 P. D. Battle, A. K. Cheetham and J. B. Goodenough, *Mater. Res. Bull.*, 1979, **14**, 1013.
16 T. Andrushkevich, G. Boreskov, V. Popovskii, L. Pliasova, L. Karakchiev and A. Ostankovitch, *Kinet. Katal.*, 1968, **9**, 1244.
17 H. Baussart, M. Le Bras and J. M. Leroy, *C.R. Acad. Sci. Paris*, 1977, **284**, C-735.
18 H. Mueller-Buschbaum and A. Tomaszewska, *Z. Kristallogr.*, 1991, **196**, 121.
19 H. Ichimura and W. Komatsu, *J. Chem. Soc. Jpn.*, 1972, **4**, 690.

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