

Short Communications

New κ -Phases with the Elements Si, Ge, P, As, S and Se

ANDERS HÅRSTA and EVA WENNEBO

Institute of Chemistry, University of Uppsala,
Box 531, S-751 21 Uppsala, Sweden

Since the first discovery of the ternary κ -phase in the Co–W–C system by Rautala and Norton,¹ the occurrence of κ -type phases in a large number of ternary systems has been reported by Nowotny, Rogl and Benesovsky.^{2–5} The ternary κ -phases invariably contain two transitional metal components, while the third component might either be a 3d transition metal (Fe, Co, Ni) or a nonmetal (B, C, O).

During studies of κ -type compounds currently being carried out at this institute,^{6–8} we decided to investigate whether κ -phases are formed in ternary systems containing nonmetals other than those already examined. For crystal-chemical reasons it seemed likely that the elements Si, Ge, P, As, S and Se might replace boron or carbon in the κ -type crystal structure. In the present communication we report the results from a brief survey of the following ternary systems: Hf–Mo–{Si, Ge, P, As, S, Se}, Hf–W–{Si, Ge, P}, Zr–Mo–{P, As} and Zr–W–P.

The starting material for the synthesis of the different alloys were: Turnings of hafnium from Materials Research S.A., London, containing 3% zirconium; turnings of zirconium from H. C. Starck, Berlin, claimed purity 99.8%; Tungsten powder from H. C. Starck, Berlin, claimed purity 99.95%; molybdenum powder from Koch Light

Laboratories, Colnbrook, England, claimed purity 99.99%; silicon powder, claimed purity 99.9%; polycrystalline ingot of germanium from Hoboken, Belgium, semiconductor grade 30 ohm cm; lumps of red phosphorus from Koch Light Laboratories, Colnbrook, England, claimed purity 99.999%; metallic arsenic from Boliden AB, Rönnskärsverken, Sweden, claimed purity 99.9%; crystalline sulfur from Kebo AB, Stockholm, *puriss* quality; selenium shot from Boliden AB, Rönnskärsverken, Sweden, claimed purity 99.4%. Ternary alloys containing silicon or germanium were prepared directly by arc melting mixtures of the constituent elements under purified argon. Due to the high volatility of the other nonmetals, samples of MoP, WP, Mo₃As₄, Hf₂S and Hf₂Se were initially prepared in evacuated and sealed silica tubes. These compounds were then mixed with appropriate amounts of the transition metal components and arc-melted. The alloy buttons were inverted and re-melted to promote homogenization. All the arc-melted alloys were subsequently annealed at 1400 °C under argon of high purity using a cold-crucible levitation technique⁹ in a high-frequency induction furnace for periods between six and twenty-four hours.

X-Ray powder photographs were recorded in a Guinier-Hägg-type focussing camera with CrK α_1 radiation ($\lambda = 2.289753$ Å) and Si($a = 5.431065$ Å)¹⁰ as internal standard. The powder patterns were indexed by comparison with the powder pattern of κ -Hf₉Mo₄Ni⁷ and the unit cell dimensions were refined using the local program CELNE.¹¹ The cell dimensions of the new κ -phases are presented in Table 1.

Table 1. Cell dimensions and cell volumes for the new κ -phases. Space group $P6_3/mmc$ (No. 194). Standard deviations are given in parentheses.

Phase	a (Å)	c (Å)	V (Å ³)
κ -Hf-Mo-Si	8.6233(4)	8.5775(9)	552.38(8)
κ -Hf-Mo-P	8.6236(4)	8.6101(6)	554.52(6)
κ -Hf-Mo-S	8.6796(3)	8.5341(3)	556.78(4)
κ -Hf-Mo-Ge	8.6396(4)	8.6827(5)	561.28(6)
κ -Hf-Mo-As	8.6559(3)	8.6646(7)	562.21(6)
κ -Hf-Mo-Se	8.6995(4)	8.6234(7)	565.19(7)
κ -Hf-W-P	8.6382(3)	8.6367(5)	558.11(5)

The phases κ -(Hf-Mo-Ge), κ -(Hf-Mo-P), κ -(Hf-W-P), κ -(Hf-Mo-As), κ -(Hf-Mo-S) and κ -(Hf-Mo-Se) are readily formed while κ -(Hf-Mo-Si) forms rather slowly. Attempts to prepare κ -phases in the other of the above-mentioned ternary systems were not successful under the conditions of synthesis employed.

In the case of κ -Hf₉Mo₄B³ the boron atoms occupy trigonal prismatic interstices between the metal atoms, while for κ -(W-Co-C)⁶ the carbon atoms occupy both trigonal prismatic and octahedral interstices. As seen in Table 1, the cellvolumes increase in the order κ -(Hf-Mo-Si)→ κ -(Hf-Mo-P)→ κ -(Hf-Mo-S) and this is also true for κ -(Hf-Mo-Ge), κ -(Hf-Mo-As) and κ -(Hf-Mo-Se). The observed trends in cellvolumes cannot be explained in terms of simple size-factor effects, since the normal atomic sizes of the nonmetals concerned decrease for both series of compounds. It therefore appears likely that the cellvolume trends are connected with changes in the nonmetal occupancy of the two types of sites. In order to clarify the structural situation in detail, we intend to carry out complete single-crystal structure refinements for a suitable number of representatives of the new κ -phases.

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1. Rautala, P. and Norton, J. T. *Trans. AIME* 194 (1952) 1045.
2. Rogl, P., Nowotny, H. and Benesovsky, F. *Monatsh. Chem.* 102 (1971) 971.
3. Rogl, P., Nowotny, H. and Benesovsky, F. *Monatsh. Chem.* 104 (1973) 182.
4. Rogl, P. and Nowotny, H. *Monatsh. Chem.* 104 (1973) 1497.
5. Rogl, P. and Nowotny, H. *Monatsh. Chem.* 108 (1977) 1167.
6. Hårsta, A., Johansson, T., Rundqvist, S. and Thomas, J. O. *Acta Chem. Scand. A* 31 (1977) 260.
7. Hårsta, A. *Acta Chem. Scand. A* 35 (1981) 43.
8. Hårsta, A., Rundqvist, S. and Thomas, J. O. *To be published.*
9. Klimecki, V., Karlsson, B., Lundström, T. and Rundqvist, S. Institute of Chemistry, University of Uppsala, UUIC-B18-103, Uppsala 1980.

10. Deslattes, R. D. and Henins, A. *Phys. Rev. Lett.* 31 (1973) 972.
11. Ersson, N.-O. University of Uppsala. *Unpublished.*

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