

Structural Investigations of CA and CA₂ by Energy-Loss Near-Edge Spectrometry and *Ab Initio* Calculations

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While the five mixed-oxide compounds that form in the CaO-Al₂O₃ system initially received attention for their roles in the cement industry, in recent years they have been recognized as candidates for optical [1] and electronic applications [2]. For example, CaAl₂O₄ (CaO·Al₂O₃, CA) glasses have infrared (IR) transmission similar to sapphire and are photosensitive to ultraviolet radiation; C₁₂A₇ with incorporated H- (C₁₂A₇:H) can be converted from an electrical insulator into an electrical conductor by illumination with UV light [2]. Despite the growing technological importance of calcium aluminate phases, there are very few studies in the literature on their crystallographic and electronic structure. In the present study, the Al-L_{2,3}, O-K and Ca-L_{2,3} energy-loss near-edge structure (ELNES) were measured experimentally for CA and CA₂ and compared with the calculated near-edge structures to obtain local symmetry fingerprints of the crystals.

A polymerized organic-inorganic complex route was used to synthesize pure crystalline CA and CA₂ powders [3]. These powders were crushed in pure ether and placed on a holey carbon film on a TEM grid. ELNES spectra were collected using a Gatan imaging filter (Gatan GIF 200) attached to a TEM operated at 200kV (FEI Tecnai F20 G2 FEG). The electronic structure of CA and CA₂ were calculated using the method of orthogonalized linear combinations of atomic orbitals (OLCAO), including the core-hole interactions [4]. The calculated edges are the weighted sum of the calculated spectra from crystallographically non-equivalent sites.

FIG.1 shows both calculated and experimentally measured Al-L_{2,3} and O-K edges from the CA₂ powders. It also includes the same edges taken from the CA powders and from a single-crystal α-Al₂O₃ sample. A power law fit was used to subtract the background from the Al-L_{2,3} and the O-K edges. All the spectra were aligned in energy scale with respect to their zero loss peaks (ZLPs).

The Al-L_{2,3} near-edge structures of CA and CA₂ show several distinct features as can be seen in FIG.1(a). While CA has 6 different locations for Al atoms, CA₂ has only 2 different locations for Al. All the Al atoms in both compounds have tetrahedral coordination. Therefore, the Al-L_{2,3} near-edge structures of these compounds are very similar to each other and very different than the Al-L_{2,3} near-edge structure of α-Al₂O₃ which contain only octahedrally coordinated Al atoms. The O-K near-edge structures of CA and CA₂ reveal several different features which indicate O sites with different coordinations. The O-K edge of α-Al₂O₃ shows a broad first peak and several smaller peaks at higher energies. For both Al-L_{2,3} and O-K edges, calculated near-edge structures of CA₂ are in good agreement with the experimentally measured ones.

Although the initial observations from two different compounds in CaO-Al₂O₃ system are reported here, the detailed analysis and calculations is being applied to each of the compounds present in this system. The promising match between the calculated and experimental spectra will provide an improved understanding of the origins of the various features in the experimental spectra which will then allow symmetry fingerprints of these compounds to be established.

[1] Wallenberger F. T., Weston N. E., and Dunn S. A. *J. Non-Cryst. Solids*, **124** (1990) 116-119.

[2] Hayashi K., Matsuiishi S., Kamiya T., Hirano M., and Hosono H. *Nature*, **419** (2002) 462-465.

[3] Gulgun M. A., Nguyen M. H., and Kriven W. M. *J. Am. Ceram. Soc.*, **82** (1999) 556-660.

[4] Mo S.-D. and Ching W.-Y. *Phys. Rev. B*, **62** (2000) 7901-7907.

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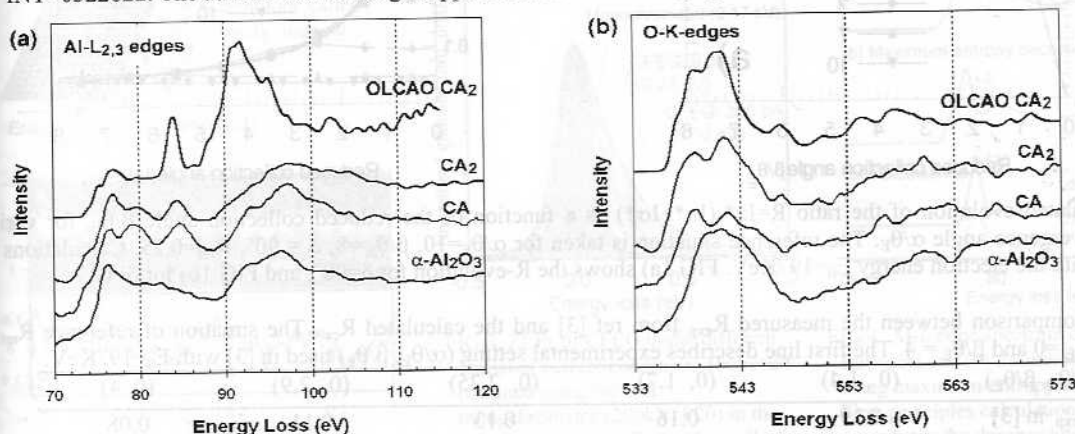


FIG. 1. Calculated (OLCAO) near-edge structure from CA₂ and experimental near-edge structures from CA and CA₂ powders and from α-Al₂O₃ single crystal. a) Al-L_{2,3} edges and b) O-K spectra edges.