Electronic Excitations and Energy Transfer in A_2SiO_5-Ce (A = Y, Lu, Gd) and Sc_2SiO_5 Single Crystals[1]

V.A. Pustovarov, V.Yu. Ivanov, E.G. Zinevich, V.L.Petrov, B.V. Shulgin, and E.I. Zinin*

Ural State Technical University, Experimental Physics Department, 620002, Ekaterinburg, K-2, Russia

* *Budker Institute of Nuclear Physics of Academy of Science, 630090, Novosibirsk, Russia*

The time-resolved emission spectra (2÷6 eV), reflection and luminescence excitation spectra (4.5÷35 eV) as well as the kinetics of luminescence have been studied for silicates A_2SiO_5-Ce (A= Y, Gd, Lu) and Sc_2SiO_5 single crystals at 10 and 293 K using synchrotron radiation of x-ray (storage ring VEPP-3) or selective vacuum ultraviolet (storage ring DORIS) range. The spectral and decay parameters of impure and intrinsic luminescence are determined. The photon multiplication effect was found for all compounds for energy E > 15 eV (E > 2.5 E_g). A role of electron-hole and exciton mechanisms of energy transfer in silicates and their dependence on temperature are discussed.

1. Introduction

The high density, high light output (comparable in same case with those for NaJ-Tl) and short emission decay time (around thirty ns) of LSO (lutetium orthosilicate, Lu_2SiO_5-Ce), GSO (gadolinium orthosilicate, Gd_2SiO_5-Ce) and YSO (yttrium orthosilicate, Y_2SiO_5-Ce) make this materials the attractive scintillators for gamma and x-ray spectroscopy and detection [1-10]. Besides, they are characterized by non hydroscopically, high temperature, chemical and radiation stability [11]. It is mainly refer to LSO-Ce (after our first publications [4, 5]) and GSO-Ce – the most radiative stable known scintillators [11]. For the successful modification of scintillation properties of known materials as well as the development of new silicate scintillators it is necessary the detail investigation of the energy transfer and dissipation as well as the structure of intrinsic and impurity electronic excitations.

In this paper we obtained and analyzed a time-resolved photoemission, luminescence excitation and reflection spectra (3.5-35 eV) of Y_2SiO_5-Ce (YSO-Ce), Gd_2SiO_5-Ce (GSO-Ce), Lu_2SiO_5-Ce (LSO-Ce), and Sc_2SiO_5 crystals using synchrotron radiation (SR) of vacuum ultraviolet range at 10 and 300 K. The spectral- kinetic parameters of Ce^{3+}-luminescence were estimated at the selective photoexcitation into the ranges of optical transmitting, around fundamental absorption edge and generation of electron-hole pairs. A lot of estimations were made using synchrotron radiation of X-ray range.

2. Experimental Detail

The monocrystals have been grown by Chohralski method by A.M. Korovkin. The samples for investigations have been prepared in shape of planes of 1-2 mm thick and around 10 mm in diameter.

The experiments were performed at the SUPERLUMI station of HASYLAB at DESY [12] using synchrotron radiation. The luminescence in the 2.0-6.0 eV region was analyzed by a Czerny-Turner mounting monochromator equipped with a photomultiplier (PM) R2059 (Hamamatsu). The investigation of an emission in VUV range was performed using a 0.5 m vacuum monochromator equipped with PM R1460 (Hamamatsu). Two in situ interchangeable gratings of the 2 m primary monochromator, Al and Pt coated, were applied in measurements of the luminescence excitation spectra over the 4-35 eV energy range. A typical spectral resolution was 0.25 nm. The luminescence excitation spectra were corrected for the equal number of the exciting photons for each energy region, but the emission spectra are presented as they are measured. Time-resolved spectra were recorded within a time window (length Δt) correlated with the arrival of synchrotron radiation pulses (delay δt). At the present experiments the delay and length were δt_1=2.2 ns, Δt_1=8.2 ns for a fast component, and δt_2=23 ns, Δ

[1] The authors are deeply grateful to U.S. Civilian Research and Development Foundation (CRDF) for partial support this work. This work was also supported by RFBR foundation (grant 00-02-16206) and Russian Ministry of Education (grant 992886).

t_2=111 ns for a slow component. Simultaneously with the excitation, the reflection spectra were recorded at an angle of incidence 17.5° by a XP2230B PM (Valvo) from a sodium salycylate coated window. For comparison the spectral-kinetics features at x-ray excitation we used SR from the VEPP-3 storage ring (Institute of Nuclear Physics, Novosibirsk) with next parameters: E = 3-62 keV, photon flux from 10^{15} to $6 \cdot 10^{16}$ $s^{-1}cm^{-2}$ [13].

3. Experimental Data and Discussion

In emission spectra of Ce-activated silicates at T= 10 K we discovered two groups of emission peaks: the first group situated in lowenergy part of the spectra (2.5-3.5 eV), the second– in highenergy part (3.5-4.5 eV), see Fig.1,2. It should be noted that only lowenergy emission is obtained in the spectra at 300K. When we are interested in the "nature" of emission bands the luminescence excitation spectra demonstrate the most informatively. Such spectra for

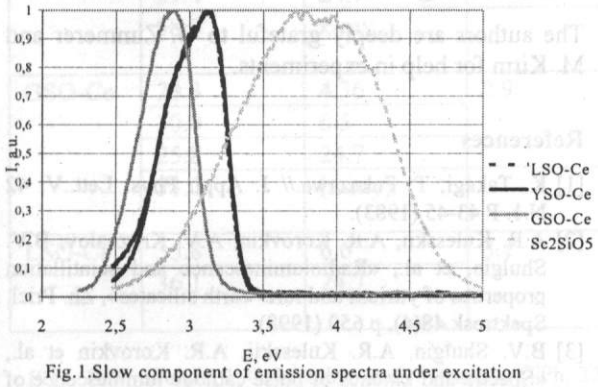

Fig.1.Slow component of emission spectra under excitation 24,7 eV at 300K

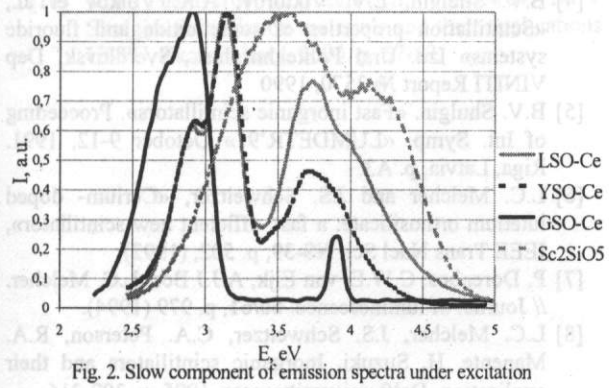

Fig. 2. Slow component of emission spectra under excitation 24,7 eV at 10 K.

our objects are presented on Fig.3. Obviously, than the 2.5-3.5 eV emission is effectively excited in the transparency region of crystals (3.5-5 eV), around fundamental absorption edge, and at higher energies. Consequently we connected this emission with impurity Ce^{3+}-luminescence. Really, this emission is absent for non-activated Sc_2SiO_5 crystal. In contrary 3.5 –4.5 eV emission present in all crystal at 10 K. The luminescence excitation spectra of this emission have not the bands in the transparency region. It should be concluded that 3.5-4.5 eV luminescence is intrinsic crystal luminescence. We didn't discovery this luminescence at 300K. The efficiency of intrinsic highenergy luminescence excitation rises with excitation energy increase (Fig. 5, 6).

The emission spectra of LSO- Ce and YSO-Ce is very similar (Fig. 1,2) , but those for GSO-Ce is

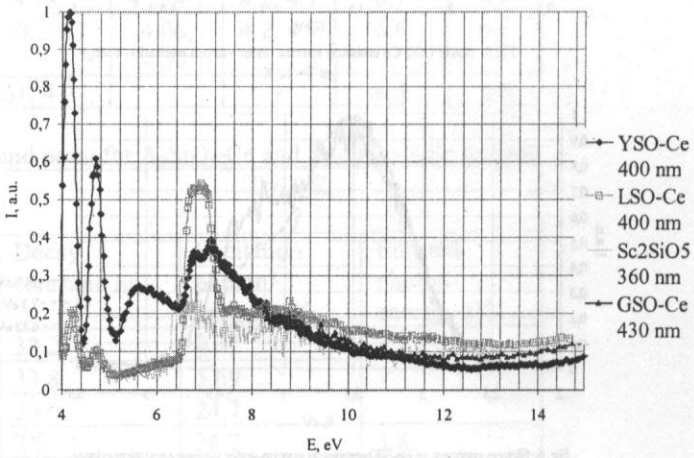

Fig. 3. Fast component of emission excitation spectra at T= 10 K.

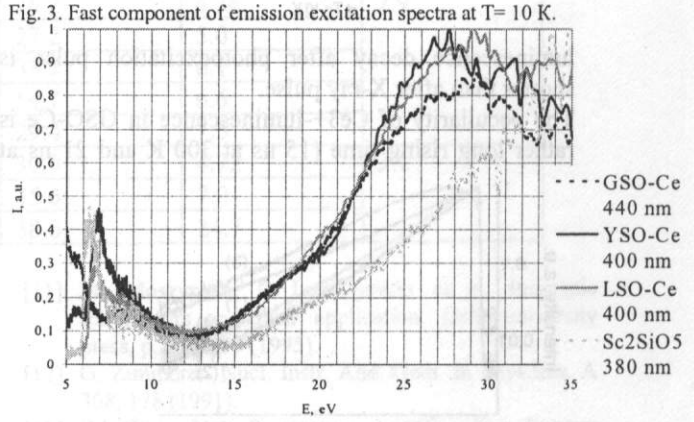

Fig.4. Fast component of emission excitation spectra at T= 300 K

differ. It is can be explained by similar crystal structure (C2/c) of LSO and YSO. Since the crystal structure of GSO is type of $P2_1/C$ [10]. It possible leads to lowenergy displacement of Ce^{3+}-emission peak (Fig.1, 2). Moreover, the spectra of intrinsic luminescence (3.5-4.5 eV) demonstrates the similar two-bands structure for LSO, YSO and Sc_2SiO_5, but has single-peak structure in GSO.

The results of decomposition of emission spectra on Gauss curves are present in Table 1.

Besides, we measured luminescence kinetic decay for intrinsic and impurity emission at various

excitation energy (Table 2, Fig.7 and 8). It should be noted than luminescence decay is usually determined by lot of exponent curves. Consequently, the fact of energy transfer from regular lattice position to Ce^{3+}-center take place. The existence of effective energy transfer determines the absence of intrinsic luminescence at 300K, Fig. 2. In the most cases the

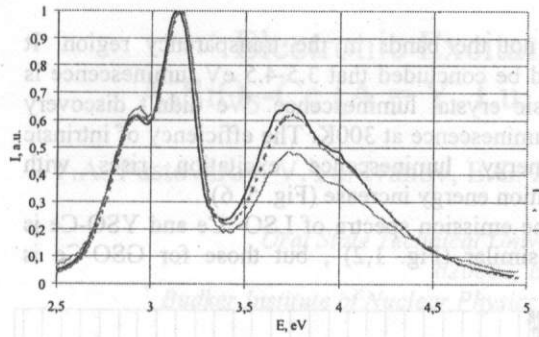

Fig.5. Static LSO-Ce emission spectra under various excitation energy at T= 10 K

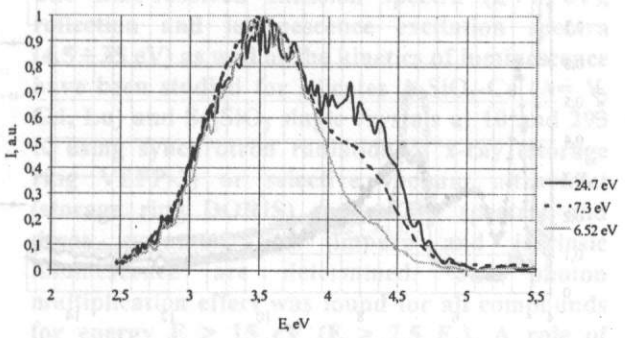

Fig. 6. Slow component of Sc_2SiO_5 emission spectra under various excitation energy at T= 10 K.

luminescence decay after photoexcitation pulse is shorter than after X-ray pulse.

The peculiarity of Ce3+-luminescence in GSO-Ce is rather long rising time (15 ns at 300 K and 21 ns at

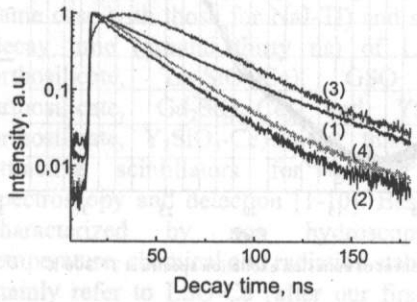

Fig.7. Kinetics of Ce^{3+}-luminescence for Lu_2SiO_5-Ce (1) and Gd_2SiO_5-Ce (2-4) crystals at T=300K: E_{exc}=24,7 eV (1,4); 4,35 eV (2); 6,5 eV (3).

10K) in comparison with other objects where those parameter is negligible. This fact early was obtained at gamma-excitation [11].

We also obtained the effect of photon multiplication (at E_{exc}>15 eV) in excitation luminescence spectra (maximum at region 25-32 eV) for the impurity crystals (see Fig. 4). Its efficiency differs for different crystals, depends from temperature, demonstrates the processes of energy transfer into impurity center and corresponds to the light output at X-rays or gamma-excitation (photon number/MeV).

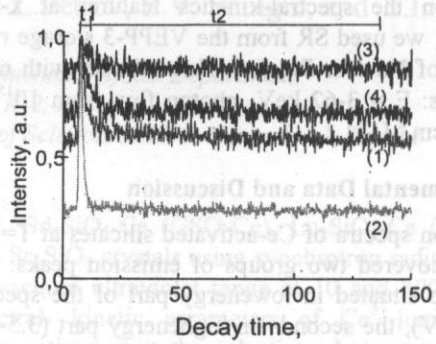

Fig.8. Kinetics of luminescence for Sc_2SiO_5 crystals at T=10K: E_{exc}=7,3 eV (1,4); 6,52 eV (2); 24,7 eV (3); $E_{emission}$=4,27 eV (1-3) and 3.54 eV (4).

4. Acknowledgments

The authors are deeply grateful to G. Zimmerer and M. Kirm for help in experiments.

References

[1] K. Takagi, T. Fukazawa.// J. Appl. Phys. Lett..V. 42 N.1. P 43-45 (1983).

[2] A.R. Kulesskii, A.R. Korovkin, A.V. Kruzhalov, B.V. Shulgin, et al., «Radioluminescence and scintillation properties of yttrium and rare- earth silicates», Zh. Pricl. Spektrosk.**48**(4), p 650 (1998).

[3] B.V. Shulgin, A.R. Kulesskii, A.R. Korovkin et al., «Spectra and kinetics of pulse cathode luminescence of Y_2SiO_5-Ce, Tb» Optica i spectroskopiya, V **68** (4) p.

[4] B.V. Shulgin, L.V. Viktorov, A.R. Volkov et al., «Scintillation properties of some oxide and fluoride systems» Izd. Ural Politekhn. Inst., Sverdlovsk, Dep VINITI Report № 3570, 1990

[5] B.V. Shulgin. «Fast inorganic scintillators». Proceeding of Int. Symp. «LUMDETR'91» October 9-12, 1991. Riga, Latvia, p. A3.

[6] L.C. Melcher and J.S. Schweitzer, «Cerium- doped lutetium orthosilicate: a fast, efficient new scintillator», IEEE Trans Nucl Sci, **NS-39**, p. 502, (1992).

[7] P. Dorenbos, C.W.E. van Eijk, A.J.J Bos, L.C. Melcher. // Journal of luminescence. **60/61**, p. 979 (1994).

[8] L.C. Melcher, J.S. Schweitzer, C.A. Peterson, R.A. Manente, H. Suzuki. Inorganic scintillators and their application. Delft university press, 1995, p. 309-316.

Table 1. Luminescence and excitation parameters for A_2SiO_5-Ce and Sc_2SiO_5single crystals

	Position of luminescence bands, eV, for 24.7 eV excitation energy				Position of luminescence bands, eV			
	Ce^{3+} luminescence		Intrinsic luminescence		Ce^{3+} luminescence		Intrinsic luminescence	
Crystal	295 K	10 K	295 K	10 K	295 K	10 K	295 K	10 K
GSO-Ce	2.78, 2.94	2.75, 2.95	-	3.9	4.2, 4.9	<3.8	6.4	6.6
YSO-Ce	2.96, 3.17	2.91, 3.16	-	3.78	4.2, 4.7	4.2, 4.7	6.7	6.8
LSO-Ce	2.96, 3.17	2.91, 3.15	-	3.70, 3.87	4.06, 4.72	4.2, 4.7	6.6	6.8
Sc_2SiO_5	-	-	3.77, 4.23	3.51, 4.27	-	-	6.3	6.6

Table 2. Decay constant for selected luminescence band point for A_2SiO_5-Ce and Sc_2SiO_5single crystals

Crystal	T=295 K			T=10 K		
	Decay constant, ns	Excitation photon energy, eV	Emitted photon energy, eV	Decay constant, ns	Excitation photon energy, eV	Emitted photon energy, eV
YSO-Ce	35.3	4.7	3.1	33.2	4.77	3.1
	39.4	24.7		33.8	5.69	
	58.0	x-ray		26.0	24.7	
				7.5	24.7	3.8
GSO-Ce	23.3	4.36	2.9	26.2	4.36	2.9
	30.0	6.5		27.2	5.0	
	25.8	24.7		33.7	6.1	
	33.0	(x-ray)		54.7	6.6	
				29.4	7.5	
LSO-Ce	35.8	6.6	3.1	30.9	4.72	3.1
	36.1	24.7		35.6	7.0	
				38.6	24.7	

[9] B.V. Shulgin, L.C. Melcher et al.// Pisma v JTPh. 22, №5 p 41 (1996).

[10] V.A. Pustovarov, E.G.Zinevich, V.L.Petrov, B. V. Shulgin. Scintillation materials and their applications. USTU, Ekaterinburg, 2000, p. 67-69.

[11] M. Moszynski, T. Ludziejevski et al. Inorganic scintillators and their application. Delft university press, p. 372-375 (1995).

[12] G. Zimmerer, Nucl. Instr. And Meth. In Phys.Res. A 308, 178 (1991).

[13] E.I. Zinin, V.A. Pustovarov, A.L. Rogaljov. Reports of VUV-89 Conf.. Irkutsk,. C.282-283. (1989).