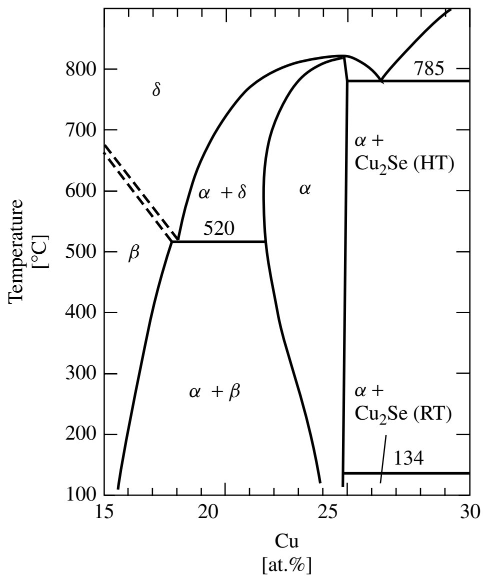

Figure 13.5 Pseudobinary In_2Se_3–Cu_2Se equilibrium phase diagram for compositions around the $CuInSe_2$ chalcopyrite phase, denoted α. The δ phase is the high-temperature sphalerite phase, and the β phase is an ordered defect phase (ODC). Cu_2Se exists as a room-temperature (RT) or high-temperature (HT) phase. (After Gödecke T, Haalboom T, Ernst F, *Z. Metallkd.* **91**, 622–634 (2000) [32])

This tolerance is one of the cornerstones of the potential of $Cu(InGa)Se_2$ as a material for efficient low-cost PV modules. Solar cells with high performance can be fabricated with $Cu/(In + Ga)$ ratios from 0.7 to nearly 1.0. This property can be understood from theoretical calculations that show that the defect complex $2V_{Cu} + In_{Cu}$, that is, two Cu vacancies with an In on Cu antisite defect, has very low formation energy, and also that it is expected to be electrically inactive [34]. Thus, the creation of such defect complexes can compensate for Cu-poor/In-rich compositions of $CuInSe_2$ without adverse effects on the photovoltaic performance. Furthermore, crystallographic ordering of this defect complex is predicted [34], which explains the observed ODC phases $Cu_2In_4Se_7$, $CuIn_3Se_5$, $CuIn_5Se_8$, and so on.

The chalcopyrite phase field is increased by the addition of Ga or Na [35]. This can be explained by a reduced tendency to form the ordered defect compounds owing to higher formation energy for Ga_{Cu} (in $CuGaSe_2$) than for In_{Cu} (in $CuInSe_2$). This leads to destabilization of the $2V_{Cu} + In_{Cu}$ defect cluster related to the ODC phases [36, 37]. The effect of Na in the $CuInSe_2$ structure has been calculated by Wei *et al.* [38], with the result that Na replaces In_{Cu} antisite defects, reducing the density of compensating donors. This theoretical result is supported by measurements of epitaxial $Cu(InGa)Se_2$ films in which Na is found to strongly reduce the concentration of compensating donors [37]. Together with a tendency for Na to occupy Cu vacancies, the reduced tendency to form antisite defects also suppresses the formation of the ordered defect compounds. The calculated effect of Na is therefore consistent with the experimental observations of increased compositional range in which single-phase chalcopyrite exists and increased conductivity [38, 39].