

# Defect adamantines: potential materials for photovoltaic applications

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Compounds of the Adamantine family includes kesterite ( $\text{Cu}_2\text{ZnSnS}_4$ ), currently the most promising material for fully inorganic thin film photovoltaic technology that is free of critical raw-materials and thus provides sustainable solutions.

Ternary adamantines like the chalcopyrites can be transferred by chemical substitution to a quaternary adamantine such as  $\text{A}^{\text{I}}_2\text{B}^{\text{II}}\text{C}^{\text{IV}}\text{X}^{\text{VI}}_4$  (e.g.,  $\text{Cu}_2\text{ZnSnS}_4$ ) and  $\text{A}^{\text{I}}\text{B}^{\text{III}}\text{C}^{\text{IV}}\text{X}^{\text{VI}}_4$  compounds, the latter are called defect adamantines (Pamplin 1981).

Defect adamantines like  $\text{Cu}\square\text{GaGeS}_4$  and  $\text{Cu}\square\text{GaSnS}_4$  can be seen as a compound within the solid solution between gallite – radvaniceite (Sejkora et al. 2022),  $(\text{CuGaS}_2)_{1-x}(\text{GeS}_2)_x$  and gallite – berndtite  $(\text{CuGaS}_2)_{1-x}(\text{SnS}_2)_x$ , at  $x = 0.5$ , respectively.

Single crystals of these defect adamantines were grown by chemical vapor transport using iodine as transport agent. Aiming for chemical compositions according to the defect adamantine, chemical analysis of the grown crystals by X-ray fluorescence (XRF) has shown, that crystals in the system  $(\text{CuGaS}_2)_{1-x}(\text{GeS}_2)_x$  show  $\text{Cu}/(\text{Ga}+\text{Ge})$  ratios between 0.45 and 0.9 as well as  $\text{Ge}/(\text{Ga}+\text{Ge})$  ratios between 0.15 and 0.6. Thus the single crystals show a quite strong deviation from the stoichiometric composition ( $\text{Cu}/(\text{Ga}+\text{Ge}) = \text{Ge}/(\text{Ga}+\text{Ge}) = 0.5$ ). We explain this behavior by the flexibility of the crystal structure of the end members and the defect adamantine. Their crystal structures are based on a corner-sharing network of tetrahedra ( $\text{CuS}_4$ ,  $\text{GaS}_4$ ,  $\text{GeS}_4$  or  $\square\text{S}_4$ ). By multiple energy anomalous synchrotron X-ray diffraction (MEAD) it was shown, that  $\text{Cu}\square\text{GaGeS}_4$  crystallizes in the tetragonal chalcopyrite-type structure. It compares to the crystal structure of gallite, but with a higher fraction of vacancies.

The single crystals grown aiming for  $\text{Cu}\square\text{GaSnS}_4$  adopt the chalcopyrite-type structure and the  $\text{Cu}/(\text{Ga}+\text{Sn})$  values are close to 1. Thus there is only a very limited solubility in the  $(\text{CuGaS}_2)_{1-x}(\text{SnS}_2)_x$  system. Berndtite ( $\text{SnS}_2$ ) crystallizes in a trigonal structure type where the  $\text{Sn}^{4+}$  cations are coordinated by 8 sulfur anions. The very limited solubility between Gallite and Berndtite may be explained by the different coordination of the four-valent cation.

The band gap energy (determined by UV-Vis spectroscopy) of the mixed crystals in the  $(\text{CuGaS}_2)_{1-x}(\text{GeS}_2)_x$  system cover a range of 2.1 to 2.4 eV, showing a strong bowing behavior in the dependency on the chemical composition parameter  $x$ . The crystals obtained in the system  $(\text{CuGaS}_2)_{1-x}(\text{SnS}_2)_x$  have band gap energies within 1.7 and 2.0 eV. Thus, such defect adamantines are interesting materials for photovoltaic applications.



Figure 1. Single crystals of off-stoichiometric  $\text{Cu}\square\text{GaGeS}_4$  (left) and  $\text{Cu}\square\text{GaSnS}_4$  (right).

Pamplin B (1981): The adamantine family of compounds. - Prog Cryst Growth Charact 3, 179

Sejkora J (2022): Radvaniceite,  $\text{GeS}_2$ , a new germanium sulphide, from the Kateřina Mine, Radvanice near Trutnov, Czech Republic. – Minerals 12, 222