This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>

Contents lists available at ScienceDirect

Radiation Measurements

journal homepage: www.elsevier.com/locate/radmeas

Intrinsic excitons in $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$

E. Feldbach*, V.P. Denks, M. Kirm, K. Kunnus, A. Maaros

Institute of Physics, University of Tartu, Riia 142, Tartu 51014, Estonia

ARTICLE INFO

Article history:

Received 17 August 2009

Received in revised form

13 September 2009

Accepted 9 November 2009

Keywords:

C12A7

Excitons

Luminescence

Time-resolved spectroscopy

ABSTRACT

Unusual crystal structure of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ is composed by a framework of positively charged nanocages, which enable accommodation of various negative ions (and even electrons) inside these cages. Different filling of cages leads to significant changes in electronic structure and as the result in luminescence properties, as well. Luminescence was studied using time-resolved spectroscopy in VUV in the temperature range from 6 to 300 K. Electron loaded samples exhibit UV luminescence band peaked at ~ 5 eV. The excitation spectrum of this emission has the onset at the energy gap value of 6.8 eV, and its decay is well described with the sum of two exponential functions with life-times of $\tau_1 = 3.7$ ns and $\tau_2 = 29$ ns, respectively. Its thermal quenching is well approximated by the sum of two Mott-Seitz type curves with the activation energies of 34 meV and 70 meV. Experimental results indicate that this luminescence is possibly due to radiative decay of two singlet self-trapped exciton states, which hole components are localized on two non-equivalent framework oxygens.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Electronic excitations of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ (C12A7) have been the subject of intensive investigations since the discovery of its conversion from a wide-gap insulator to electronic conductor (Hayashi et al., 2002). One of remarkable properties of C12A7 is its high stability under irradiation – no amorphization was detected at doses up to 600 dpa (Sushko et al., 2006). Therefore, this material is of interest as potential scintillator for harsh conditions.

The unit cell of stoichiometric C12A7 contains two molecules and can be rewritten as $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} + 2\text{O}^{2-}$. The first part of this formula denotes framework of positively charged cages (12 cages per unit cell) and 2O^{2-} part is referred to “free oxygen”, which due to charge neutrality requirement occupies 1/6 of the total number of cage sites. There is an inner free space of 0.4 nm diameter inside cages and a 0.1 nm wide opening by means of which each cage is connected to 8 nearest neighbors. There are two non-equivalent positions of framework oxygen ions in this lattice – 48 out of 64 are coordinated by two Ca and two Al ions while 16 of them are coordinated by one Al and three Ca ions. Depending on the preparation conditions “free oxygen” can be replaced by other negative ions and even by electrons. In this latter relatively unusual case electrons behave as anions and this type of compound is called electride (Dye, 2003). These encaged electrons are loosely bound to the crystal lattice and induce the electrical conductivity, which type

depends on the concentration of accommodated electrons (Kim et al., 2007). At concentrations below $10^{20}/\text{cm}^3$ electrons are well localized resulting in the polaron-type cage-to-cage hopping conductivity. Several luminescence bands in visible and UV spectral range have been detected and the energy gap (E_g) value of ~ 6.8 eV has been determined using photostimulated luminescence method in our previous study (Feldbach et al., 2009). The possible exciton formation energy in C12A7 was estimated as ~ 6.6 eV from the Urbach tail study (Hayashi et al., 2007), which also agrees well with our estimation for E_g . The main aim of our present work was to analyze possible evidences of excitons using time-resolved luminescence spectroscopy and further investigation of unique band structure of C12A7 in general. Such information is primarily needed for evaluation of applications prospects of C12A7 as a transformer of ionizing radiation.

2. Experimental

Time-resolved photoluminescence investigations of C12A7 were carried out using synchrotron radiation at the SUPERLUMI station of HASYLAB at DESY (Hamburg, Germany) (Zimmerer, 2007). Luminescence spectra are not corrected to the spectral response of the detection system. Ceramic samples were synthesized using a melt solidification method in reducing atmosphere at the Institute of Physics, University of Tartu (Feldbach et al., 2009). According to (Kim et al., 2007) this method enables to achieve the concentration of encaged electrons up to $\sim 3 \times 10^{19}/\text{cm}^3$, which means partial replacement of encaged ions. Investigated ceramic

* Corresponding author. Tel.: +372 737 4786; fax: +372 738 3033.
E-mail address: eduard.feldbach@ut.ee (E. Feldbach).

Fig. 1. Typical photoluminescence spectrum at 9 K ($h\nu_{\text{exc}} = 7$ eV) for electron loaded samples (blue circles) in comparison with the oxygen treated samples (red circles). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

pieces were cleaved and a half of samples were treated at 1273 K in oxygen atmosphere (oxygen treated samples) for comparison with the electron loaded ones.

3. Results and discussion

Typical photoluminescence spectrum at 9 K excited by 7 eV photons for electron loaded samples (blue circles) in comparison with oxygen treated samples (red circles) is depicted in Fig. 1 and the corresponding excitation spectra for 5 eV and 3.3 eV bands of electron loaded C12A7 in Fig. 2. Several electron loaded polycrystalline ceramics were investigated and the UV band peaked at ~ 5 eV was always reproducibly detected. Spectral composition of luminescence at lower energies is strongly dependent on sample synthesis route, which is very likely related to the encaged oxygen ions of various types (O^{2-} , O^- , O_2^- , O_2^{2-} , OH^-). Nevertheless, some assumptions on the origin of 3.3 eV band can be drawn from our spectroscopic data. The excitation of 3.3 eV emission has onset at ~ 5.1 eV with foreseeable doublet structure. The splitting and position of this excitation band is rather close to the calculated values for encaged O^{2-} 2p levels above the top of the valence band (Sushko et al., 2006). Therefore, this doublet is assigned to the direct excitation of encaged O^{2-} oxygen and the emission band peaks at ~ 3.3 eV is related to the recombination of electrons with the holes localized on the encaged O^{2-} oxygen. The next onset at

Fig. 2. Luminescence excitation spectra of electron loaded C12A7 for 5 eV (blue circles) and 3.3 eV (red line) bands at 9 K. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

~ 7 eV corresponds obviously to the beginning of band-to-band transitions with the subsequent hole localization on encaged oxygen and radiative recombination.

More detailed study was performed for 5 eV band. Our recent result showed that 5 eV luminescence has the excitation onset at $\sim E_g$ (Feldbach et al., 2009), i.e. resulting only from electron-hole pair creation, led us to the hypothesis of excitonic nature of this emission. Further, the decay curve for 5 eV photoluminescence ($h\nu_{\text{exc}} = 7$ eV) recorded at 9 K is depicted in Fig. 3a. The experimental data (blue circles) can be well approximated with the sum of two exponential decays (red solid line). The following values for life-times (τ) were obtained: $\tau_1 = 3.7$ ns and $\tau_2 = 29$ ns. The ratio of light sums for these two decay components is $\approx 1:3$ (the ratio of fast to slow component), which is in agreement with the proportion of two non-equivalent oxygen positions in the framework of C12A7. It is a clear indication that the holes created on the both kind of framework O^{2-} ions are definitely involved in the formation of intrinsic electronic excitations. Lifetimes in nano-second range are typical for allowed transitions and enable to assume that both belong to singlet exciton state. There is a strong evidence in favour of exciton formation in (Hayashi et al., 2007), where the Urbach tail analysis of fundamental absorption edge points to strong electron-phonon interaction in C12A7, which is necessary condition for self-trapping of excitations. There is $\sim 50\%$ of free space in the volume of C12A7 structure, which according to theoretical considerations (see e.g. Shluger and Itoh, 1990) is also prerequisite for self-trapping of excitations. In stoichiometric C12A7 there is a huge amount ($\sim 10^{21}/\text{cm}^3$) of encaged oxygen ions and all free holes created in the valence band tend to localize

Fig. 3. (a) Decay of 5 eV luminescence ($h\nu_{\text{exc}} = 7$ eV) of electron loaded sample at 9 K (blue circles). Red solid line is a fit consisting of the sum of two exponential decays with life-times of $\tau_1 = 3.7$ ns and $\tau_2 = 29$ ns. (b) Thermal quenching of 5 eV luminescence band ($h\nu_{\text{exc}} = 7$ eV) of electron loaded sample (blue circles). Red solid line is a fit consisting of the sum of two Mott-Seitz equations with activation energies of $E_1 = 34$ meV and $E_2 = 70$ meV. Curves I_1 and I_2 denote the individual components of the fit. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. Schematic representation of C12A7 band structure according to (Hayashi et al., 2007) with indicated ground states of encaged O^{2-} ions and electrons. Red arrows correspond to the excitation maxima for 3.3 eV luminescence band and blue arrow to the excitation onset for 5 eV band. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

on the encaged ions, where it is energetically more favorable. This prohibits localization of holes on the framework oxygens and recombination emission at 3.3 eV is dominant feature in luminescence.

The behavior of thermal quenching of ~ 5 eV luminescence and its subsequent Mott-Seitz analysis (see Fig. 3b) also points to the situation that two types of holes are involved in the luminescence process. The experimental data was fitted with the sum of two Mott-Seitz equations having activation energies of $E_1 = 34$ meV and $E_2 = 70$ meV.

Fig. 4 represents schematically band structure according to (Hayashi et al., 2007), which is in good agreement with our time-resolved luminescence spectroscopy results. Red and blue arrows denote excitation onsets for 3.3 eV and 5 eV emission bands for centers related to recombination of electrons with holes localized on encaged oxygen ions and with ones on framework oxygens, respectively.

Based on experimental data we propose that in nanoporous C12A7 compound already partial replacement of encaged oxygen

with electrons suppresses the dominating trapping channel for valence band holes on the encaged oxygens and, consequently, the efficient self-trapping of holes, which reside at two different non-equivalent framework oxygen ions becomes feasible. Subsequent recombination with conduction band electrons leads to formation of intrinsic self-trapped excitons in singlet states, which radiative decay results in ~ 5 eV luminescence band with ns decay times revealed in our experiments.

Acknowledgements

The support for luminescence investigations in VUV using synchrotron radiation by the European Community European Community's Seventh Framework Programme (FP7/2007–2013, grant 226716) is gratefully acknowledged as well as funding by Estonian Science Foundation (Grant 8306).

References

- Dye, J.L., 2003. Electrons as anions. *Science* 302, 607–608.
- Feldbach, E., Denks, V.P., Kirm, M., Liblik, P., Maaroos, A., Mändar, H., Avarmaa, T., Kunnus, K., 2009. VUV and cathodoluminescence spectroscopy of $12CaO \cdot 7Al_2O_3$. *J. Mater. Sci. Mater. Electron.* 20, S260–S263.
- Hayashi, K., Matsuishi, S., Kamiya, T., Hirano, M., Hosono, H., 2002. Light-induced conversion of an insulating refractory oxide to persistent electronic conductor. *Nature* 419, 462–465.
- Hayashi, K., Sushko, P.V., Ramo, D.M., Shluger, A.L., Watauchi, S., Tanaka, I., Matsuishi, S., Hirano, M., Hosono, H., 2007. Nanoporous crystal $12CaO \cdot 7Al_2O_3$: a playground for studies of ultraviolet optical absorption of negative ions. *J. Phys. Chem. B* 111, 1946–1956.
- Kim, S.-W., Matsuishi, S., Miyakawa, M., Hayashi, K., Hirano, M., Hosono, H., 2007. Fabrication of room temperature-stable $12CaO \cdot 7Al_2O_3$ electride: a review. *J. Mater. Sci. Mater. Electron.* 18, S5–S14.
- Shluger, A., Itoh, N., 1990. Models of electronic defects and self-trapped excitons in Li_2O . *J. Phys. Condens. Matter* 2, 4119–4125.
- Sushko, P.V., Shluger, A.L., Hayashi, K., Hirano, M., Hosono, H., 2006. Mechanism of oxygen ion diffusion in a nanoporous complex oxide $12CaO \cdot 7Al_2O_3$. *Phys. Rev. B* 73, 014101.
- Zimmerer, G., 2007. SUPERLUMI: a unique setup for luminescence spectroscopy with synchrotron radiation. *Radiat. Meas.* 42, 859–864.