



Characterizing CA_2 and CA_6 using ELNES

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ARTICLE INFO

Article history:

Received 29 December 2008

Received in revised form

20 April 2010

Accepted 22 May 2010

Available online 27 May 2010

Keywords:

Calcium aluminates

ELNES

STEM

TEM

Ab initio calculations

EELS

X-ray diffraction

ABSTRACT

Calcium aluminates, compounds in the $CaO-Al_2O_3$ phase system, are used in high-temperature cements and refractory oxides and have wide range of potential technological applications due to their interesting optical, electrical, thermal, and mechanical properties. They are used in both crystalline and glassy form; the glass is an isotropic material while the crystalline materials may be highly anisotropic. This paper will consider two particular crystalline materials, CA_2 and CA_6 , but the results should be applicable to all calcium aluminates. Although CA_2 and CA_6 crystals contain the same chemical species, Ca, Al, and O, the coordination and local environments of these species are different in the two structures and hence they show very different energy-loss near-edge structures (ELNES) when examined by electron energy-loss spectroscopy (EELS) in the TEM. The data obtained using ELNES can effectively provide a fingerprint for each compound and a map for their electronic structure. Once such fingerprints are obtained, they can be used to identify nano-sized particles/grains or material at interfaces and grain boundaries.

In the present study, the local symmetry fingerprints for CA_2 and CA_6 structures are reported combining experimental spectra with electronic-structure calculations that allow the different features in the spectra to be interpreted. Al- $L_{2,3}$ and O-K edge core-loss spectra from CA_2 and CA_6 were measured experimentally using electron energy-loss spectroscopy in a monochromated scanning transmission electron microscope. The near-edge structures were calculated for the different phases using the orthogonalized linear combination of atomic-orbitals method, and took account of core-hole interactions. It is shown that CA_2 and CA_6 structures exhibit distinctive experimental ELNES fingerprints so that these two phases can be separately identified even when present in small volumes.

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1. Introduction

Although the binary compounds of the $CaO-Al_2O_3$ system have long been used in high-temperature cements [1] and refractory oxides [2], they also have a wide range of potential technological applications due to their optical, electrical, thermal, and mechanical properties. Calcium aluminate glasses are attractive candidates for low-loss optical fibers [3]. They transmit electromagnetic radiation moderately far [4] into the infrared region (25% at $5.5 \mu m$ for a 2 mm optical path) [5] and they are photosensitive [6]. Crystalline $CaAl_4O_7$ ($CaO \cdot 2Al_2O_3$, CA_2) has a very low coefficient of thermal expansion ($1.2 \times 10^6 K^{-1}$ up to 372 K [7]) and thus, it has been used as a thermal-shock-resistant refractory material. Crystalline $CaAl_{12}O_{19}$ ($CaO \cdot 6Al_2O_3$, CA_6) [8] is

a known interface phase in fiber-reinforced ceramic-oxide composites that facilitates the fiber pull-out and improves the strength of the material [9]. Lacerda et al. [10] reported that $Ca_{12}Al_{14}O_{33}$ ($12CaO \cdot 7Al_2O_3$, $C_{12}A_7$) is an ion conductor at high temperatures. More recently, Hayashi et al. [11] reported that when hydrogen is incorporated, $C_{12}A_7$ can be converted from an electrical insulator into an electrical conductor by UV-light illumination.

Despite the growing technological importance of calcium aluminate phases, there have been a limited number of studies of their crystallographic and electronic structure. Early crystallographic investigations were carried out using various XRD techniques [12–17]. More recently, multinuclear solid-state NMR studies have reported the structure and atomic environment of these phases [18,19]. Undoubtedly, most illuminating studies of the electronic structure of calcium aluminates resulted from XANES were reported by Weigel et al. [20] and Henderson et al. [21] in the past few years using SGM beamline at the Canadian Light Source (CLS).

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It is not trivial to calculate the electronic structures of calcium aluminate phases theoretically due to the large and complicated structures of these phases. Previously, theoretical calculation of the electronic structure of CaAl_2O_4 (CA) has been reported [22]; however, until this study theoretical calculations of the electronic structures of CA_2 and CA_6 including the core–hole interactions have not been reported. In this paper, electron energy-loss spectroscopy in the TEM has been combined with calculations of the electronic structure to provide a method for identifying these phases when other techniques are problematic.

2. Materials and methods

2.1. Calcium di-aluminate (CaAl_4O_7 , $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$, CA_2)

The occurrence of $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ was initially reported by two independent studies in 1937 [23,24]. Goldsmith [25], and Gorla and Burdese [26] stated that CA_2 is monoclinic according to X-ray diffraction results, but Goldsmith's optical properties indicated that the compound should be either hexagonal or tetragonal. Filonenko and Laurov [27] reported that CA_2 crystallizes in the tetragonal state. Controversy over the exact crystal structure of the CA_2 was not resolved for many years. Boyko and Wisnyi [17] reported that CA_2 forms a monoclinic crystal with a space group C2/c ; Cockayne and Robertson [15] concluded that this phase is complex hexagonal. Goodwin and Lindop [16] confirmed the monoclinic structure and the results reported in that study are now the accepted crystal data for CA_2 . Structural data for CA_2 and the atomic positions in the crystal are listed in Tables 1 and 2, respectively.

2.2. Calcium hexa-aluminate ($\text{CaAl}_{12}\text{O}_{19}$, $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$, CA_6)

CA_6 is a stable aluminate found at the alumina-rich end of the binary phase diagram [28]. It also occurs in nature as the mineral hibonite. (Paul Hibon discovered the mineral in 1956 [29].)

The crystal structure of CA_6 was studied by Kato and Saalfeld [30], and confirmed to be isostructural with the mineral magnetoplumbite (MP) [12,31]. CA_6 belongs to the hexagonal space group $\text{P6}_3/\text{mmc}$ and can be represented symbolically as $\text{CaAlO}_3[\text{Al}_{11}\text{O}_{16}]$. The portion in brackets represents the spinel block and the remainder is the inter-spinel layer. In the CA_6 structure, the Ca ions are dodecahedrally (12-fold) coordinated in the inter-spinel layer. Al ions are distributed over three crystallographically independent octahedral sites, one tetrahedral site, and one bi-pyramidal site. The exact location of the Al atom in the trigonal bi-pyramidal site was first explained using the split-atom model [13] (see also [32]). It was shown that the Al^{3+} ion statistically occupies one of the two equivalent sites displaced from the mirror plane [13]. Structural data for the CA_6 crystal and the atomic positions with coordination values are given in Tables 3 and 4, respectively.

Table 1
Structural information for CA_2 [16].

Formula: $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$	Lattice parameters
Space group: C2/c	$a = 12.8398 \text{ \AA}$
Volume: 591.54 \AA^3	$b = 8.8624 \text{ \AA}$
No. of formula units/unit cell: 4	$c = 5.4311 \text{ \AA}$
Density: 2.915 g cm^{-3}	$\alpha = \gamma = 90^\circ, \beta = 106^\circ$

Table 2
Atomic positions for CA_2 [16].

Atom	Position (Wyckoff)	Coordination	x	y	z
Al(1)	8f	4	0.16410	0.08670	0.30300
Al(2)	8f	4	0.11980	0.44060	0.24100
Ca	4e	6 ^a	0	0.80910	0.25000
O(1)	4e	4 Al	0	0.52310	0.25000
O(2)	8f	2 Al+2 Ca	0.11550	0.05120	0.56590
O(3)	8f	2 Al+1 Ca	0.11850	0.25530	0.14910
O(4)	8f	3 Al	0.19240	0.44360	0.57970

^a Although the Ca coordination is known to be 7 in CA_2 crystal, based on the bond-length criteria used for the interpretation of the data in this study Ca coordination is listed as 6-fold.

Table 3
Structural information for CA_6 [13].

Formula: $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$	Lattice parameters
Space group: $\text{P6}_3/\text{mmc}$	$a = 5.5587 \text{ \AA}$
Volume: 585.83 \AA^3	$b = 21.8929 \text{ \AA}$
No. of formula units/unit cell: 2	$\alpha = \beta = 90^\circ$
Density: 3.79 g cm^{-3}	$\gamma = 120^\circ$

2.3. Structural investigations using ELNES

The low-energy portion of the electron energy-loss spectrum (EELS) is known by the acronym ELNES (energy-loss near-edge structure). ELNES is sensitive to the density of unoccupied states (DOS) above the Fermi energy (E_F) around the central atom [8,33–36]. The energy level of the unoccupied states is strongly influenced by the interaction of the central atom with its close neighbors. Therefore, ELNES can provide information about the structural and chemical properties of the atom undergoing excitation. It can thus be used as a probe of the bonding and nearest-neighbor coordination, and therefore the local symmetry [37,38]. These near edge structures are also sensitive to the valence state of the excited atom [39,40]. The combination of these information makes ELNES a technique that provides a fingerprint of a particular crystal structure.

An unsurpassed advantage of EELS/STEM combination over other analytical techniques is its sub-nanometer spatial resolution. This advantage allows the fingerprinting by the ELNES method in order to identify the structure of the small feature being probed by the STEM. The methodology behind this technique should be supported by both systematic measurements on suitable reference materials, and by electronic calculations [22,41]. This combination of experimental study and theoretical calculation which gives the fingerprint, can then help to identify the local bonding in unknown phases and can be associated with spatially localized structural features such as interfaces and defects [42,43].

When the ELNES fingerprints of two different coordinations of the same element have been determined, it is, in principle, possible to use these fingerprints to analyze compounds where both coordinations coexist and thus to determine the relative site occupancies via an algorithm or fitting procedure. This technique has mainly been applied to light elements to determine the proportion of sp^2 -bonded carbon atoms in amorphous diamond films [44,45] and the proportion of BO_3 and BO_4 groups in various compounds containing boron–oxygen polyhedra [46]. The possibility of using Al K- and Al $L_{2,3}$ -ELNES fingerprints to extract the site occupancies in mixed-coordination materials has also been investigated [47].

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