

Point defects and transport mechanisms in transparent conducting oxides of intermediate conductivity

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Abstract

The layered delafossite structure *p*-type transparent conducting oxides (TCOs) and the mayenite cage-structure *n*-type transparent conducting oxides represent enabling materials for novel technological applications. In the present work, isovalent replacement of the delafossite B-site cation (i.e., B=Sc and Y for Al in CuBO₂) and isovalent substitution of the mayenite Ca-cations by Mg in C₁₂A₇ (12CaO·7Al₂O₃) were undertaken to probe the conduction mechanisms and defect structures of these novel materials. Both classes of materials exhibit small polaron conduction with comparable activation energies and conductivities. In the delafossites, increasing B-cation radius increases the hopping energy without changing the pre-exponential factors. An upper limit for mobility is estimated at ~1 cm² V⁻¹ s⁻¹ for these materials. In terms of carrier generation mechanisms, there is a changeover from aluminum anti-site/oxygen interstitial associates in CuAlO₂ to oxygen interstitials in CuScO₂ and CuYO₂. In Mg-doped mayenite, substitution produces no change in activation energy but a precipitous drop in the pre-exponential factor. This behavior is linked to magnesium ions blocking critical conduction paths in the mayenite structure.

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1. Introduction

The recent discoveries of *p*-type transparent conducting oxides (TCOs) [1] and UV light-activated *n*-type TCOs [2] represent enabling materials for novel technological applications. For example, the development of a *p*-type TCO with properties (especially mobility) comparable to the best *n*-type TCOs, such as tin oxide and indium-tin oxide (ITO), would enable all-oxide and all-transparent electronics and optoelectronics [3]. Additionally, a high-mobility UV light-activated TCO would enable direct writing of conducting lines and semiconductor elements, with potential for invisible-circuit technology, high-density optical recording, etc. [2].

The materials of interest in this study have quite different crystal structures, but share common features in terms of their conduction mechanism. The delafossite ABO₂ structure (Fig. 1) is comprised of alternating layers of slightly distorted edge-shared B³⁺ O₆ octahedra sandwiching two-dimensional close-packed A-cation planes forming linear O–A¹⁺–O “dumbbells” [4,5]. Two types of stacking are possible, the 2H polytype (P6₃/mmc, No. 194) with AaBbAaBb stacking and the 3R polytype (R $\bar{3}$ m, No. 166) with AaBbCcAaBbCc stacking (as shown in Fig. 1). The mayenite C₁₂A₇ structure (Fig. 2) is comprised of 12 cages (2 formula units) per unit cell [6–8]. Two of the cages are displayed in Fig. 2. Its empirical formula can be expressed as [Ca₂₄Al₂₈O₆₄]⁴⁺+2O²⁻. The two “free oxygens”, which are necessary for charge neutrality, are found in two out of the 12 cages per unit cell (as in Fig. 2b). The positively charged cages (without free oxygen, Fig. 2a) and negatively charged cages (with free oxygen, Fig. 2b) are believed to be essential for the hydrogen dissociation and doping of this

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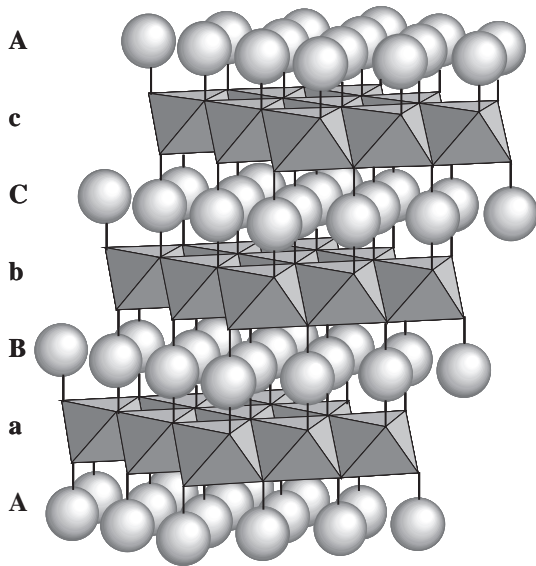


Fig. 1. The delafossite structure ($R\bar{3}m$, No. 166) having alternating layers of Cu^{+1} (shaded spheres) and distorted BO_6 edge-shared octahedral (shaded polygons) along the c -axis.

material (see below). In spite of their disparate crystal structures, both systems share common features insofar as transport is concerned. Both exhibit variable range hopping at low temperatures (i.e., below room temperature) [1,2] and small polaron conduction at higher temperatures (see below). As a result, electronic mobility in both classes of materials is limited ($<1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and conductivities are in an intermediate range (10^{-2} to 10^1 S/cm) between insulating transparent oxides and conventional n -type TCOs ($>10^3 \text{ S/cm}$).

The present study employed isovalent replacement of the B-cation in CuBO_2 ($\text{B}=\text{Sc}$ and Y for Al) and isovalent substitution of Ca-cations in C_{12}A_7 by Mg to probe both the transport mechanisms and carrier generation processes in these important materials. In the case of the delafossite structure (Fig. 1), it is well known that the c -axis length is governed by the A-cation size or the Cu-cation in the copper-based delafossites. On the other hand, the a -axis length and thus the Cu–Cu spacing is governed by the B-cation size. These structural features modify the wave function overlap between Cu species, and thereby the activation energy for hopping. Furthermore, a changeover in prevailing point defect mechanisms is presented. In the case of the mayenite structure (Fig. 2), recent first-principles electronic structure calculations suggest that Mg is an effective “killer” for hopping conduction via Ca-sites in cages involved in the conduction path; the band structure of $\text{Ca}_{12-x}\text{Mg}_x\text{Al}_{14}\text{O}_{33}$ ($x=1$) was found to be that of an insulator [9]. Systematic replacement of Ca by Mg allows us to probe the conduction path in this UV light-activated material. Although the present work pertains to bulk ceramics, the lessons learned are equally applicable for film growth and optimization.

2. Experimental

Bulk delafossite specimens were made by conventional high-temperature solid-state reaction of ultrapure oxides (Aldrich Chemical, USA; 99.99–99.999%). In the case of CuAlO_2 and CuScO_2 , copper (I) oxide was found to be a suitable copper source; in the case of CuYO_2 , copper (II) oxide provided better results. Component oxides were dried at 400°C and stored in a desiccator prior to mixing. Stoichiometric quantities were mixed in agate mortar and pestle under acetone, dried, and pressed into pellets at 175–400 MPa. Pellets were surrounded by a sacrificial powder of the same nominal composition to prevent any reaction with the alumina crucibles employed. Firing took place at 1100°C (1373 K) (CuAlO_2 and CuScO_2) in air for 24–36 h, followed by air-quenching. This process was repeated, with intermediate re-grinding and pelletizing, until the product was phase-pure by X-ray diffraction (XRD). In the case of CuYO_2 , the initial firing took place at 1000°C (1273 K) in air for 24 h to form the intermediate phase, $\text{Cu}_2\text{Y}_2\text{O}_5$. This step proved necessary owing to the sluggish rate of delafossite formation from the constituent oxides. The $\text{Cu}_2\text{Y}_2\text{O}_5$ phase was subsequently reduced to delafossite at 1000°C under flowing Ar, again with multiple re-grinding and firing steps (24–36 h). The Sc- and Y-specimens

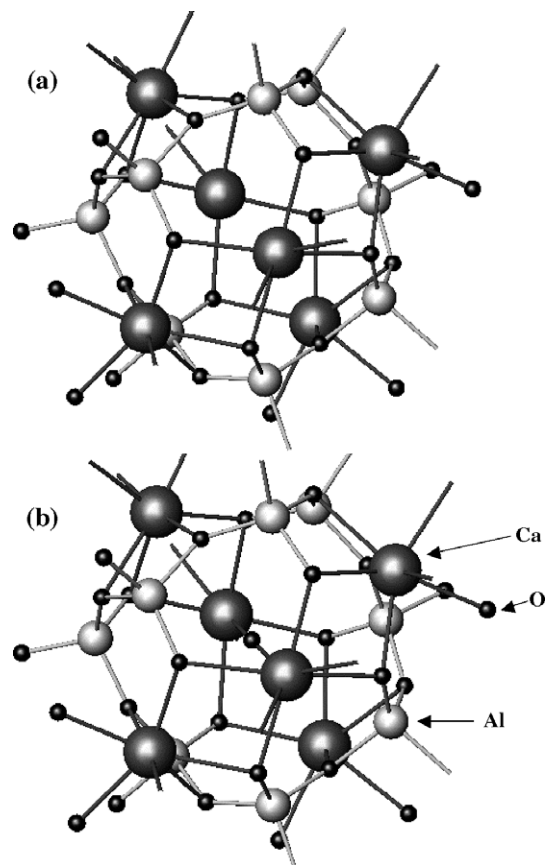


Fig. 2. The cage structure of mayenite C_{12}A_7 ($[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} + 2\text{O}^{2-}$) is shown. (a) A positively charged cage. (b) A negatively charged cage including a free O^{2-} ion.

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