

# Crystal Structures and Properties of $\text{Eu}_2\text{GeSe}_4$ and $\text{Eu}_2\text{Ge}_2\text{Se}_5$

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Europium selenogermanate(IV) and Europium selenogermanate(III) were synthesized by direct reactions of the elements at 1023 K and their crystal structures determined by single crystal methods.  $\alpha\text{-Eu}_2\text{GeSe}_4$  ( $P2_1$ ,  $a = 6.964(1)$ ,  $b = 7.055(2)$ ,  $c = 8.400(2)$  Å,  $\beta = 108.12(2)^\circ$ ,  $Z = 2$ ) crystallizes as a polar variant of the monoclinic  $\text{Sr}_2\text{GeS}_4$ -type at room temperature. At 673 K, the structure is centrosymmetric ( $\beta\text{-Eu}_2\text{GeSe}_4$ ,  $P2_1/m$ ,  $a = 6.969(1)$ ,  $b = 7.059(2)$ ,  $c = 8.516(2)$  Å,  $\beta = 107.99(2)^\circ$ ,  $Z = 2$ ), and a phase transition  $P2_1 \rightarrow P2_1/m$  as known from  $\text{Eu}_2\text{GeS}_4$  is highly probable.  $\text{Eu}_2\text{Ge}_2\text{Se}_5$  ( $P2_1/n$ ,  $a = 8.421(4)$ ,  $b = 12.235(4)$ ,  $c = 9.127(3)$  Å,  $\beta = 93.67(4)^\circ$ ,  $Z = 4$ ) crystallizes in the  $\text{Sr}_2\text{Ge}_2\text{Se}_5$  type, mainly characterized by complex  $[\text{Ge}_4\text{Se}_{10}]^{8-}$  anions with homonuclear Ge-Ge bonds. Both compounds are deep red Zintl phases according to  $(\text{Eu}^{2+})_2\text{Ge}^{4+}(\text{Se}^{2-})_4$  and  $(\text{Eu}^{2+})_2(\text{Ge}^{3+})_2(\text{Se}^{2-})_5$ . Magnetic susceptibility measurements show paramagnetic behavior above 20 K with magnetic moments of  $8.00(5) \mu_{\text{B}}/\text{Eu}$  and  $8.10(5) \mu_{\text{B}}/\text{Eu}$ , respectively, indicating  $\text{Eu}^{2+}$ .  $\text{Eu}_2\text{Ge}_2\text{Se}_5$  orders antiferromagnetically at  $T_{\text{N}} = 4.2(2)$  K and undergoes a metamagnetic transition at 2 K at a critical field of  $0.5(3)$  T. The saturation moment at 2.2 K and 5.5 T is  $7.00(2) \mu_{\text{B}}/\text{Eu}$ .  $\text{Eu}_2\text{GeSe}_4$  is a ferromagnet with  $T_{\text{C}} = 5.8(2)$  K and a saturation moment at 2.2 K and 5.5 T of  $6.92(2) \mu_{\text{B}}/\text{Eu}$ .  $^{151}\text{Eu}$  Mössbauer spectroscopic measurements of  $\text{Eu}_2\text{GeSe}_4$  and  $\text{Eu}_2\text{Ge}_2\text{Se}_5$  at 78 K show isomer shifts of  $-12.43(4)$  mm/s and  $-12.69(5)$  mm/s, respectively, in accordance with divalent europium.