Determination of the composition of binary systems by the ratio method employing SEM-EDAX

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Abstract. By employing x-ray emission in a scanning electron microscope (SEM), it has been shown that compositions of binary systems such as As-Se glasses, Al-Zn alloys and copper sulphides can be determined.

1. Introduction

Phase identification and determination of phase composition are major problems in solid state synthesis especially when the product is in the form of a polycrystalline powder or compact. It has been recently shown (Cheetham and Skarnulis) that analysis of characteristic x-ray emission from thin sections of the sample in a transmission electron microscope provides a reliable method for determining the composition of individual crystallites in a polycrystalline mixture. The method is based on the fact that the ratio of concentration C_x/C_y of two elements x and y in a given crystal is proportional to the ratio of intensities (I_x/I_y) of their characteristic x-ray emission lines.

$$C_x/C_y = K_{xy} (I_x/I_y)$$

where K_{xy} is a constant for the particular pair of elements. K_{xy} can be evaluated using either a known compound or from the ionization cross-section, fluorescence and specimen-detector geometry (Russ 1976).

This so called ratio method has been successfully applied to several classes of solids such as alloys, minerals, metal oxides and sulphides by carrying out x-ray microanalysis in a transmission electron microscope (Cliff and Lorimer 1975; Goldstein 1979 and Cheetham 1980). We have examined whether the ratio method is applicable for the determination of phase composition of solids by making use of x-ray emission in a scanning electron microscope.

2. Experimental

We have selected three different binary systems for our study (i) As-Se glasses (ii) Al-Zn alloys and (iii) Cu-S sulphides. Samples of (i) and (ii) were in the form of sheets,
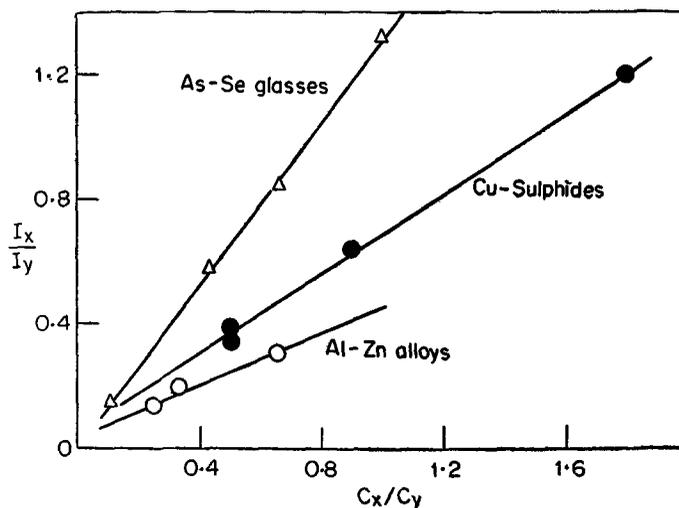
Figure 1. X-ray emission intensity ratio *vs* molar concentration ratio.

while samples of (iii) were polycrystalline powders. Specimens pertaining to each system were mounted on a single holder. As-Se glasses were coated with carbon to make them conducting. X-ray microanalysis were carried out in a cambridge stereoscan S-150 microscope fitted with a Philips x-ray detector at 20 keV electron energy. The sample holder was tilted by about 40° w.r.t. electron beam and rotated about beam axis so that the holder was directly facing the x-ray detector.

X-ray spectra were obtained for a preset time (40-100 sec) with separate windows set for each k-peak and to the base line on the left side of each peak (to correct for the background intensity). For samples of (i) and (ii) both area and point analysis were carried out; for samples of (iii) only point analysis was made. In each case x-ray emission intensities were determined in at least three different regions of the sample to ensure compensational homogeneity.

3. Results and Discussion

The intensity ratios k_α (As)/k_α (Se) for (i), k_α (Zn)/k_α (Al) for (ii) and k_α (Cu)/k_α (S) for (iii) are plotted in figure 1 against the molar concentration ratios which are already known (i and ii) or have been determined by other methods (iii). From figure 1 we see that the plots are linear in all the three cases over the composition range investigated. In the case of Cu-S system two different samples having the same Cu/S ratio *viz* $LaCuS_2$ and $CaFeS_2$ (chalcopyrite) were investigated. We see that the data points are close together in the figure indicating that the influence of the third constituent on the ratio is only minimal.

We have also examined ternary compounds such as MgV_2O_4 and MgV_2S_4 in which the ratio of two elements is constant, but the third element is different. By this method, we have found that the k_α (Mg)/k_α (V) ratio is the same in both the cases, 0·081 and 0·09 respectively indicating that the influence of the third constituent on the intensity ratios is marginal.

The present study shows that just as with TEM x-ray emission in SEM can be made use of for characterization of complex materials.

Acknowledgements

References

Cheetham A K 1980 *Nature* **288** 469
Cheetham A K and Skarnulis A J 1981 *Anal. Chem.* **53** 1060
Cliff G and Lorimer G W 1975 *J. Microsc.* **103** 203
Goldstein J I 1979 *J. Metals* **31** 66
Russ R C 1976 EDAX EDITor **6** 42