

## A Ternary Germanium Tungsten Oxide of the $\text{Mo}_5\text{O}_{14}$ Type

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During recent years attempts have been made to understand the factors which govern the formation of oxides with crystallographic shear (CS), bronze or pentagonal column (PC) structure types, particularly in oxide systems having tungsten or molybdenum as a major component.<sup>1</sup> The present authors have been systematically mapping a series of ternary M–W–O systems in the phase region close to  $\text{WO}_3$ . Some results for the Ti,<sup>2</sup> Zr,<sup>3</sup> V,<sup>4</sup> Cr,<sup>5</sup> Nb and Ta<sup>6</sup> systems have already been presented. In addition it is known that non-transition elements can also induce the formation of some of the structure types listed above.<sup>7–9</sup> With this background we thought it of interest to study the Ge–W–O system.

Samples were heated for up to five weeks in sealed, evacuated silica tubes at 1400 K. It was found by electron microscopy and X-ray diffraction analysis that samples of gross composition between  $\text{WO}_3$  and  $(\text{Ge,W})\text{O}_{2.9}$  were essentially made up of CS phases, regardless of heating time. For compositions in the range  $(\text{Ge,W})\text{O}_{2.9}$  to  $(\text{Ge,W})\text{O}_{2.7}$  several compounds containing PC's as well as CS phases were found. The proportion of PC structures formed depended upon heating times and it appears that at least some of these phases form very slowly at this temperature.

One of the PC phases observed in these preparations is a ternary phase possessing the  $\text{Mo}_5\text{O}_{14}$  structure.<sup>10</sup> Monophasic samples of an oxide  $(\text{Ge,W})_5\text{O}_{14}$  were obtained in samples of gross compositions where about 5 atomic % of the metal content was Ge, heated for 5 weeks at 1400 K. The new  $(\text{Ge,W})_5\text{O}_{14}$  phase has been characterized using Guinier-Hägg X-ray powder photographs. A visual comparison of the X-ray pattern of this new oxide and that of the binary  $\text{Mo}_5\text{O}_{14}$  oxide clearly shows that the two phases are isostructural. The two patterns have the same indexed diffraction lines and the same intensity distribution. A powder pattern of the observed  $(\text{Ge,W})_5\text{O}_{14}$  oxide extracted from a sample of overall composition  $\text{Ge}_2\text{W}_{16}\text{O}_{49}$ , which only contained minor amounts of other oxides, gave the unit cell dimensions  $a = 23.27(1)$  Å and  $c = 3.791(1)$  Å.

This is the first time this structure type has been observed to be formed in any system other than a binary or ternary molybdenum

oxide.<sup>1</sup> In addition, it appears to be quite stable at 1400 K once having formed. All the molybdenum oxides form very quickly, but prove to be of rather low stability and decompose at temperatures of the order of 900–1200 K. The stability of the  $(\text{Ge,W})_5\text{O}_{14}$  oxide is therefore somewhat surprising, and it is possible that the germanium has a particular role to play in this context.

The existence of this phase suggests that PC or tunnel compounds may be more prevalent in the binary and ternary tungsten oxides than previously thought. Already one new oxide of this type has been found in the binary W–O system<sup>11</sup> in samples heated for several weeks. The present result suggests that others may be found in binary and ternary systems if long heating times are employed. This is an interesting difference with the closely related molybdenum oxides where the PC structures tend to form at low temperatures and to decompose rather easily at moderate temperatures.<sup>1</sup>

Further experiments need to be carried out in ternary systems involving non-transition metals from groups 3B, 4B and 5B of the periodic table and such studies are planned. In addition the role that Ge plays in substituting for W and thus stabilizing the  $\text{Mo}_5\text{O}_{14}$  structure of  $(\text{Ge,W})_5\text{O}_{14}$  is not yet clear. To this end, a careful study of the homogeneity range of the  $(\text{Ge,W})_5\text{O}_{14}$  phase is at present being completed. These and other relevant results from the Ge–W–O system will be the subject of a further communication.

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