21 Compounds of Thorium with Germanium
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21.1 Binary Germanides

21.1.1 The Th–Ge Binary System

In the binary system thorium–germanium the compounds Th₂Ge, Th₃Ge₂, ThGe, a phase with stoichiometries of Th₆Ge₁₋₂ₓ, designated as “Th₆Geₓ”, ThGe₂, and Th₀.₉Ge₂ are established and confirmed by different preparation techniques, and metallographic and crystallographic examinations. The existence of the compounds Th₃Ge and ThGe₃ has not been confirmed.

The transformation of pure, face-centered cubic α-thorium to body-centered β-thorium occurs at 1636±10 K (recommended value) and pure β-thorium melts at 2028±10 K (recommended value) [1]. There is no information available on a possible effect of germanium on the α to β transformation. A small solubility of germanium in thorium is postulated [2].

The thorium–ThGe₂ two-phase region is formed by a eutectic reaction at about 20 at% germanium and 1500°C [3]; see also [4 to 6]; or at 12 at% germanium and 1450°C [2]; see also [7, 8]. Th₂Ge crystallizes in a body-centered CuAl₂-type structure and decomposes at about 1750°C [3]. Th₃Ge₂ crystallizes in a tetragonal structure and melts congruently at about 1800°C [2] or nearly 2000°C [3]. At 48 to 49 at% germanium a eutectic mixture of Th₂Ge₂ and ThGe was observed [2]. The existence of this eutectic formation is not confirmed [3]. ThGe crystallizes in a cubic NaCl-type structure and melts congruently at approximately 1800°C [2]. Contrarily, peritectic decomposition into Th₂Ge₂ and liquid at about 1700°C is reported [3]. “Th₆Geₓ” crystallizes with a germanium-deficient distorted AlB₂-type [9] or α-ThSi₂-type structure [10], in which the distortion generates an orthorhombic structure [2]. “Th₆Geₓ” decomposes at 1600°C into a phase with α-ThSi₂-type (“α-Th₆Geₓ”) and liquid [3] or melts incongruently at about 1650°C [2]. “α-Th₆Geₓ” is reported to melt congruently near 1900°C [3].

ThGe₂ crystallizes in a face-centered orthorhombic ZrSi₂-type structure and decomposes at about 1600°C into ThGe₁.₈ and Th₀.₉Ge₂ [2, 11]. Th₀.₉Ge₂ crystallizes in a face-centered orthorhombic structure and melts incongruently at about 1600°C [2] or is presumed to decompose above 1500°C into Th₆Ge₁.₆₂ and liquid [3]. The Th₀.₉Ge₂-germanium two-phase region is formed by a eutectic reaction at 90 at% germanium and 900°C [2].

Pure germanium melts at 1210.4 K [1].

Tentative phase diagrams were established in 1963 involving the existence of Th₃Ge [2]; see also [7]; and in a revised but still tentative form given by [3]; see also [5, 6, 8, 12]. This phase diagram is shown in Fig. 139.
The Th–Ge System

Fig. 139 Tentative thorium–germanium phase diagram [12] from [3].

References for 21.1.1:


21.1.2 Trithorium Monogermanide, "\(\text{Th}_3\text{Ge}\)" (?)

The formation of a thorium-rich compound with the composition of \(\text{ThGe}_{0.3\pm0.1}\) was first reported in 1958 [1] and confirmed as \(\text{Th}_3\text{Ge}\) by metallographic and thermal examinations during a reinvestigation of the thorium–germanium systems [2]. Contrarily, it was suggested