Realizing new, efficient solar absorbers containing earth-abundant elements represents a critical component for expanding the reach of photovoltaic (PV) technologies, meeting growing energy needs, and ameliorating atmospheric CO_2 concentrations. Among all of the elements, Fe is ranked fourth in terms of abundance in the earth's crust, and it is the least expensive metallic element to extract from Nature. The use of Fe in PV was proposed more than 25 years ago in the form of FeS_2 pyrite. Unfortunately, the material has been plagued by performance problems that to this day are both persistently present and not well understood. Considering the current level of understanding and the recent resurgence of interest in Fe-bearing PV materials,[1,2] we have undertaken a concerted and integrated theoretical and experimental study that provides new insight into the problem of FeS_2. We use this insight to propose and then implement design rules for identifying new Fe-containing materials. These rules have led us to consider the new materials Fe_2SiS_4 and Fe_2GeS_4, which may well circumvent the limitations of pyrite.

[illegible]: In addition to its abundance, FeS_2 exhibits a useful band gap ($E_g = 0.9$ eV)[3] and an absorption coefficient that rises to a remarkable level above 10^5 cm^{-1} at $E_g + 0.1$ eV. This high absorption coefficient (as strong as that of organic dyes at visible photon energies!) provides a unique opportunity among inorganic materials to incorporate a very thin absorber layer (<0.1 μm) in a solar cell to capture most of the incident solar radiation. This thickness can be compared to 1.5–3 μm for current thin-film technologies and >200 μm for single-crystal Si cells. Such thin layers not only conserve material, but they also provide an avenue to high efficiency through efficient charge separation associated with a high internal electrical field. But, like its common name, fool's gold, FeS_2 as the promised golden solution for PV has not come true. While the material exhibits exceptional optical and electrical properties, a photo response representative of the intrinsic band gap has not been observed. Single crystals are commonly observed to be -type. In photoelectrochemical cell measurements, the open-circuit voltage, $_{oc}$, is generally measured to be a mere 0.01 V, rising to 0.2 V with surface treatments,[4] i.e., well below the measured optical band gap. In contrast, thin films are commonly -type, and they exhibit no photoelectrochemical response. After nearly a decade of effort,[5] work on FeS_2 largely ceased as the PV community turned its attention to thin-film materials such as $Cu(In,Ga)Se_2$[6] and CdTe,[7] spawning technologies that have now reached commercial module production with efficiencies greater than 10 percent.[8] Yet, the toxicity of Cd and scarcity of In continue to pose a threat to these

Facile S-vacancy formation in FeS_2 has commonly been invoked to address the observed properties. Such vacancy formation has been supported by various studies, e.g., X-ray diffraction, indicating S deficiency as high as 7.5% (FeS_{2-x}, x = 0.15), and thermogravimetric data, revealing possible S loss on heating to temperatures as low as 400 °C. Indeed, observed [illegible] (relative to the ideal FeS_2 stoichiometry) has almost universally been interpreted to imply microscopic [illegible] in otherwise perfect FeS_2. The notion that FeS_2 is prone to high S vacancy concentrations is rooted in much earlier unsuccessful attempts to use it as a semiconductor in electronic devices.[3] This model of bulk S vacancies, however, is not without contradictions. Indeed, on the basis of a very careful analysis of the literature, Ellmer and Hopfner[10] have concluded that FeS_2 is actually a stoichiometric compound. Given these contradictory conclusions, the nature of S deficiencies in FeS_2 remains uncertain.

[illegible]$_2$? To address the likelihood that S vacancies can exist in FeS_2, we have calculated the formation energies of all possible isolated and associated intrinsic defects as a function of the chemical potential (reflecting T and pressure-dependent growth conditions such as Fe-rich/S-poor) (Figure

From TGA measurements, we find that Fe_2GeS_4 and Fe_2SiS_4 begin to lose mass only above 725 and 1000 °C, respectively. The former mass loss corresponds to the volatilization of GeS_2, while the latter is correlated with the volatilization of SiS_2. The formation of Fe_2GeS_4 thin films by sputtering is confirmed by X-ray diffraction (Figure S3) and electron-probe microanalysis (S/Fe = 1.96, Ge/Fe = 0.51). They exhibit a resistivity of 2.3 kΩ cm and -type majority carriers. This resistivity is similar to that measured on single crystals, . ., 840 Ω cm, where a carrier concentration of 5×10^{18} cm^{-3} is estimated from the measured Seebeck coefficient of +750 μV/K.[24] Unlike FeS_2, the characteristics of the bulk powders and thin films are equivalent, and they support the calculations with respect to phase stability. The ternary compounds do not readily decompose into S-deficient binary phases. This material choice then satisfies the new design principle.

A ? The band structure for Fe_2SiS_4 (Figure 4a) reveals a valence band dominated by S character and a conduction band dominated by Fe character. The direct gaps calculated for Fe_2SiS_4 and Fe_2GeS_4 are 1.55 and 1.40 eV, respectively. These values compare well to the direct gaps, 1.54 and 1.36 eV (Figure 4b), measured by diffuse reflectance from pressed pellets of Fe_2SiS_4 and Fe_2GeS_4, respectively. An equivalent gap is observed for the Fe_2GeS_4 thin film (Figure S4). All of these band gaps are more than 0.4 eV greater than FeS_2, providing considerable advantages with respect to absorption of the solar spectrum.[25

understanding the material as a potential photovoltaic absorber. We find from calculations and experimental observations that S deficiencies are a common trait of FeS_2, but they are manifest through coexistence of secondary phases rather than bulk S vacancies in FeS_2. We learn from these findings that deposition of thin films will be a particularly challenging problem. Approaches that rely on high-temperature sintering of high surface -area nanoparticles, for example, are especially problematic.

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