Synthesis and luminescence properties of Ce³⁺ doped nanoporous 12CaO·7Al₂O₃ powders and ceramics

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ABSTRACT

Ce³⁺ doped nanoporous 12CaO·7Al₂O₃ (C12A7) was synthesized using the self-propagating combustion method and solid state reaction. Ceramics of high density were produced using the melt-solidification process in a carbon crucible. The obtained samples were characterized using XRD and SEM methods and studied by means of low temperature time resolved luminescence under laser and synchrotron radiation excitation. It was shown that the Ce³⁺ ion in C12A7 emits broad-band 5d–4f luminescence peaked at ~3.0 eV. The decay curves of Ce³⁺ emission in the studied samples have complicated nature depending on the excitation energy with the main decay component of 20–30 ns life time, typical for parity and spin allowed transitions of Ce³⁺. The emission of Ce³⁺ ions is efficiently excited through the intra-centre as well as in the intrinsic absorption region of C12A7.

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1. Introduction

The compound of 12CaO·7Al₂O₃ (C12A7) has an outstanding position among calcium aluminates due to its unique nanocage crystal structure (12 cages per unit cell) with inner cage diameters of ~0.4 nm, inducing a nanoporous macroscopic material. These cages are positively charged (+1/3 per cage), and to maintain charge neutrality part of these cages are occupied by negative ions (O²⁻ in the stoichiometric case). These negative ions can be replaced easily by other anions like F⁻, OH⁻, H⁻, etc., and even by electrons [1,2], which make this compound very attractive as functional material with highly variable properties. The unique nanocage structure results in very peculiar electronic properties among other wide gap materials. Theoretical and experimental studies of C12A7 reported in Refs. [2,3] outline that a cage conduction band (CCB) due to overlapping s-like states associated with empty cages is formed within the energy gap. Also ground states of various encaged ions are often located not far from the top of the valence band of C12A7. This circumstance can cause perturbation of the associated electronic states and have a significant influence on electron–hole processes in C12A7. It is obvious that such a material with the possibility to precisely control electron and hole processes has a high potential in a variety of applications based on luminescence, which still have been rather

modestly investigated. There are only a few reports published, which concern luminescence properties of Au-implanted [4] and undoped C12A7 by our group [5,6]. In particular, rare earth ions play a special role in this application area as active centres for lasers, in materials for lighting, scintillation, dosimetry as well as in displays and optoelectronic devices. Rare earth doped aluminates are also materials of interest in persistent phosphor applications [7]. The only reports that we are aware of concern luminescence and optical properties of Er³⁺ ions doped C12A7 from infrared up to ultraviolet spectral region with the main aim in optoelectronic applications [8,9].

The central goal of the present study was to develop efficient synthesis routes introducing Ce³⁺ ions into C12A7 and to perform the characterization of the materials obtained in the form of powders and ceramics. Special attention was paid to determination of luminescence properties, which includes specific properties (wavelength, decay kinetics, etc.,) related to the emission centre and its excitation mechanisms. The Ce³⁺ ion has a central role among other rare earths as its spectral characteristics can be utilized to predict the spectroscopic properties of other rare earth ions according to the methodology developed by Dorenbos [10]. Due to parity and spin allowed 5d–4f transitions in Ce³⁺ resulting in short decay times, it is widely used in various scintillators and other ionizing radiation converters. Presently, there is a rising demand for materials used in visualization and characterization of ultrahigh intensity photon beams with femtosecond range pulse duration generated by free electron lasers or laser-based high harmonic generation systems (see e.g. [11]).

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2. Experiment

Time resolved low temperature photoluminescence experiments were carried out at the SUPERLUMI station of HASYLAB at DESY using 4–20 eV synchrotron radiation (SR) from the DORIS storage ring for excitation [12]. The excitation spectra were recorded with an instrumental resolution of ~ 0.3 nm. Sodium salicylate luminescence was used as reference signal to account for incident photon flux. Emission in UV/visible spectral range was detected by using a 0.3 m Czerny–Turner monochromator-spectrograph SpectraPro-308i (Acton Research Inc.) equipped with a photomultiplier tube (R6358P, Hamamatsu), which was also used in recording of excitation spectra. The typical spectral resolution used was 10–20 nm selected upon the signal intensity depending on excitation energy and sample under excitation. Recorded emission spectra were not corrected for the spectral response of the detection system. C12A7 powders and ceramics were mounted onto a copper sample holder attached to a cold finger of a flow-type liquid helium cryostat. All measurements were performed under ultrahigh vacuum conditions. The pulsed nature of synchrotron radiation allowed to record all spectra in time integrated (TI) mode as well as in such one, where spectra were stored within a selected time window with length Δt delayed by time interval δt in respect of arrival of excitation pulse.

Some studies in UV range at room temperature were performed using a laser spectroscopy setup [13], based on an optical parametric oscillator NT 342/1/UVE (EKSPLA, Lithuania) providing short pulses of 5 ns duration with the spectral resolution of <5 cm^{-1} , which are tuneable in the energy range of 0.6–6.0 eV. The luminescence spectra were recorded using a Shamrock SR-303i imaging spectrograph equipped with an Andor DH-501CCD camera on the imaging exit port and on the another exit port the Hamamatsu H3177-51 PMT was mounted, output signal of which is stored in Tektronix TDS 380 digital scope. Emission spectra were also recorded within time window $\Delta t = 200$ ns delayed by $\delta t = 20$ ns in respect of the exciting laser pulse. XRD patterns were recorded on a Bragg–Brentano type X-ray powder diffractometer using Cu K α radiation and θ – 2θ step scanning mode.

3. Preparation routes of Ce^{3+} doped C12A7

Compounds with the general formulas $\text{Ca}_{12-x}\text{Al}_{14}\text{O}_{33}:\text{Ce}_x$ ($x = 0.001$) (further on as C12A7: 0.1% Ce) and $\text{Ca}_{12-x}\text{Al}_{14}\text{O}_{32}\text{F}_2:\text{Ce}_x$ ($x = 0.001$; 0.01) (C12A7:F 0.1% and 1% Ce) were produced via combustion synthesis elaborated in [14] and solid state reaction method, respectively. For the combustion method, urea was used as an energetic fuel and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.98%, AlfaAesar), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.999%, AlfaAesar) and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%, AlfaAesar) as oxidative components. Stoichiometric mixture of metal nitrates and urea, calculated accordingly to the total reducing and oxidizing valences, was dissolved and stirred thoroughly for 0.5 h. The clear solution in a quartz beaker was placed into a vertical tube furnace preheated to 500 °C. A few minutes after the completion of water evaporation, self-ignition occurred and a white spongy powder of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}:\text{Ce}$ was obtained. The powder was annealed at 1000 °C for 4 h in air. Afterwards pellets were pressed and calcined at 1100 °C for 4 h in a slightly reducing atmosphere of Ar and for comparison in air.

The fluorinated ceramic samples were prepared in two stages. In the first stage, the solid state reaction method was used. Well mixed chemicals of CaCO_3 (99.997%, AlfaAesar), $\gamma\text{-Al}_2\text{O}_3$ (99.997%, AlfaAesar), CaF_2 (99.95%, AlfaAesar) and CeF_3 (99.9%, AlfaAesar) in ratios 11:7:1: x ($x = 0.01$; 0.001) were milled using agate grinding media. The powder was pressed into pellets and heated at 1350 °C for 8 h in Ar. These samples as well as the pellets

made by the combustion method were characterized by XRD. In the second stage, the obtained pellets were used as a starting material in the melt-solidification process in a reducing carbon crucible [15]. Such procedure is also used for partial substitution of encaged ions with electrons and the colour of the insulating C12A7 compound changes from white to dark green, which is typical for C12A7 electride (i.e., a system, where electrons are anions in the cages). As a result of the above-mentioned process, dark green ceramics were obtained, which indirectly indicates that cages of C12A7 are partially filled with electrons and the proper phase of Ce doped C12A7 is formed. The density of the obtained ceramics was determined to be ~ 2.8 g/cm^3 , which value is between the reduced glass (2.92 g/cm^3) and crystalline C12A7 (2.68 g/cm^3) as reported in [15].

4. Results and discussion

According to the phase diagram [16,17] multi-phases of calcium aluminates can easily form depending sensitively on reaction conditions and the compositional ratio of $\text{CaO-Al}_2\text{O}_3$. This is also confirmed in our case by XRD pattern of powder samples shown in Fig. 1. The best phase purity was obtained for C12A7:F 0.1% Ce, which resulted nearly phase pure C12A7 and some amount of residual CaO formed during reaction (Fig. 1a). At higher (1%) Ce concentration, also some amount of the $\text{Ca}_3\text{Al}_2\text{O}_6$ (C3A) phase was found along with the main C12A7 (Fig. 1b). Surprisingly to us, the combustion synthesis gave the worst result with presence of C3A, a small amount of CaAl_2O_4 , and some other unidentified phases. Our previous experience in producing of stoichiometric C12A7 was in favour of the latter method, yielding phase pure powders. Fig. 2 presents a SEM image of ceramic C12A7:F 1% Ce sample. The ceramic piece consists of large crystallite domains with the size of a few hundred μm , which means that the samples can be considered as macroscopic ones from point of view of luminescence studies.

Fig. 1. XRD patterns of fluorinated C12A7:F 0.1% Ce (a), C12A7:F 1% Ce (b) produced by solid state reaction and C12A7: 0.1% Ce (c) produced using combustion synthesis. Miller indices HKL of reflections for the following identified crystalline phases CaO, $\text{Ca}_3\text{Al}_2\text{O}_6$ and C12A7 are shown at the patterns (a), (b) and (c) correspondingly. Diffraction intensity is shown in absolute units of counts per 5 s (cp5s).

Fig. 2. SEM image of a C12A7:F 1% Ce ceramic sample. The image was taken with the TESCAN VEGA 5136 SEM system.

Fig. 3 shows emission spectra from the studied Ce doped C12A7 samples. Under 4.6 eV laser excitation the C12A7: 0.1% Ce pellet at room temperature has a single broad luminescence band at 3 eV. The pellets synthesized by combustion method were treated in Ar as well in air. The oxidative character of combustion reactions itself and annealing in air favoured the formation of Ce^{4+} , which was revealed by the lack of emission under the same excitation. Samples which exhibit intense 3 eV emission at room temperature were investigated also under excitation by 7 eV photons at 10 K, which creates electron–hole pairs in pure C12A7 [6] and causes appearance of bands extending to the UV like those reported in [5]. The low energy side of the dominating luminescence band consists mostly of fast luminescence, as **Fig. 3a** (symbols) demonstrates. A practically analogous picture is observed for time-integrated luminescence of C12A7:F 1% Ce ceramics at similar excitation conditions. Resonant excitation by 3.8 eV (**Fig. 3b**) and 4.3 eV photons (**Fig. 3c**) of the states in the energy gap of C12A7 results again in a single luminescence band peaked at 3 eV independently of sample temperature. All results obtained confirm that the main luminescence peak of C12A7:Ce is revealed in similar position independently of the synthesis routes used for sample preparation. This emission is interpreted as the well-known transition from the lowest 5d level to the spin–orbit split 4f ground state ($^2\text{F}_{5/2}$, $^2\text{F}_{7/2}$) of Ce^{3+} ions. The typical doublet structure of 5d–4f luminescence is not observed because of strong electron–phonon interaction of 5d states in this host and also because of inhomogeneous broadening effects typical for C12A7 [6]. The latter effects are due to randomly distributed various encaged species (oxygen and fluorine ions or electrons), influencing the physical size of cages, thereby varying the crystal field strength. Also substituted Ce^{3+} ions located in the sample area with minority phases of other aluminates present in the sample contribute to the broadening.

The most important factor influencing luminescence properties of Ce ions in C12A7 arises from the circumstance that Ce^{3+} ions substitute Ca^{2+} ions in C12A7 host because of similar ionic radii (0.1 and 0.101 nm in octahedral coordination [18], respectively). The Al^{3+} ions have significantly smaller size (0.039 nm) in tetrahedral coordination and cannot be replaced by rare earths. Each cage has six Ca^{2+} ions built into its walls and for empty cages all these

Fig. 3. Emission spectra of various C12A7 samples: (a) luminescence of C12A7: 0.1% Ce at 300 K excited by laser 4.6 eV (1). Time-integrated luminescence (2) and short component (3; $\delta t = 1.6$ ns, $\Delta t = 14$ ns) of the same sample at 10 K excited by 7 eV photons using synchrotron radiation (SR). (b) Time-integrated luminescence of C12A7:F 1% Ce at 10 K (4) and 300 K (5) excited by 3.8 and 7.0 eV photons (6; $T = 10$ K), respectively, using SR. (c) Time-integrated luminescence of C12A7:F 1% Ce at 10 K (7) and its short component (8; $\delta t = 12$ ns, $\Delta t = 20$ ns) and TI emission at 300 K (9) excited by 4.3 and 7.0 eV photons using SR. Spectra are scaled for better visualization.

sites are equivalent. Implementation of encaged species (oxygen ions, electrons, etc.) causes a considerable deformation of the cage along its S_4 symmetry axis [2] and two axial Ca^{2+} sites will be distorted and feel a different crystal field strength compared to the other 4. This introduces two kinds of Ce^{3+} centres in C12A7 with slightly different spectral properties resulting in a broadened luminescence band. Due to the unique structure of C12A7, the charge compensation needed for Ce^{3+} ions (extra +1 charge in respect of Ca^{2+} ions) can be achieved in an original way by negative species (oxygen and fluorine ions as well as electrons in particular case) positioned within cages. On the other hand, this circumstance can be disadvantageous, if the total charge neutrality of lattice becomes partly unbalanced, which favours formation of phases other than C12A7. This could explain the result of combustion synthesis where the phase rich mixture of aluminates was formed.

Fig. 4a demonstrates excitation spectra of time integrated and fast components of 3.3 eV luminescence of C12A7: 0.1% Ce pellet at 10 K. The excitation onset of this emission is at 5.5 eV without

Fig. 4. Excitation spectra of various C12A7 samples using SR excitation: (a) excitation spectra of TI (line) 3.3 eV luminescence and its short component (o; $\delta t = 1.6$ ns, $\Delta t = 14$ ns) of C12A7: 0.1% Ce at 10 K. (b) excitation spectra of TI (line) 3.0 eV luminescence and its short component (o; $\delta t = 1.6$ ns, $\Delta t = 14$ ns) of C12A7:F 1% Ce at 300 K. (c) excitation spectra of TI (line) 2.8 eV luminescence, its short component (o; $\delta t = 1.6$ ns, $\Delta t = 14$ ns) and 2.14 eV emission (dashed line) of C12A7:F 1% Ce at 10 K.

any pronounced excitation bands below that energy, which could be assigned to Ce^{3+} 4f–5d absorption. The absence of Ce^{3+} 4f–5d transitions is explainable by optical transitions of encaged species as shown in [2], where absorption of active oxygens in C12A7 starts at 3.7 eV, practically prohibiting excitation of Ce^{3+} ions. On contrary, for the emissions 3.0 and 2.8 eV of C12A7:F 1% Ce ceramics (at 300 and 10 K, respectively), there is an excitation band peaked at 4.4 eV, which is followed by an analogous onset at 5.5 eV as in the combustion synthesized sample. This band at 4.4 eV is assigned to the 4f–5d absorption of the Ce^{3+} ion. At 300 K, the intra-centre 4f–5d excitation (the maximum of the peak is shifted to 4.3 eV due to thermal effects) is more efficient than through intrinsic absorption, but at 10 K the latter process dominates, indicating rather good energy transfer to the Ce^{3+} centres by electron–hole pairs. This means that Ce^{3+} doped C12A7 is applicable in radiation converters.

Even though our direct goal was not the determination of absolute scintillation intensities of the prepared materials, some preliminary estimate can be given. The comparison of Ce-luminescence intensities shows that under similar conditions (under band to

band excitations by 7 eV photons), the powder sample synthesized by combustion method (0.1% Ce) has a factor of 5 higher yield than that of ceramics of dark green colour (1% Ce). It is obvious that the yield is influenced by the efficiency of the energy transfer processes and optical properties of samples. The combustion synthesized white powder sample is more favourable for scintillation applications than strongly coloured ceramics with considerable self-absorption.

Fig. 5 depicts decay curves of Ce emission informing about the dynamics of luminescence centres. Under 5.3 eV laser excitation of C12A7: 0.1% Ce pellet at 300 K, the decay of 3.0 eV luminescence can be approximated by a single exponential with a decay time of ~ 32 ns. Exciting the same sample at 10 K by 5.8 eV photons, which corresponds to near intrinsic edge absorption of C12A7 [5], the decay of 3.3 luminescence has a more complicated shape and can be modelled by two-exponential functions with characteristic times of 7 and 51 ns. Under the intra-centre excitation by 4.3 eV photons, the 3.0 eV luminescence of C12A7:F 1% Ce ceramics at 300 K has also a two-exponential decay with time constants of 7 and 20 ns. It is obvious that the longer decay component in all cases is typical for Ce^{3+} 5d–4f transitions, providing an additional proof of the origin of 3.0 eV emission. The appearance of the shorter component needs further detailed studies, but it is very likely that such behaviour is related to the existence of two kinds of Ce^{3+} centres in C12A7. The shortening of decay times of luminescence centre also occurs if there is another channel competing with the radiative decay. One of the centres should have efficient energy transfer channel, whereas the other one is “off-resonance”, providing a typical lifetime of Ce^{3+} in the range of 20–30 ns. In the case of the C12A7: 0.1% Ce sample, such a channel can be due to an overlap of Ce^{3+} d-states with those formed due to excitations of the C12A7 host near the intrinsic absorption. In the case of C12A7:F 1% Ce ceramics, localized energy levels of encaged electrons are at the distance approximately ~ 5 eV from the top of valence band. The energy transfer from the excited 5d states of Ce^{3+} ions to these electrons, causing their transition to the framework conduction band, is sufficient under resonant condition to shorten the decay time to 7 ns for one kind of Ce centre. This is supported by the experimental fact that already excitation into the lowest 5d state creates the short component in Ce^{3+} luminescence.

Fig. 5. Decay curves for emission at 3.1 eV of the C12A7: 0.1% Ce at 300 K excited by laser 5.4 eV (1) and for 3.3 eV emission (3) of the same sample at 10 K excited by 5.8 eV SR photons. Decay curves for 3.0 eV emission (2) of the C12A7:F 1% Ce at 300 K excited by 4.3 eV SR photons. Symbols mark initial experimental data and lines represent results of fitting procedure. Decay curves are shifted in respect of each other for their better visualization.

The determination of 4f ground state positions of rare earths in the energy gap and exact locations of 5d levels is a sophisticated task (see [19] and references therein). For example, according to [20], where such energy level scheme has been constructed for SrAl_2O_4 , which has slightly larger energy gap than C12A7, the Ce^{3+} ground state is positioned ~ 2.8 eV above the top of valence band. In the excitation spectra of C12A7:Ce one can clearly identify Ce 4f–5d peaked at 4.4 eV and thereafter the onset 5.5 eV, above of that both Ce^{3+} and 2.14 eV luminescence of C12A7 host are well excited (see Fig. 4c). Therefore, the electronic excitations above this threshold are related to a superposition of Ce 5d states with those arising from C12A7 host. This is also confirmed by changes in the emission spectra and in the decay kinetics of Ce luminescence in this region. It means also that the ground state position of Ce 4f levels is definitely lower than in SrAl_2O_4 , because of clearly observed 5d excitation band of Ce^{3+} with the high-energy edge at 4.7 eV. The latter one for obvious reasons cannot be located within the conduction band ($E_{4f} < E_g - E_{5d} = 7 - 4.7$ eV = 2.3 eV).

5. Conclusions

We prepared Ce^{3+} doped C12A7 using combustion synthesis and solid state reaction. The samples of latter process were turned into ceramics in the melt-solidification process and were studied by means of luminescence spectroscopy under laser and VUV excitation. It was shown that the revealed luminescence peaked at 3.0 eV is due to Ce^{3+} 5d–4f transitions. This emission is excited through intra-centre Ce^{3+} 4f–5d absorption as well as through host absorption of C12A7 open good perspectives to use this material in luminescence related applications. The decay kinetics of Ce^{3+} emission is complicated possessing the main component of 20–30 ns and fast one of ~ 7 ns.

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