driving force for bulk and grain-boundary interdiffusion of CdTe and CdS. It has been widely reported that a continuous CdTe–CdS solid-solution alloy series can be formed by codeposition of CdTe and CdS at temperatures less than 200°C. The optical band gap of these alloys varies with the composition according to $E_g(x) = 2.40x + 1.51(1 - x) - bx(1 - x)$, with bowing parameter, $b \sim 1.8$, as shown in Figure 14.13 [139]. However, thermal treatment of alloy films above 400°C can induce phase segregation, with the miscibility gap found for equilibrated CdTe–CdS mixed crystals.

Numerous references have established the T–x phase relations in CdTe–CdS mixed crystals at temperatures above 625°C, which exceeds the temperatures typically used to deposit and process thin-film CdTe/CdS structures. This has been extended down to 360°C by lattice-parameter determination of equilibrated $CdTe_{1-x}S_x$ alloy films, as shown in Figure 14.14 [146]. Thermodynamic analysis of the asymmetric phase boundaries using nonideal solution thermodynamics reveals positive values of excess-mixing enthalpies $\Delta H^{EX} = 3.5$ kcal/mol for CdS into CdTe and $\Delta H^{EX} = 5.6$ kcal/mol for CdTe into CdS. For CdS dissolved in CdTe, the experimentally obtained excess-mixing enthalpy supports those calculated from first principles band structure theory for the CdTe–CdS system [147].

The crystallographic forms of the solid alloys are the zincblende (F-43 m) structure for $CdTe_{1-x}S_x$ and the wurtzite ($P6_3mc$) structure for $CdS_{1-y}Te_y$. The zincblende transition to the wurtzite structure in metastable films occurs at $x = 0.3$, and the lattice parameter within each structure type follows Vegard's rule. Metastable and equilibrated $CdTe_{1-x}S_x$ alloy films exhibit the same dependence of E_g, with minimum at 1.39 eV, corresponding to the zincblende–wurtzite transition.

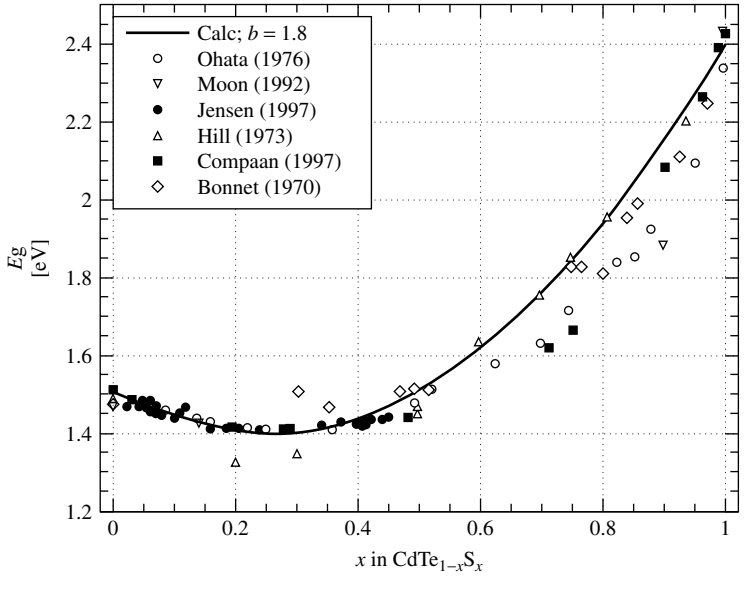

Figure 14.13 Optical band gap of $CdTe_{1-x}S_x$ alloy thin films versus composition. (Data listed in order from References [140–145])