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X-Ray Fluorescence Study of Manganese Compounds at Stoichiometric Compositions

M. Ghodsi,* P. H. Duvigneaud, and G. Glade
Service de Chimie Industrielle et Chimie des Solides, Université Libre de Bruxelles, Belgium

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Manganese oxides and other inorganic compounds were studied by electron induced X-ray fluorescence. Mn $L\alpha$ energy shifts were measured with respect to pure manganese $L\alpha$ maximum. Those shifts were shown to be a smooth function of manganese partial charge if the latter is calculated from Sanderson's electronegativity scale. The results are in good agreement with Yokokawa's previous work on oxides.

Increasing interest in X-ray analysis methods in such field as industry and research is duly justified by numerous advantages they offer. For example, X-ray fluorescence allows the study of amorphous substances and detection limits of heavy elements can be reduced to a very low level (*ca.* 100 ppm) by use of an ultrathin counter window (polypropylene 1 μm). The cold cathod tube (windowless tube) appears as a very efficient tool for the electronic excitation of K bands of light elements (boron included) and of L bands of heavier elements ($Z>20$). On the other hand, electronic excitation permits the surface analysis of samples in connection with the low penetration depth of the rays.[1]

Furthermore, this method gives access to the stoichiometric composition of samples owing to the energy shift of the characteristic bands (the so-called chemical shift) and can be successfully applied to the study of transition metal oxides[2] the importance of which is well known. Particulary, Mn $L\alpha$ energy shifts (corresponding to the transition L_{III} $M_{\mathrm{IV},\,\mathrm{V}}$) can be linked with partial charge of manganese in its compounds.

Experimental

The spectrometer is an "INEL-Alpha 2020" model allowing the study of light elements owing to the use of an electron tube ("Elent 20"). This device, working under a primary vacuum, has been described elsewhere.[3] Table 1 gives the conditions of use of the spectrometer for the Mn $L\alpha$ measurements.

Table 1. Experimental conditions for the study of Mn L_α

Excitation source	Electron tube
Voltage	3kV
Intensity	800μA
Analyzing crystal	RbAP(2d=26.12Å)
Detection	Flow proportional counter (90% Argon–10% methane)

Table 2. X-Ray diffraction analysis of the samples

Chemical species	Name	Lattice
MnO synth.	Manganosite	Cubic
MnO (RDH)	MnO 90% manganosite MnO_2 10% pyrolusite	
Mn $(OH)_2$	Pyrochroite	Hexagonal
Mn_2O_3	Partridgeite	Orthorhombic
Mn_3O_4	Hausmannite	Tetragonal
MnO_2	Pyrolusite	Tetragonal

Materials. Each of the synthesized systems has been duly characterized by X-ray diffraction analysis. Results are summarized in Table 2. Manganosite[4] is prepared by a careful decarbonation of precipitated $MnCO_3$. Precipitation is obtained under pure N_2 atmosphere by the reaction

$$Mn(NO_3)_2 + (NH_4)_2CO_3 \longrightarrow MnCO_3 + 2NH_4^+ + 2NO_3^-. \qquad (1)$$

After Reaction 1 has been completed, $MnCO_3$ is washed and decomposed at 500 °C in presence of N_2 96%–H_2 4%. Operation is complete after 48 h. Manganese(II) oxide (Riedel-De Haen-high grade purity) has also been investigated. X-Ray diffraction analysis gives a composition of 90% manganosite and 10% MnO_2 (pyrolusite). Dimanganese trioxide has been synthesized by modifying a method initially proposed by Krull.[5] $Mn(OH)_2$ is precipitated from manganese(II) acetate according to the reaction

$$Mn(CH_3COO)_2 + 2OH^- \longrightarrow Mn(OH)_2 + 2CH_3COO^-. \qquad (2)$$

Initial reactives concentration is chosen as high as possible in order to obtain very small particles[6] and hence to improve the oxidation kinetics. The oxidation step has been performed for 6 h under pure oxygen. The system consists of Partridgeite, as shown by X-ray analysis. Mn_3O_4 is prepared by a prolonged heating of MnO_2 in presence of air (1050 °C) and characterized as Hausmannite.[7] $Mn(OH)_2$ is precipitated in an oxygen-free dilute aqueous ammonia, starting from $MnCl_2$. The hydroxide is vacuum dehydrated in presence of P_2O_5 for 48 h. Electrolytic manganese (99.99%) is polished up to complete disappearance of superficial oxide. Evolution of the surface state is measured by the intensity of the O $K\alpha$ peak. Other samples ($MnSO_4$, $MnCl_2$) though of high purity grade, have been recrystallized. In order to avoid granulometry effects,[8] a mixture of oxides (MnO 50%–MnO_2 50% and MnO 80%–MnO_2 20%) has been prepared from sieved powders (size less than 30 μm).

Energy Shifts. One of the most interesting characteristics of low energy X-ray emission bands is the change occurring in spectra when the valence state of the element under study is modified.[9,10] Since emitted soft X-rays are connected with transitions finding their origin in external levels of an atom, corresponding photon energy must be sensitive to the oxidation state of the element. Hence, significant changes in energy position of the intensity maxima can occur. Furthermore, new transitions unobserved in pure elements, can

Table 3. Mn L_α Energy shifts in manganese compounds

Compound	E/eV	ΔE Mn L_α/eV
Mn	634.7	—
MnO	635.4	+0.7
MnO(RDH)	635.4	+0.7
$Mn(OH)_2$	635.7	+1.0
Mn_3O_4	635.6	+0.9
Mn_2O_3	636.0	+1.3
MnO_2	636.1	+1.4
MnO 50%-MnO_2 50%	636.0	+1.3
MnO_2 20%-MnO 80%	635.7	+1.0
$MnCl_2$	636.0	+1.3
$MnSO_4$	636.3	+1.6

appear in their compounds.[11] If ΔE represent the energy shift of the element band maximum in a compound compared with that of the pure element, one generally finds:

$$\Delta E(K\alpha) < \Delta E(K\beta) < \Delta E(L). \tag{3}$$

If the element's oxidation state increases. As a rule, the higher the formal positive change, the more energetic the electronic transition. In the opposite case (element negatively charged), ΔE will be negative. This is only in case of light elements compounds (sulfides[12] oxides[13]) that K shifts can easily be observed. For heavier elements, only the L energy shifts can provide the required information.

Results and Discussion

Mn $L\alpha$ maxima positions (transitions between L_{III} and $M_{\text{IV,V}}$ levels) have been measured. Each point of the curve intensity *versus* angle is provided by a hundred seconds counting time, angular increment being equal to 0.01°.[2] ΔE (eV) is obtained by comparison with pure manganese $L\alpha$. Table 3 shows the observed energy shifts. All ΔE's correspond to an energy increase of the transition and appear to be directly linked with the manganese oxidation state. It is worthwhile to remark that MnO (Riedel-De Haen) behaves in the same way as pure manganosite despite the high MnO_2 concentration revealed by X-ray diffraction. This can be explained by the relatively low excitation depth. As shown by Feldman,[14] the penetration depth of the electrons in the sample is given by:

$$R(\text{Å}) = \frac{250<A>}{\rho<Z>^{n/2}}E^{n/2} \tag{4}$$

where n=1.2 (1−0.29 log$<Z>$), $<A>$ is the mean atomic weight and ρ the specific mass gr/cm^3) of the sample. $<Z>$ is the mean atomic number and E (keV) is the electrons kinetic energy. Accordingly, excitation depth is *ca.* 800 Å in case of MnO. It seems obvious to assume that the particle nucleus consists of undetected MnO_2 as a result of uncompleted particle reduction. It can be pointed out that the mixture (MnO 50%-MnO_2 50%) exhibits the same overall chemical shift as Mn_2O_3.

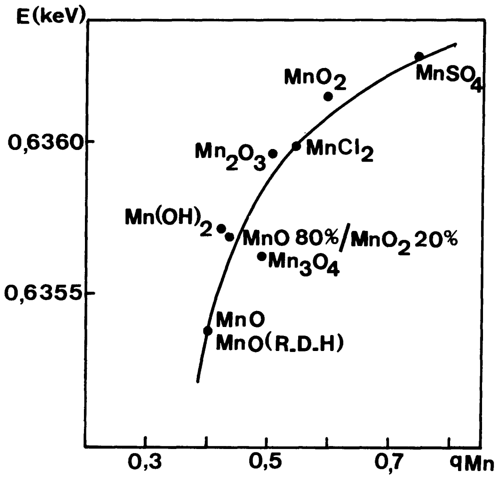

Fig. 1. MnL_α Energy shifts *versus* manganese partial charge in its compouds.
As an example, the solid line is a fifth order polynomial approximation (correlation coefficient: 0.94).

Figure 1 represents the observed energy shift as a function of manganese partial charge calculated from Sanderson electronegativities scale[15] which appears to give a better correlation with experimental evidence than Pauling's scale.[16,17] As a matter of fact, one observes a smooth variation of ΔE as a function of q_{Mn}. Those results are in good agreement with those of Yokokawa *et al.*[18] on Si $K\alpha$ and Al $K\alpha$ chemical shifts in oxide glasses.

Conclusions

Soft X-ray fluorescence is an useful tool in the study of transition metal compounds. Particularly, L energy shifts give a rapid estimate of the mean stoichiometry of a compound or mixtures of compounds. Furthermore, the use of the electrons tube gives access, in contrast with Auger spectroscopy, to a relatively important analysis depth (*ca.* 1000 Å); accordingly, the contribution of possible superficial impurities is highly reduced. Finally, in view of the industrial importance of manganese and transition compounds, study of the L energy shifts provides a useful method for the rapid determination of mineral ores and metallurgy products.

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