

# VUV and cathodoluminescence spectroscopy of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$

Eduard Feldbach · Viktor P. Denks · Marco Kirm · Peeter Liblik ·  
Aarne Maaroos · Hugo Mändar · Tea Avarmaa · Kristjan Kunnus

Received: 20 July 2007 / Accepted: 4 January 2008 / Published online: 23 January 2008  
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**Abstract** Reflection, photo- and cathodoluminescence of  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  (C12A7) were investigated. Smooth features observed in VUV reflection spectrum of monocrystalline C12A7 evidence its complicated crystalline structure and lattice disorder. Two luminescence bands peaking at 4.9 and 3.35 eV were revealed in C12A7 ceramics having encaged electrons and  $\text{O}^{2-}$  ions. The 4.9 eV emission has an excitation onset at 6.8 eV, i.e. near the threshold of free electron-hole pair creation, and is assigned to the recombination of encaged electrons with valence band holes. The 3.35 eV emission is ascribed to the recombination of electrons with the holes localized at the encaged  $\text{O}^{2-}$  ions.

## 1 Introduction

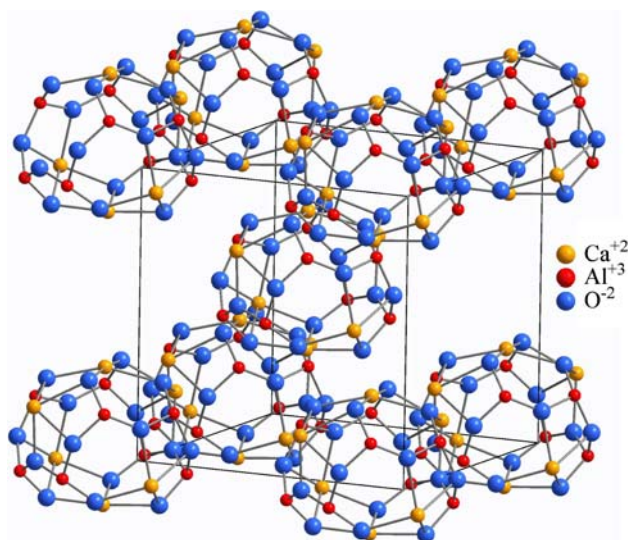
$12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  (C12A7) compound has rather complicated crystal structure. C12A7 can be considered as a structural analogue of nanoporous zeolites/sodalites on the one hand, while on the other hand the analysis of properties of electronic excitations of C12A7 should be carried out in relation to the constituent parts of this compound—simple oxides of CaO and  $\text{Al}_2\text{O}_3$ , all studied earlier by us [1–4]. There are two different groups of ions in the C12A7 structure. Most of ions belong to the regular lattice, which can be considered as a joint framework of cages (12 cages per unit cell,  $\sim 7 \cdot 10^{21}$  cages/cm<sup>3</sup>); a fragment of it is

depicted in Fig. 1. Important point is, that this framework is positively charged (+4 per unit cell) and in order to maintain charge neutrality it has to be compensated by another group of ions i.e. negative ions occupying free space inside these cages. It should be emphasized that the encaged ions are rather natural intrinsic component of the lattice than impurities. This can result in the disorder of both chemical composition and spatial distribution of lattice constituents. In the case of stoichiometric C12A7 there are  $\text{O}^{2-}$  ions in every sixth cage on average, that means the concentration of encaged ions to be as high as  $\sim 1.2 \cdot 10^{21}$  cm<sup>-3</sup>. Another important point is the possibility of encaging various ions by using different preparation methods. In the outstanding particular case even electrons can be introduced replacing usual negative ions, that opens the possibility of tuning conductivity of this material in a very wide range [5, 6]. This kind of compositional engineering leading to such dramatic changes of the material properties, makes C12A7 very attractive for numerous applications.

According to theoretical calculations [7, 8] the unique crystal structure of C12A7 causes two main peculiarities in the electronic structure, which are the main subject of present investigation. Firstly, there is an s-like state associated with each empty cage and due to the overlap of these states so-called cage conduction band (CCB) is formed inside the framework band-gap. Secondly, the occupied states connected with the encaged ions, located near the top of the valence band, strongly perturb it. Hence, changing the chemical composition of encaged species enables the modification of electronic structure of C12A7.

Luminescence spectroscopy using tunable synchrotron radiation sources in VUV is indispensable tool for investigation of electronic excitations and optical properties of wide-band-gap solids. Our first results on luminescence

E. Feldbach (✉) · V. P. Denks · M. Kirm · P. Liblik ·  
A. Maaroos · H. Mändar · T. Avarmaa · K. Kunnus  
Institute of Physics, University of Tartu, Riia 142, Tartu 51014,  
Estonia  
e-mail: eduard.feldbach@ut.ee



**Fig. 1** Cages of the same chirality form a bcc lattice. The whole framework consists of 6 interlocked bcc lattices of different chiralities

properties of C12A7 were published recently in [9]. The aim of the present study is to elucidate the electronic structure of this unique compound benefiting from the recent progress in synthesis and post-synthesis treatment of C12A7 ceramics and single crystals.

## 2 Experimental details

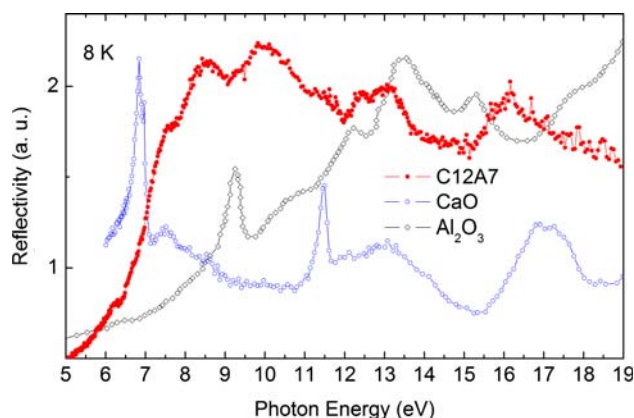
Polished C12A7 single crystals grown by the Czochralski method at the Tokyo Institute of Technology [10] were used for reflectivity measurements. Due to technological reasons these crystals contained considerable amount ( $\sim 5 \cdot 10^{19} \text{ cm}^{-3}$ ) of  $\text{Ir}^{4+}$  ions, which presumably occupy  $\text{Ca}^{2+}$  sites. It is obvious that such amount of impurities influences luminescence properties. This was very likely the reason for low luminescence efficiency of these crystals with regard to that of polycrystalline ceramic samples. The ceramic samples, which were used in luminescence experiments, were synthesized at our institute in two stages. During the first stage insulating powder was synthesized using the self-propagating combustion method [11] followed by 5 h annealing at 1,000 °C in dry air atmosphere. Ca- and Al-nitrates of high purity (99.999%, Alfa-Aesar) were used as starting materials. According to the XRD study this method gives phase pure samples contrary to the conventional solid-state reaction method, which almost always yields the desired C12A7 along with the variety of other calcium aluminates together with some amount of unreacted CaO and  $\text{Al}_2\text{O}_3$  found as impurity phases. In the second stage, this powder was used as the starting material in the melt-solidification process in reducing atmosphere [12] to get electrical conductive

ceramic samples. In this process, negative encaged ions are partly replaced by electrons. According to [12] this kind of samples has a dark green color and exhibits conductivity up to 5 S/cm at 300 K, which corresponds to electron concentration of  $\sim 3 \cdot 10^{19} \text{ cm}^{-3}$  (i.e. far below the theoretical maximum of  $\sim 2.3 \cdot 10^{21} \text{ cm}^{-3}$ ).

Photoluminescence and its excitation spectra as well as VUV reflectivity (at the incidence angle of  $17.5^\circ$ ) were investigated at the SUPERLUMI station [13] of HASYLAB (Hamburg, Germany) with a spectral resolution of 0.3 nm. Cathodoluminescence (CL) was studied at the set-up of our home institute in Tartu. This set-up consists of an electron gun with variable accelerating voltage (1–30 kV), two double monochromators (for VUV and UV-VIS region) with the respective detectors covering the spectral range from 1.7 to 11 eV and a He-cryostat for low temperature measurements.

## 3 Results and discussion

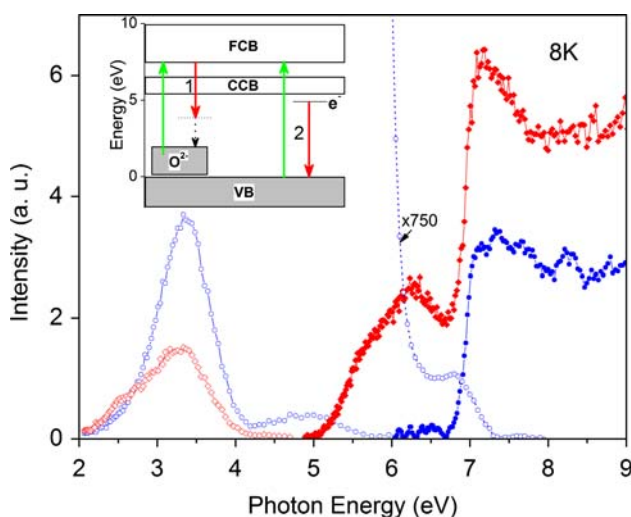
The reflection spectrum of C12A7 is shown in Fig. 2 along with literature data for CaO and  $\text{Al}_2\text{O}_3$  [3, 14]. It does not change significantly between 8 K and room temperature. No sharp excitonic features typical of simple oxides (the features at 6.8 and 9.1 eV in CaO and  $\text{Al}_2\text{O}_3$ , respectively) are observed. This can be explained by a large unit cell (116 atoms) similar to  $\text{Y}_3\text{Al}_5\text{O}_{12}$ , which has 160 atoms in the unit cell [15]. Another plausible reason is the significant disorder in the lattice of C12A7 causing inhomogeneous broadening effects in the spectra. The encaged ions, influencing the physical size of the cages, are arbitrarily distributed in the C12A7 lattice and thereby modulate also electronic properties. Nevertheless, a sharp increase of reflectivity is observed above 6 eV, being a circumstantial piece of evidence that the band gap energy ( $E_g$ ) for C12A7 is close to that of CaO (indirect gap



**Fig. 2** Reflection spectra recorded at 8 K for C12A7 (filled circles), CaO (open circles) [3] and  $\text{Al}_2\text{O}_3$  (open diamonds) [14]

$E_g \sim 6.4$  eV [3]). This allows assuming that the bottom of the C12A7 framework conduction band (FCB) is formed by  $\text{Ca}^{2+}$  states. Further smooth features of C12A7 reflectivity in the energy range from 7 to 19 eV are attributed to interband transitions in the CaO and  $\text{Al}_2\text{O}_3$  sublattices. It is obvious from Fig. 2 that the direct comparison with the reflection spectra of CaO and  $\text{Al}_2\text{O}_3$  is not helpful. For the precise identification of transitions the band structure calculations extended into the energy range exceeding the band gap region are required.

Nanoporous crystal structure of C12A7 serves as a unique environment for studying the electronic structure of negative ions. For example, to the best of our knowledge, the ultraviolet absorption spectrum of  $\text{O}^{2-}$  in C12A7 reported in [8] is the only published experimental result on its absorption in solids. At the same time this is the most common constituent of luminescence centers (hole component) in simple oxides like MgO [16]. C12A7 synthesized in an oxidizing atmosphere can accommodate a large amount of active oxygen ions ( $\text{O}^-$ ,  $\text{O}_2^-$ ,  $\text{O}_2^{2-}$ ). According to the Ref. [8], their energy states, strongly influence the top of the valence band (VB) of C12A7 and consequently modulate the electronic structure. Samples of C12A7 thermally treated in the atmosphere of various oxygen content were investigated in our previous work [9], where we got preliminary estimate for  $E_g \sim 6.5$  eV by means of the photostimulated luminescence method. In



**Fig. 3** Cathodoluminescence, photoluminescence and luminescence excitation spectra under photoexcitation of the encaged electrons containing C12A7 ceramics at 8 K. Photoluminescence excited by 7.75 eV photons (open circles + solid line) and by 6.3 eV photons (open diamonds). The tail of cathodoluminescence (electron energy 15 keV, beam current 1  $\mu\text{A}$ ; open circles + dashed line). In the inset—the schematic band structure with the indicated (up and down arrows) excitation and luminescence processes attributable to 3.35 eV emission band (1) and 4.9 eV emission band (2). Energy level indicated by  $e^-$  designates the occupied cage level

present work, we used samples where the encaged oxygen was partly replaced by electrons using the melt-solidification process in reducing atmosphere [12]. The emission and excitation spectra of these samples are shown in Fig. 3. The emission band peaked at 3.35 eV always dominates in as-grown insulating C12A7 samples, whereas the luminescence band with the maximum at 4.9 eV appears only in the conductive (treated in reducing atmosphere) samples. The energy distance from a one-electron state occupied by an encaged electron to the top of the VB was estimated theoretically to be  $\sim 4.9$  eV [7]. These facts strongly support the interpretation of this emission band as the recombination of encaged electrons with VB holes. Moreover, the excitation spectrum of the 4.9 eV emission (filled circles in Fig. 3.) has a sharp onset at 6.8 eV and exhibits the highest excitation efficiency above 7.0 eV. This value is in good agreement with the upper limit ( $\sim 6.8$  eV) calculated for the framework band gap [7, 8] and is attributable to the VB  $\rightarrow$  FCB transitions. According to the analysis of the Urbach tail performed in [8], the value of the focal point  $E_0$  is 6.6 eV.  $E_0$  is a characteristic parameter close to the energy of the lowest excitonic states in ionic crystals [17], favouring the  $E_g$  value  $\geq 6.8$  eV. By applying a powerful electron beam excitation (15 keV, 1  $\mu\text{A}$ ) and registration through a double VUV monochromator we succeeded in detection of a very weak emission tail in the cathodoluminescence spectrum of C12A7 extending up to 7.2 eV with a well-pronounced hump at 6.8 eV (see Fig. 3, dashed line with open circles). On the short wavelength side, the spectrum is modulated by intrinsic absorption. Similar kind of a weak emission was found by us earlier in BeO [18], and it was interpreted as the recombination luminescence of hot (non-relaxed) carriers during their relaxation. Peculiarities can appear on top of a broad spectrum (like the hump at 6.8 eV) in the case of the existence of a potential barrier separating an initially populated excited state and a relaxed state contributing to the luminescence spectrum at lower energies. At low temperatures the emission nearly resonant with the absorption occurs near the band edge because of the barrier prohibiting non-radiative depopulation of the excited state. Thus, we can conclude that the framework energy gap of C12A7 is  $\geq 6.8$  eV and the variation of this value can be expected due to the structural disorder (the random distribution of encaged species). The most surprising result is the fact that no excitation bands were found within the energy gap for the 4.9 eV luminescence. It means that the probabilities of the transitions of VB electrons to the localized states of encaged electrons via the empty CCB states are not very high.

The excitation spectrum for the 3.35 eV emission (Fig. 3, filled diamonds) has the onset at 5.1 eV and forms a band peaked at 6.3 eV. These bands are attributed to the

$O^{2-} \rightarrow$  FCB transitions in agreement with calculations of [8]. The second sharp rise of the excitation spectrum at 7 eV belongs (analogously to the 4.9 eV emission) to the  $VB \rightarrow$  FCB transitions. Thus, the creation of holes on the encaged  $O^{2-}$  via direct intra-centre excitation of these ions or via  $VB \rightarrow$  FCB transitions has comparable efficiency. This observation is in agreement with the calculated strong lattice distortion induced by these encaged ions that split several framework O 2p states from the top of the VB and result in the effective narrowing of the band gap of a stoichiometric C12A7 up to  $\sim 2$  eV [7]. The experimental data obtained strongly support the suggestion that the 3.35 eV emission takes place after the relaxation of created holes on the  $O^{2-}$  centres (dashed arrow in the inset of Fig. 3) and their recombination with electrons (arrow 1 in the inset of Fig. 3). This interpretation was also supported by a subsequent thermal treatment of investigated conductive samples during 4 h in oxygen flow at 1,200°C, which turned them back to insulating state and increased amount of  $O^{2-}$  ions. The emission intensities were significantly affected by this treatment, whereas the intensity of the 3.35 eV emission was increased and that of the 4.9 eV emission decreased.

#### 4 Conclusions

For the first time the reflection spectrum of a C12A7 single crystal was measured in VUV spectral range (5–19 eV). No sharp features of excitonic origin were found, which is typical for the system with a big unit cell and provides the evidence of significant disorder in the crystal lattice of C12A7. In the samples with encaged electrons (approximately at concentration of  $\sim 3 \cdot 10^{19} \text{ cm}^{-3}$ ), the recombination of these electrons with VB holes, resulting in the emission band peaked at 4.9 eV, was detected. The onset of the excitation for this emission at 6.8 eV and the tail of the “hot” emission taking place during the relaxation of hot carriers refer to the framework energy gap value of  $E_g \geq 6.8$  eV. No evidences of the involvement of CCB states into excitation of the 4.9 eV emission was detected. Holes localized on encaged  $O^{2-}$  ions can be created both via direct intra-centre excitation of these ions and via  $VB \rightarrow$  FCB excitations. The emission peaked at 3.35 eV takes place after relaxation of these holes and their recombination with the electrons originating from the FCB. The

lowest excitation energy (at 5.1 eV) of this band is in good agreement with the calculated “narrowing” of the energy gap of a stoichiometric C12A7 by  $\sim 2$  eV.

**Acknowledgements** The support for luminescence investigations in VUV using synchrotron radiation by the European Community under Contract RII3-CT-2004-506008 (IA-SFS), and support by the Estonian Science Foundation (grants 6538 and 6010) is gratefully acknowledged. We also thank Professors M. Hirano, H. Hosono and Dr. P. V. Sushko for several fruitful discussions and for kindly providing us with C12A7 single crystals.

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