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Sulfosalts — A new class of compound semiconductors for photovoltaic applications

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Abstract

A short historical outline of sulfosalts with respect to their mineralogical origin and their possible technical applications is given. The high number of more than 200 species results from their chemical and structural definition. The modular crystal structures of sulfosalt compounds base on superstructures of diverse construction units. Physical properties of mineral samples as well as deposited thin films show promising results with respect to photovoltaic application. As a proof of concept, first sulfosalt thin film solar cells were prepared. The efficiency of this cell is reported to be 1%. Further efforts will be done to improve efficiency.

Keywords: Sulfosalts; Structural properties; Physical properties; Thin film deposition; Solar cells

1. Introduction

Sulfosalts are well known mineral species since those days, when they where highly respected for their silver content in medieval mining activities on hydrothermal vein deposits all over the world. They do occur not only in vein deposits, but also in "black and white smokers" on tectonical active ocean floor regions and in exhalative deposits correlated to active volcanism. They are even considered to be responsible for low radar emissivities on Venus observed by Magellan and Pioneer Venus missions [1]. Many classical ore deposits have yielded a large variety of sulfosalt mineral phases. The actual number of sulfosalt mineral species has crossed the 200 mark. Many of these minerals are widespread in sulphide ore deposits — some of them being quite rare. Up till now, the technical importance of sulfosalts is mostly restricted to being a raw material carrier with respect to silver, tin, lead, copper, sulphur, selenium and other elements.

To a large extent, the basic scientific research work on sulfosalts has focussed on thermodynamic properties and crystal structures for mineralogical classification.

The knowledge about their electronic properties is extremely scarce. Since Shuey [2] who mentioned only 4 representatives of the sulfosalts, until the detailed Landolt–Börnstein tables [3], the total number of publications is marginal. Semiconducting band-gaps of sulfosalts were reported by Lomelino et al. [4], Boldish et al. [5], and Dittrich et al. [6–8].

Application oriented research work was reported in the fields of phase change memory devices [9], thermoelectric energy conversion applications [10], X-ray detectors [11], and thin film solar cells [12].

2. Definition of sulfosalts

The basic chemical definition of the sulfosalt minerals can be given as ternary compounds of 4th and 5th main group elements with chalcogens of the 6th main group in the periodic system (in principle: IV-V-VI compounds). The occurrence in nature (under ambient conditions) indicates thermodynamic stability. Additional transition metals can be introduced by coupled isoelectronic substitution leading to quaternary and more complex multinary compounds. A formal definition can be given by:

$$\mathbf{A}_x\mathbf{B}_y\mathbf{C}_z$$

with:

A = Cu^{1+}, Ag^{1+}, Pb^{2+}, Sn^{2+}, Sn^{4+}, Fe^{2+}, Mn^{2+}, Hg^{2+}, Tl^{1+}... (in synthetic material also alkali and alkaline earth metals, and lanthanides)
B = As^{3+}, Sb^{3+}, Bi^{3+} (formal 3-valent cations in non-planar 3-fold coordination, occasionally also Te^{4+})
C = S^{2-}, Se^{2-}, Te^{2-}

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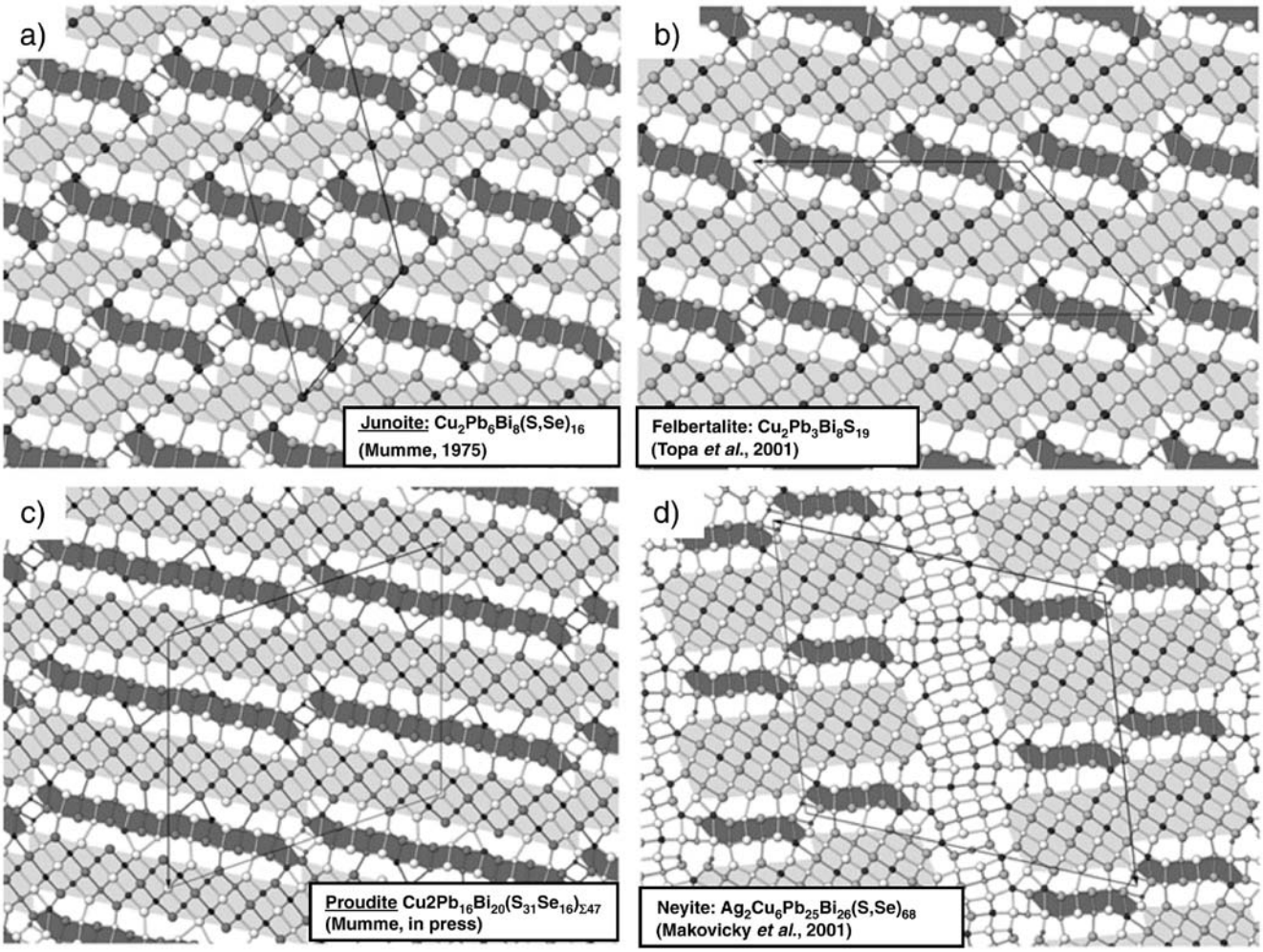

Fig. 1. Demonstration of the modular construction of sulfosalt crystal structures by (i) variable unit dimensions, (ii) connectivity of units, and (iii) combination of units (for detailed explanation see text).

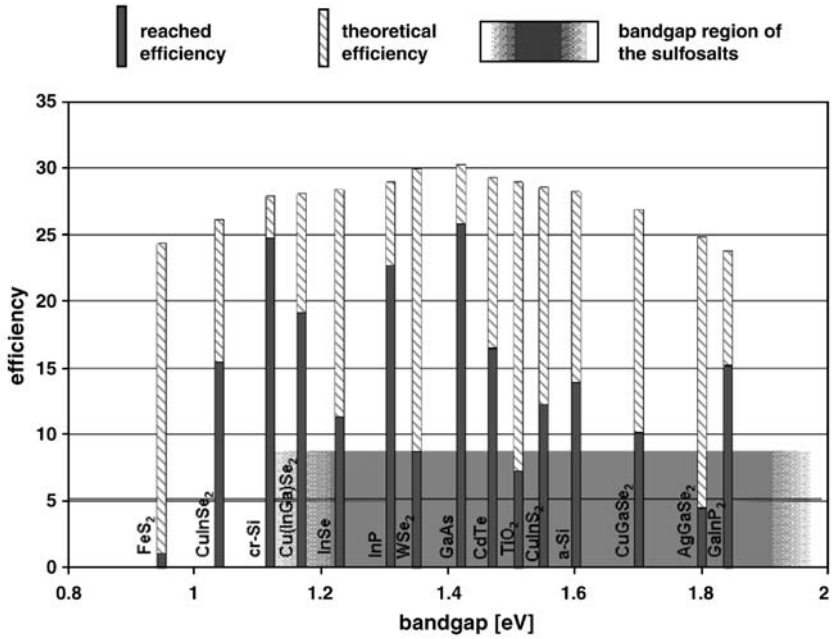

Fig. 2. Bandgap region of sulfosalts compared to standard photovoltaic materials.