

Research Article

The Lattice Compatibility Theory: Arguments for Recorded I-III-O₂ Ternary Oxide Ceramics Instability at Low Temperatures beside Ternary Telluride and Sulphide Ceramics

K. Boubaker

École Supérieure de Sciences et Techniques de Tunis (ESSTT), Université de Tunis, 63 Rue Sidi Jabeur, 5100 Mahdia, Tunisia

Correspondence should be addressed to K. Boubaker; mmbb11112000@yahoo.fr

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Some recorded behaviours differences between chalcopyrite ternary oxide ceramics and telluride and sulphides are investigated in the framework of the recently proposed Lattice Compatibility Theory (LCT). Alterations have been evaluated in terms of Urbach tailing and atomic valence shell electrons orbital eigenvalues, which were calculated through several approximations. The aim of the study was mainly an attempt to explain the intriguing problem of difficulties of elaborating chalcopyrite ternary oxide ceramics (I-III-O₂) at relatively low temperatures under conditions which allowed crystallization of ternary telluride and sulphides.

1. Introduction

I-III-VI₂ ternary ceramics are attractive materials in possible photovoltaic and optoelectronic applications [1–9] like coating films for IR reflection, smart windows, functional glasses, transparent electrodes in flat panel displays, and solar cells [10, 11]. During the last two decades, p-type ternary transparent conducting oxide ceramics, like CuAlO₂, CuInO₂, AgAlO₂, and ZnAlO₂, have attracted more and more attention for their high absorption coefficient as well as their band gap energy (1.8–3.5 eV). Currently, many experimental efforts are underway to search for new p-type TCOs. In 1997, Kawazoe et al. [12] elaborated p-type CuAlO₂ films resistivity of 10.5 Ω cm, which is ten times less than that of typical ZnO [13], the most available candidate for similar applications.

p-type Cu-Al-O-like ceramics have been prepared by several techniques. Pulsed laser deposition [14], sputtering [15], more information of these two techniques will be introduced in the following sections.

In our laboratories, we tried to elaborate Cu-Al-O-like ceramics using wet techniques (Spray, vaporization, etc.) at relatively low temperatures (300–450°C). After hundreds of attempts, we came to the conclusion that such temperature

ranges are not suitable but for elaborating ternary oxides. Dlala et al. [16], succeeded to stabilize Ag₂S thin films; Amlouk et al. [17] elaborated SnO₂:F and CdS airless sprayed layers Khélia et al. [18], Kamoun et al. [19], and Amlouk et al. [20] fabricated and characterized β-SnS₂ and β-In_{2-x}Al_xS₃ compounds at low temperatures. Binary sulphide compounds such as Ag₂S, Cu₂S, SnS₂, and In₂S₃ have been obtained in our laboratory in 200–320°C domain of temperature. Later, ternary sulphide compounds based on copper and silver which generally crystallized in chalcopyrite structure I-III-VI₂ (CuInS₂, AgInS₂, AgInS_{2-x}Se_x) were prepared, by Guezmir et al. [21], Kamoun et al. [22, 23], Aissa [24, 25], and Lazzez et al. [26], in substrate temperature lying in 340–420°C. Finally, Bouaziz et al. [27, 28] obtained Cu₂SnS₃ and Cu₃SnS₄ ternary compounds in 300–400°C domain.

The subject of this paper is an attempt to explain, starting from experimental facts, why was it impossible to stabilize ternary oxides under humid condition below 450°C, while both binary and ternary sulphides were easily obtained. This paper is arranged as follows. In Section 2, we present some experimental details concerning ternary oxide ceramics fabrication. In Section 3, the fundamentals of the lattice Compatibility Theory (LCT) are presented as

a plausible explanation to ternary oxide ceramics unexpected instability at low temperatures. Conclusion will be appeared in Section 4.

2. Experimental Details

CuAlS₂ thin films ceramics have been deposited on glass substrates using chemical bath deposition CBD technique with CuSO₄, (NH₂)₂SC and hydrated Al₂(SO₄)₃ as precursors. Commercial solutions of 0.10 M CuSO₄(NH₂)₂, and 1.0 M (NH₂)₂SC, 0.1 M Al₂(SO₄)₃·14H₂O were used. A primal solution of CuSO₄(NH₂)₂ with an excess triethanolamine was stirred for few minutes until colour changed, before adding a stirred Al₂(SO₄)₃ solution. Substrate slides were finally immersed in the obtained dark orange black solution for 22 hours. Removal of the slides was carried out at room temperature and was followed by a few rinsing-drying stages. CuAlTe₂ layers have been synthesized by annealing, under vacuum in an argon-rich medium, a multilayer structure of thin Cu, Al, and Te layers which were deposited by evaporation. A mixture of pure copper, aluminium, and tellurium weighed in stoichiometric ratios was sealed in a vacuum quartz tube. The tube was subjected to several 35 h annealing stages. CuAlTe₂ layers were consecutively grown by the evaporation of the obtained powder under vacuum. More details about experimental procedure can be found elsewhere [21, 23, 24, 26–28]. Similar techniques and disposals have been used in order to synthesize CuAlO₂. A wide variety of precursors, including mineral CuFeO₂, high-purity CuO, Al₂O₃, and metallic Aluminium have been tried unsuccessfully in our laboratories, particularly at temperatures beyond 450°C.

3. Oxygen Beside Sulfur-Like Structural Disparity

3.1. Atomic Scale Patterns. In order to explain the mentioned paradox (Section 2), a quick comparative review of oxygen-sulfur properties is needed. While both elements have the same valence, oxygen electronegativity is 3.44, less than that of sulfur (2.58). Some other differences can be outlined:

- (i) O=O double bonds are stronger than S=S.
- (ii) S–S single bonds are almost twice as strong as O–O.
- (iii) Sulfur can expand its valence shell to hold more eight to twelve electrons.

The last difference has been illustrated by Carelli et al. [29] who stated that in combined media, “sulfur can expand its valence shell to produce a soft nucleophilic center” which refers to the so-called S-nucleophilicity. This property, accounts, in the case of I-III-O₂ and I-III-S₂ compounds for the ability of sulfur to expand its valence shell from 8 to 10 or 12 electrons using its available 3d orbitals, allowing oxidation states not available to its oxygen analogs (Figure 1).

Moreover, opposite to Cu–O bonding patterns, which obey a simple oxidation state formalism, Cu–S bonding systems have a high degree of delocalization resulting in additional electronic band structures (Figure 1) and are hence covalent rather than ionic.

Moreover, calculation of atomic valence shell electrons orbital eigenvalues for sulfur, oxygen, and tellurium in delafossite structures confirms this delocalization plausibility. Orbital eigenvalues were calculated through local density (LDA) [30] and scalar-relativistic local density (ScRLD) [31] approximations using OPIUM code [32, 33]. In the first approach, the many-electron configuration is approximated by a set of single-particle equations while the second takes into account some of the effects of relativity, such as Darwin shift and mass-velocity term.

Table 1 gathers atomic orbital eigenvalues (in eV) for oxygen, sulfur, and tellurium according to (LDA) and (ScRLD) approximations.

According to (LDA) and (ScRLD) calculations, most of Tellurium bonding in the valence region is accomplished by the 5p orbitals. The in-plane locally π -type 5p orbitals (Figure 2) form a narrowband between -0.2 and -0.3 eV, which is far below the Fermi energy. This range confirms the diffuse character of tellurium p-orbitals, which also confers to the lattice a covalent rather than ionic aspect.

(Figure 3) shows the two-dimensional arrangement with Cu⁺ ions located between layers of B^{III}O₂ octahedra. The structure is characterized by alternating layers of slightly distorted edge-shared B^{III}O₂ (or B^{III}S₂) octahedra sandwiching planes of close-packed A⁺ cations (here Cu⁺) in linear or “dumbbell” coordination to oxygen anions in the adjacent octahedra.

The difference in length between Cu–O and Cu–S bonds (24%) has been ascribed to the electrons being shifted to the orbital 3d. All these observations plea on favor of the presence of a delocalized valence “hole” favorizing natural bonding between two opposed octahedra planes (Figure 3) at low temperatures. If we consider the results of Liang et al. [34, 35], which stated that the Cu–Cu bonding character was very weak in such structures, we can conclude that the crystalline behavior of A^IB^{III}O₂ (Figure 3) and A^IB^{III}S₂ lattices depends mainly on is the status of A⁺ ion (here Copper). According to Landolt-Börnstein [36–38] and Greenwood and Earnshaw [39], any formulation of copper monosulphide as Cu^{II}S with no meaningful S–S bonds is incompatible both with the crystal structure, and the observed diamagnetism as a Cu(II) compound would have a d⁹ configuration and be expected to be paramagnetic. An alternative formulation as (Cu⁺)₃(S²⁻)(S₂)⁻ was proposed and supported by other studies.

3.2. Urbach Energy and Lattice Compatibility Theory (LCT) Consideration. An additional argument can also be formulated through the recently proposed Urbach energy-related Lattice Compatibility Theory (LCT) [40–42]. Urbach energy E_u has been determined, for the ternary oxides and telluride and sulphides samples through the equations:

$$\begin{aligned} \ln(\alpha(h\nu)) &= \ln(\alpha_0) + \frac{h\nu}{E_u}, \\ E_u &= \alpha(h\nu) \left(\frac{d[\alpha(h\nu)]}{d[h\nu]} \right)^{-1} = h \left[\frac{d}{d\nu} (\ln\alpha(\nu)) \right]^{-1}, \end{aligned} \quad (1)$$

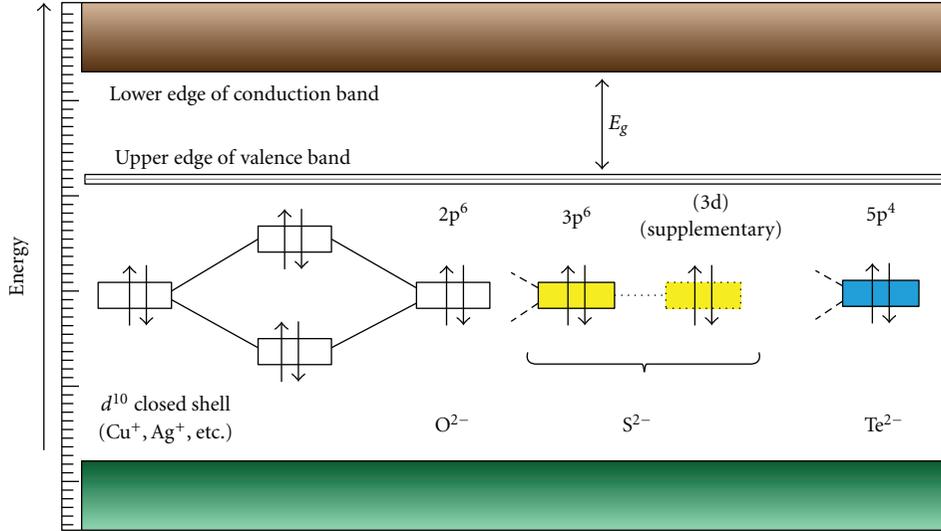
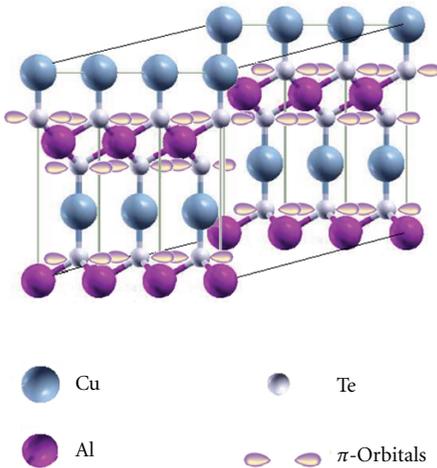


FIGURE 1: Sulfur-oxygen-tellurium different outer shell configuration inside a Cu-like combination.

TABLE 1: Atomic orbital eigenvalues (in eV) for oxygen, sulfur, and tellurium.

Oxygen Structure: [He] 2s ² 2p ⁴			Sulfur Structure: [Ne] 3s ² 3p ⁴			Tellurium Structure: [Kr] 4d ¹⁰ 5s ² 5p ⁴		
Orbital	LDA	ScRLD	Orbital	LDA	ScRLD	Orbital	LDA	ScRLD
1s	-18.7582	-18.7585	1s	-87.78993	-87.94937	4s	-5.57284	-6.00853
2s	-0.87136	-0.87246	2s	-7.69994	-7.737587	4p	-4.10008	-4.19056
2p	-0.33838	-0.33816	2p	-5.75125	-5.749477	4d	-1.60838	-1.53477
			3s	-0.63091	-0.634502	5s	-0.52099	-0.56288
			3p	-0.261676	-0.261260	5p	-0.22659	-0.22459

FIGURE 2: CuAlTe₂ ceramics crystal structure.

where $\alpha(h\nu)$ represents, for each sample, the experimentally deduced optical absorption profile.

Urbach energy E_u has been defined as an aggregated for the evaluating of the intrinsic disorder and atomic scale

dispersion inside structures as it indicates the width of the band tails of the localized states in presence of defects. The width of the localized states (band tail energy or Urbach energy E_u) has been estimated from the slopes of the plots of $(\ln \alpha(h\nu))$ versus energy $h\nu$ (Figure 4).

It can be noticed that the atomic-scale intrinsic disorder is higher in CuAlS₂ and CuAlTe₂ than in films, and disposals have been used in order to synthesize CuAlO₂ matrices. This result is in good agreement with the precedent analyses and with the fundamentals of the Lattice Compatibility Theory (LCT) [40–42].

Finally, additional investigation should be carried out in order to explain the need of calcination (at 1200°C [43], 800°C [44], and 900°C [45]), as an avoidable step for establishing A^IB^{III}O₂ stable structures, while A^IB^{III}S₂ are autostabilized at low temperatures apparently, thanks to the above-described valence “hole.”

4. Conclusion

In this study, we tried to give some explanation to the intriguing problem of the impossibility of elaborating chalcopyrite ternary oxide ceramics (I-III-O₂) at relatively low temperatures in wet media. Contrast has been highlighted with regard to ternary telluride and sulphide ceramics.

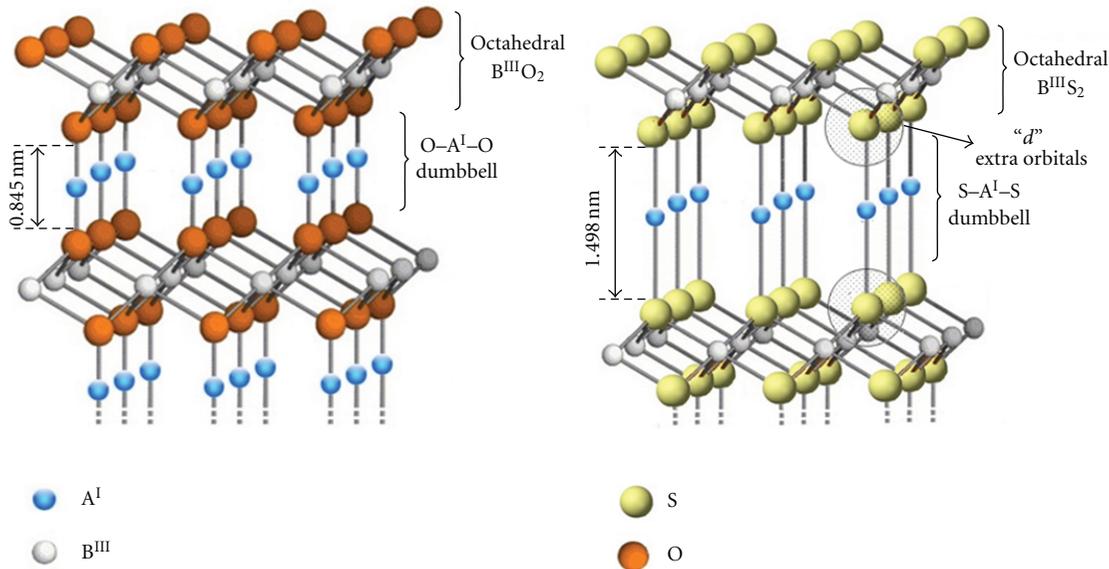


FIGURE 3: $A^I B^III S_2$ and $A^I B^III O_2$ ceramics Delafossite type structure (with additional sulfur orbitals).

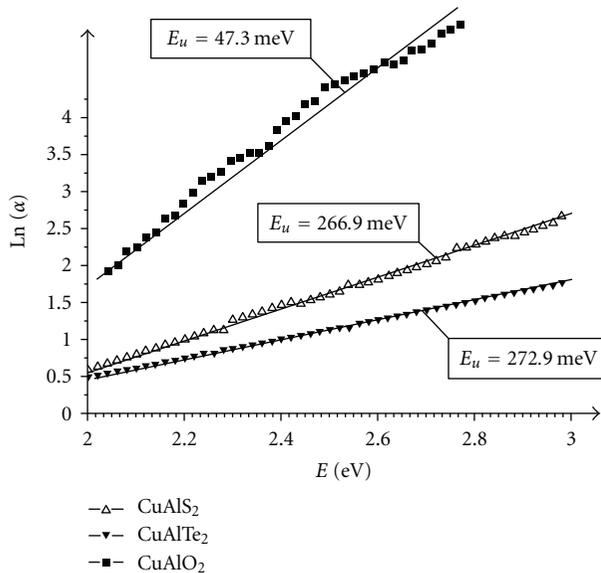


FIGURE 4: Plots of $(\text{Ln} \alpha(v))$ versus energy $h\nu$ (as guides for evaluating E_u).

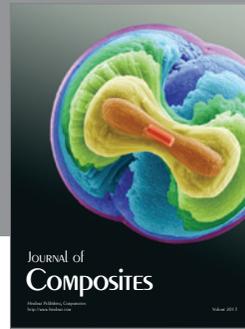
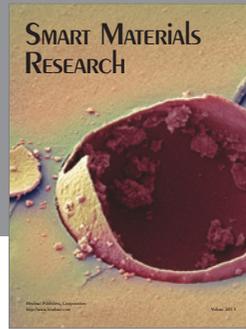
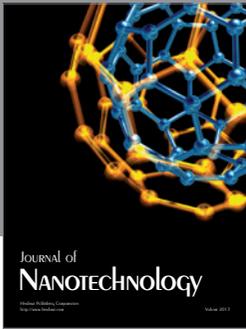
An attempt to explain this paradox has been formulated in terms of particularities of $A^I B^III O_2$ and $A^I B^III S_2$ ceramics delafossite structure and bonding interaction.

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