Quantitative Light Element Analysis by Analytical Electron Microscopy

Anthony K. Cheetham,*[a] A. Jerome Skarnulis,[a] Diane M. Thomas,[a] and Katuhiko Ibe[b]
[a] *University of Oxford, Chemical Crystallography Laboratory, 9 Parks Road, Oxford, OX1 3PD, U.K.*
[b] *Jeol Ltd., 1418 Nakagami, Akishima, Tokyo 196, Japan*

Quantitative analyses of a series of metal oxides have been performed by *X*-ray emission spectroscopy in an analytical electron microscope equipped with a thin window *X*-ray detector.

The characterisation of polycrystalline materials is one of the most challenging problems in solid state chemistry. The need for such characterisation usually arises because it is not possible to prepare single crystals, but in some instances it is of specific interest to examine samples in a finely divided form, for example as supported catalysts. The characterisation, itself, may range from the determination of the chemical composition of a phase to the investigation of its structure, and a range of sophisticated methods is open to the chemist, including electron microscopy,[1] powder neutron diffraction,[2] and magic angle spinning n.m.r. spectroscopy.[3] This paper describes the application of analytical electron microscopy[4] to the analysis of powder samples containing light elements.

X-Ray emission spectroscopy in the transmission electron microscope (*i.e.* TEM) is one of the most effective techniques for analysing polycrystalline materials, particularly mixtures, but applications to oxides and other light element systems are limited by the inability of most *X*-ray detectors to measure emissions from elements that are lighter than sodium. This stems from the need to protect the solid state detector by using a beryllium window, which, unfortunately, absorbs the emissions (<1 keV) from light elements. In a mixed metal oxide, therefore, it is only possible to determine the cation ratio, unless the oxidation states of the metallic elements are known from other observations. In the Bi–Re–O system, for example, samples of $BiReO_4$, $Bi_3Re_3O_{11}$, and $BiReO_5$ give identical spectra.[5] This is a serious limitation because it inhibits the definitive characterisation of large classes of materials, including some very important catalysts, in circumstances where a knowledge of the oxidation states is essential. There are two possible approaches to the analysis of light elements in the electron microscope: electron energy loss spectroscopy (EELS), which promises to yield both analytical and structural information,[6] and *X*-ray spectroscopy using detectors that are fitted with ultra-thin windows, or none at

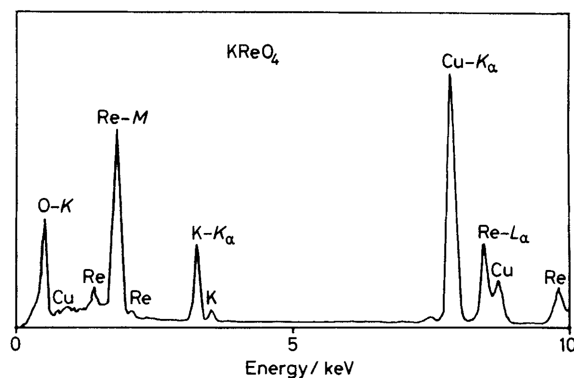

Figure 1. *X*-Ray emission spectrum of $KReO_4$, obtained at 200 keV. The sample was supported on a copper grid.

all. The thin window approach has been considered previously,[7] but only very recently have such detectors become available commercially. Here, we illustrate the use of this technique in a quantitative analysis of a series of oxides and mixed oxides of rhenium.

Polycrystalline samples of ReO_2, ReO_3, $KReO_4$, and Ba_2ReO_5 were prepared by standard, solid state methods and characterised by *X*-ray powder diffraction. Finely ground samples were dispersed on holey carbon supports, held on 3 mm copper grids, and their *X*-ray emission spectra were examined at 200 keV on a Jeol 2000EX analytical electron microscope equipped with a Tracor Northern Micro-Z *X*-ray detector. Analysis was carried out by means of the ratio method,[8] which assumes that the specimen is infinitely thin and that absorption and other corrections can be safely ignored. In the present work, the thickness of the crystallites was monitored empirically by measuring the Re-M:Re-L_α ratio, which varies sharply with crystal thickness but tends to a constant value for very thin crystals. This value (approx. 2.4) was determined by making measurements on ReO_2 crystals with differing thicknesses. Up to ten small crystallites of each compound were analysed using the procedure described in reference 4.

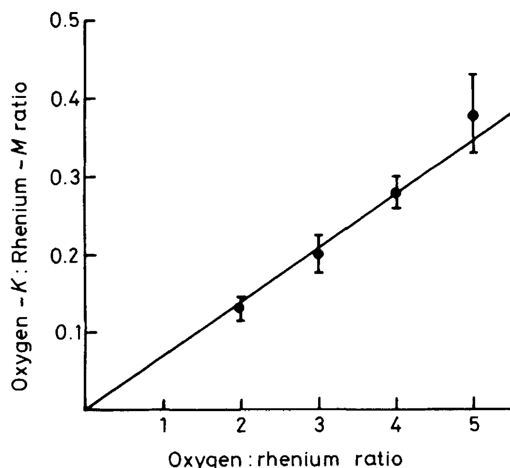

Figure 2. Ratios of *X*-ray emission intensities, oxygen-*K*: rhenium-*M*, plotted *vs.* the oxygen: rhenium atomic ratios for ReO_2, ReO_3, $KReO_4$, and Ba_2ReO_5. The error bars represent the spread of observed ratios.

A typical spectrum is shown in Figure 1 and oxygen-*K*: rhenium-*M* ratios are plotted against O:Re atomic ratios in Figure 2. The linearity of the plot in Figure 2 confirms that oxide analysis can be performed quantitatively using the ratio method if sufficient care is taken to select thin crystals. This was found to be straightforward for all the samples except ReO_2, for which the particle size was rather large. However, after exclusion of the data from thicker crystals, as described above, the ReO_2 data were in excellent agreement with the rest. The data for Ba_2ReO_5 appear to be slightly affected by fluorescence of the oxygen-*K* line, probably by the Ba-*M* lines at approximately 790 eV. This would account for the larger spread of values and the rather higher O-*K*: Re-*M* ratios. However, our results indicate that it is possible to determine oxygen content to a precision of approximately one-half an oxygen atom per rhenium, *i.e.* one unit of Re oxidation state, although it may be difficult to obtain reproducible data in systems that offer no opportunity to monitor crystal thickness. Greater sensitivity to oxygen might be achieved by working at a lower electron energy, but we preferred to make measurements at the voltage that would be used to obtain electron diffraction, TEM, and EELS data. Our results augur well for the quantitative analysis of light elements (C to Na) in a wide range of chemical systems.

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