Deep VUV Scintillators for Detectors Working in Cryogenic Environment

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Abstract—The properties of various inorganic scintillator materials with different origin of their VUV luminescence have been studied under pulsed excitation by XUV (50–1000 eV) synchrotron radiation. A comparison of spectral and timing characteristics of these crystalline VUV emitters has been performed. The processes of energy transfer from the host crystal to the luminescence centers of different nature were analyzed from the features of excitation spectra in the regions of inner-shell absorption.

Index Terms—Crossluminescence, excitons, fast VUV luminescence, inorganic scintillators, rare earth ions, synchrotron radiation.

I. INTRODUCTION

THERE exists a growing demand for VUV inorganic scintillators working at low temperatures. For example, experiments on dark matter detection use liquid xenon and argon scintillators, which emit at 175 and 128 nm, respectively [1]. For the development of detection units working in a cryogenic environment, it is very important to have a compact test set-up using scintillator emission in the VUV range at low temperatures with a constant luminescence yield.

Several inorganic scintillator materials with low-temperature VUV luminescence can be proposed for such a test facility. Crossluminescence (CL) materials based on KF binary compounds (KMgF_3 , KYF_4 , KLuF_4) emit fast broadband emission ($\tau \sim 1$ ns) in the range of 140–200 nm [2], [3]. The light yield of such scintillators is rather low, which is characteristic for CL. The crystals also emit slow luminescence originating from self-trapped excitations (STE), but at lower energy in the UV region. In MgO very fast (decay time in picosecond range) and intense VUV emission at 162 nm is observed due to edge luminescence of excitons, accompanied by other slow emissions in the longer wavelength region [4], [5]. Al_2O_3 crystals possess fast (~ 7 ns) excitonic luminescence at 166 nm in addition to other fast and slow emissions in the UV region, originating from F^+

and F centers, respectively [6], [7]. Many wide band gap crystals (mainly fluorides but also some oxides) doped with Nd^{3+} , Er^{3+} , or Tm^{3+} emit VUV luminescence due to interconfigurational $5d - 4f$ transitions of the respective ion. This luminescence occurs in the range of 160–200 nm depending on the matrix and on the particular ion (see, e.g., [8], [9]). In most cases, the light yield of such scintillators is also quite low. In addition, Er^{3+} and Tm^{3+} doped crystals emit mainly slow VUV luminescence. Our recent studies [10]–[12] have shown that several wide band gap materials containing Gd^{3+} ions emit VUV luminescence at ~ 125 nm due to $5d - 4f$ transitions in Gd^{3+} with decay times in the range from ~ 1 to 8.5 ns, depending on the matrix. To the best of our knowledge, this is the shortest-wavelength (fast) emission observed from ionic materials.

In the present work, low-temperature luminescence of materials mentioned above was studied under tunable XUV excitation (50–1000 eV) by synchrotron radiation from an undulator source at the DORIS storage ring to investigate the scintillators under realistic conditions.

II. EXPERIMENTAL DETAILS

The experiments were carried out using a low temperature luminescence set-up for the VUV spectral region connected to the undulator beam-line BW3 of HASYLAB at DESY [13]. Photons generated by two interchangeable undulators are tunable in the energy range of 30–2000 eV by means of Zeiss SX700 monochromator. Luminescence was detected with a 0.4-m monochromator in Seya–Namioka mounting equipped with a microchannel plate type PMT (Hamamatsu 1645 U-09). The spectral working range $\lambda = 110$ –500 nm of this device was limited on the short-wavelength side by the transmission of the MgF_2 window of the PMT, and on the long-wavelength side by the mechanics of the monochromator. The effective time resolution of the detection system was 300 ps (FWHM), with a 130 ps length of the exciting synchrotron pulses. Discrimination between the fast and slow emission was achieved by measuring signals within “short” and “long” time windows (Δt) delayed (by δt) with respect to the excitation pulses of synchrotron radiation. The optical resolution of the analyzing monochromator was typically 2 nm.

The following single crystalline samples were studied in this work under XUV excitation: KMgF_3 , MgO , Al_2O_3 , LiGdF_4 , and GdF_3 . To ensure clean surfaces, most of the crystalline samples were cleaved prior to mounting onto the sample holder, which was attached to a flow-type liquid helium cryostat. The typical size of the irradiated surface of the samples was 5×5 mm² and the thickness ~ 1 mm.

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Fig. 1. Fast component (dashed curve, $\Delta t = 5.6$ ns, $\delta t = 0.15$ ns) and time-integrated (solid curve) luminescence spectra of KMgF_3 measured under excitation by 130 eV photons at a temperature of 10 K. Inset shows decay of fast component (crossluminescence) with gradual shortening of the decay under excitation by photons with increasing energies: 50, 80, and 302 eV. Solid lines are the best fits of decay curves by two-exponential decay law for excitation by 50 and 302 eV photons (Log scale is used).

III. RESULTS AND DISCUSSION

The luminescence properties and processes of the energy transfer in different VUV-emitting scintillator materials were compared through the analysis of emission and excitation spectra, as well as luminescence decay curves obtained under excitation in the spectral regions corresponding to inner-shell absorption.

In the excitation spectra measured in the XUV region a characteristic decrease of luminescence intensity is usually observed at photon energies corresponding to maxima of absorption. This behavior of the spectra is explained by increased nonradiative near-surface losses of excitations for higher absorption coefficients. Accordingly, excitation and absorption spectra show opposite behavior. In addition, some changes of luminescence decay times are usually observed under variation of excitation energy because of the different quenching mechanisms. However, the influence of these factors strongly depends on the nature of luminescence in a particular crystal and on the mechanisms of the energy transfer from the host crystal to the luminescence centers.

A. Crossluminescence From KMgF_3

CL is a specific kind of intrinsic luminescence of ionic crystals, which is also called core-valence luminescence, or Auger-free luminescence. It is due to radiative recombination of electrons from the valence band with the holes in the uppermost core band. CL exists in those ionic crystals, in which the Auger-decay of the holes in the uppermost core band is energetically forbidden. CL is observed only from 6 binary ionic crystals (BaF_2 , CsF , CsCl , CsBr , RbF , KF), but is also observed from many ternary and multi-component crystals based on combinations of these 6 binary compounds. The shortest-wavelength radiation is emitted by KF-based CL crystals.

Emission spectra of the fast component (CL) and time-integrated luminescence (CL + STE) obtained from a pure KMgF_3 crystal at 10 K under 130 eV excitation are presented in Fig. 1.

Fig. 2. Decay times of crossluminescence from KMgF_3 (at a temperature of 10 K) showing shortening of the decay under excitation by photons with increasing energies. Decay curves were fitted by two-exponential decay function. The lines are drawn only for better visualization of data.

Fig. 3. Excitation spectra of crossluminescence ($\lambda_{\text{em}} = 150$ nm, dotted curves) and self-trapped exciton emission ($\lambda_{\text{em}} = 325$ nm, solid curves) from KMgF_3 crystal at 10 K in the range of the $K\ 2p$ and $F\ 1s$ absorption. Note the different energy scale for two parts of the Figure.

The CL spectrum consists of two bands centered at 150 and 170 nm. The STE emission band has its maximum at 325 nm. The decay time of CL is of the order of 1 ns, but the decay law is not single-exponential for any of the excitation energies (see Fig. 2). The decay becomes shorter with increasing excitation energy in the range up to ~ 300 eV and practically does not change for higher excitation energies, including the region above the $F^- 1s$ absorption. The decay curves can be fitted well by a two-exponential decay function with decay components shown in Fig. 2.

Fig. 3 shows the excitation spectra for CL (150 nm) and STE (325 nm) emission in a pure KMgF_3 in the energy ranges covering the $K^+ 2p$ and $F^- 1s$ absorption edges. Maxima in the absorption coefficient cause minima in the excitation spectra at 298.5 and 301 eV corresponding to the doublet of $K^+ 2p_{3/2}$ and $2p_{1/2}$ states, in accordance with typical behavior of excitation spectra under inner-shell absorption. However, the depth of minima is larger for STE luminescence. This is due to the much shorter lifetime of excitations for CL (~ 1 ns) compared to STE luminescence (at least many μs). Accordingly, the diffusion length $L = (D\tau)^{1/2}$, where D is diffusion coefficient, is much smaller for CL, leading to a weaker influence of near-surface losses on CL compared to STE emission. The intensity of

Fig. 4. Luminescence spectra of MgO single crystal measured under excitation by 130 eV photons at 10 K. The bandwidth is determined here by the spectral resolution of the monochromator which is ~ 1 nm. Inset shows decay of edge luminescence of excitons (Log scale is used).

STE luminescence decreases also at the $F^- 1s$ edge, whereas that of CL increases in this spectral region. Such a behavior of the excitation spectrum of CL near $F^- 1s$ absorption edges has been reported earlier for a BaF_2 crystal [14], [15].

A peculiar behavior of the excitation spectrum for CL in a $KMgF_3$ crystal at the $F^- 1s$ edge can be interpreted similar to a BaF_2 crystal [15] as an inter-atomic (F-K) cross-relaxation process of holes. The increase of CL intensity above the $F^- 1s$ edge means that the Auger decay of the $F^- 1s$ core hole finally creates the $K^+ 3p$ shell holes needed for CL. The mechanism behind the process was proposed in [16], which explains the effect by resonant electron-transfer relaxation between the outer np level of the metal ion and the $2p$ level of fluorine ion studied for alkali metal and alkaline-earth fluorides using Auger spectroscopy. Among all alkali fluorides this effect is strongest just for potassium fluoride.

B. Edge Luminescence of Excitons From MgO

Pure MgO emits narrow-band luminescence at 162 nm (Fig. 4) under XUV excitation at low temperature. This emission is due to edge luminescence of excitons [4], [5] which is interpreted as luminescence of free or bound excitons of large radius in regular or defect-related sites of the crystal. Although the peak intensity of narrow-line excitonic emission from MgO is rather strong, the integrated emission intensity in comparison with lower energy luminescence bands (see [5] and references therein) is not very high. The decay time of the luminescence of large radius excitonic states of MgO is in picosecond range, i.e., very high time resolution can be obtained with this scintillator material. As depicted in the inset of Fig. 4, the dominating ultrafast component conforms to the instrumental response of the detection system. The edge luminescence of excitons is practically quenched at $T = 120$ K. However, rather weak and thermally broadened structures in VUV can be detected in MgO at room temperature as well, but the efficiency of this emission is too small for any applied purpose.

Luminescence properties of MgO have already been investigated under excitation by XUV radiation covering the Mg $2p$ and $O 1s$ absorption edges [13]. The excitation spectrum of MgO excitonic luminescence shows a typical “inverted”

Fig. 5. Luminescence spectra of non-irradiated and electron-irradiated α - Al_2O_3 single crystals measured under excitation by 535 eV photons at 10 K.

behavior with respect to the absorption spectrum at the Mg $2p$ edge. Recently, MgO crystals have been studied near the $O 1s$ edge using X-ray fluorescence spectroscopy, resulting in high quality absorption spectra [17]. A detailed comparison (not shown) with that one confirms that the efficiency of edge exciton luminescence has a positive jump at the $O 1s$ edge, whereas other emissions exhibit normal behavior. This effect was interpreted in [13] as the result of an increased probability of valence exciton formation under excitation at the $O 1s$ edge, since the main decay channels of the $O 1s$ core hole create mainly valence holes, which thereafter tend to form excitons.

C. Luminescence of Self-Shrunk Excitons From Al_2O_3

Emission spectra of α - Al_2O_3 single crystals under 535 eV excitation at 10 K are shown in Fig. 5. The measurements were performed in particular for a crystal which was previously irradiated in air at room temperature by 50 MeV electrons with a fluence of 6×10^{17} e/cm². The fast broadband VUV intrinsic emission at 166 nm dominates in the spectrum of non-irradiated α - Al_2O_3 . It is well known that this emission is effectively excited at the direct optical creation of excitons in the region 8.8–9.3 eV or at the recombination of free electrons and free holes under high-density excitation by electron beam [6], [7]. Since no evidence of self-trapping for both electrons and holes has been obtained for Al_2O_3 , the 166 nm emission was ascribed to the radiative decay of self-shrunk excitons (see [6] and references therein). Such kind of immobile excitons can exist in a system where an electron and a hole do not separately undergo self-trapping, while the sum of their deformation potentials is sufficient for the recombination formation of a localized exciton. Various exciton formation mechanisms from free and self-trapped carriers (i.e., electron and holes) in the field of acoustic phonons have been theoretically analyzed in [18]. The studied crystal shows also luminescence of F^+ (325 nm) and F (400 nm) centers primarily resulting from electron irradiation.

The excitation spectra of both excitonic (166 nm) and F^+ center (325 nm) luminescence were measured in the energy range of the Al $2p$ -edge (75–130 eV) and O $1s$ -edge (535–575 eV). The obtained excitation spectra of those emissions (not shown) are similar to the spectra obtained in [13] for excitonic luminescence of (non-irradiated) α - Al_2O_3 and its

Fig. 6. Decay curves of excitonic luminescence (at 166 nm) from Al_2O_3 measured at a temperature of 10 K under excitation by photons with different energies: 77, 79, 92, 100, 120, 126 and 150 eV. Solid curves are best fits with three-exponential decay for excitation energies 77 and 150 eV.

features are “inverted” with respect to absorption spectrum of $\alpha\text{-Al}_2\text{O}_3$ at both edges.

The decay curves of excitonic emission from $\alpha\text{-Al}_2\text{O}_3$ are presented in Fig. 6. No remarkable difference was found for decay curves measured from non-irradiated and electron-irradiated samples under excitation by photons with the same energies. The decay law is always non-exponential with a considerable contribution of the slow emission component. Remarkable changes of decay kinetics can be seen under excitation by photons of different energies. In particular, the initial stage of decay becomes faster for excitation by photons of higher energies. The decay curves can be well simulated by a three-exponential decay function, e.g., for excitation by 77 eV with $\tau_1 = 1.06$ ns, $\tau_2 = 7.8$ ns, $\tau_3 = 56.3$ ns and for excitation by 150 eV with $\tau_1 = 1.05$ ns, $\tau_2 = 7.1$ ns, $\tau_3 = 53.7$ ns (see Fig. 6). These features indicate a rather complicated mechanism of creation of self-shrunk excitons under XUV excitation, as well as the presence of some quenching of excitonic luminescence for excitation by high-energy photons. For comparison, in highly pure Czochralski grown $\alpha\text{-Al}_2\text{O}_3$ the decay of the 7.6 eV intrinsic excitonic emission observed after excitation with 8.98 eV photons has a lifetime of 7 ns. The luminescence decay is well described by a single exponential [19].

D. $5d - 4f$ Luminescence of Gd^{3+} Ions in Fluoride Matrices

Recently it has been found that several Gd^{3+} containing wide band-gap fluoride crystals possess fast luminescence in the VUV spectral range due to interconfigurational $5d - 4f$ transitions in Gd^{3+} [10]–[12]. It is well known that some trivalent rare earth (RE) ions show radiative decay from their mixed $4f^{n-1}5d$ electronic configuration, i.e., such RE ions emit so called $5d - 4f$ luminescence. This luminescence is caused by transitions from the lowest level of $4f^{n-1}5d$ electronic configuration ($5d$ level) to the ground state or some excited levels of $4f^n$ electronic configuration of the RE^{3+} ion. For the first half of the lanthanide series, transitions from the lowest $5d$ level into the $4f$ levels are spin-allowed and $5d - 4f$ luminescence is fast with typical lifetimes in the nanosecond range. In the

Fig. 7. VUV luminescence spectra of three Gd^{3+} containing compounds measured at 10 K. Spectra were recorded under VUV excitation with a spectral resolution of 0.05 nm [10]–[12].

Fig. 8. Decay curves of VUV luminescence from different Gd^{3+} containing compounds measured under direct $4f - 5d$ excitation. The respective decay times are indicated in the Figure. The time profile of SR excitation pulse (including instrumental response) is also shown.

second half of series, transitions from the lowest $5d$ state are spin-forbidden, and such $5d - 4f$ luminescence is slow with lifetimes in the μs range.

Examples of VUV emission spectra due to $5d - 4f$ transitions in Gd^{3+} are shown in Fig. 7. The spectra from the LiGdF_4 and $\text{CaF}_2 : \text{Gd}^{3+}$ crystals have maxima at ~ 126.5 and 129.5 nm respectively and show well-pronounced fine structure due to zero-phonon lines and vibronics. The spectrum from $\text{LiYF}_4 : \text{Gd}^{3+}$ (not shown here) has nearly the same shape as that from the LiGdF_4 crystal but is slightly shifted to longer wavelengths. The VUV emission spectrum of GdF_3 is situated at shorter wavelengths than all other studied crystals and shows a single structureless band centered at ~ 125 nm. A similar emission spectrum is observed from $\text{YF}_3 : \text{Gd}^{3+}$ (not shown). The decay times of VUV luminescence from all Gd^{3+} -containing samples are in the nanosecond range. Fig. 8 presents the survey of data from [10]–[12] on $\text{Gd}^{3+} 5d - 4f$ luminescence decay under VUV excitation in different Gd^{3+} -containing compounds. At $T \sim 10$ K, the following decay times were obtained: 8.5 ns for $\text{CaF}_2 : \text{Gd}^{3+}$, 2.8 ns for LiGdF_4 , 2.5 ns for $\text{LiYF}_4 : \text{Gd}^{3+}$, 0.97 ns for GdF_3 , and 1.1 ns for $\text{YF}_3 : \text{Gd}^{3+}$.

VUV luminescence from all Gd^{3+} compounds is observed only at low temperatures. As an example, the temperature dependence of VUV luminescence from $\text{LiYF}_4 : \text{Gd}^{3+}$ (10%) is shown in Fig. 9. The emission spectra were measured here with

Fig. 9. Temperature dependence of the VUV luminescence from $\text{LiYF}_4 : \text{Gd}^{3+}(10\%)$. In the inset, the integrated intensity of the emission is plotted as a function of temperature, together with the simulation curve obtained as the best fit with the Mott formula. E_a is activation energy of thermal quenching.

a moderate spectral resolution in order to prevent possible radiation damage, and accordingly the fine structure in the spectra was not revealed. The dependence of integrated luminescence intensity on temperature was approximated by the Mott formula, $I(T)/I(0) = (1 + A \exp(-E_a/k_B T))^{-1}$ (shown in the inset of Fig. 9). An activation energy $E_a \sim 65$ meV for thermal quenching was obtained from the fit. Around 250 K, the VUV luminescence is quenched completely. Thermal quenching of $\text{Gd}^{3+}5d-4f$ luminescence is attributed to phonon assisted non-radiative relaxation from the lowest $\text{Gd}^{3+}5d$ level to lower-lying $4f$ levels (many $4f$ levels are located in the same energy region as the $5d$ state). The direct $5d-4f$ non-radiative transitions (at low temperature) are heavily spin-forbidden [10]–[12].

The possible dependence of decay properties of VUV luminescence from Gd^{3+} containing materials upon photon energy of irradiation has been analyzed under excitation of the samples around the $\text{Gd}^{3+}4d$ absorption edge (see Fig. 10). The absorption coefficient is strongly increased in this region (known as “giant resonance” [20]), resulting in smaller thickness of the layer in which radiation is absorbed and accordingly to stronger near-surface losses. Indeed, excitation and absorption spectra show “inverted” behavior in this region. However, no remarkable changes of decay curves (shown in the inset of Fig. 10) have been observed for different excitation photon energies although some shortening of decay (the appearance of the faster initial stage of decay) is observed under XUV excitation compared to direct $4f-5d$ excitation by VUV radiation.

One more type of VUV emitters exists which is based on $5d-4f$ luminescence of Lu^{3+} ion incorporated into wide band-gap fluoride matrices [10], [11]. The wavelengths of these emissions are even shorter (124 nm) than those of Gd^{3+} based emitters. However, the decay for such kind of luminescence is slow because it is due to spin-forbidden $5d-4f$ transitions.

E. General Consideration

The main characteristics of VUV luminescence from the studied crystals are listed in Table I. The estimation of the relative light outputs of different scintillator materials under

Fig. 10. Excitation spectra of fast (circles, $\Delta = 1.75$ ns, $\delta = 0.37$ ns) and time-integrated (solid curve) VUV luminescence from GdF_3 crystal at 9 K in the range of the $\text{Gd } 4d$ absorption. The inset shows decay curves of VUV luminescence measured under excitation by photons of different energies.

TABLE I
MAIN PROPERTIES OF DIFFERENT VUV EMITTERS

Crystal	Emission wavelength (nm)	Decay time (ns)
KMgF ₃	150, 170	~1.5
MgO	162	<0.2
Al ₂ O ₃	166	~7
LiGdF ₄	126.5	2.8
LiYF ₄ :Gd	127	2.5
GdF ₃	125	1

XUV excitation is not an easy task, since the studied scintillators show narrow emission lines as well as broadband luminescence with very different efficiencies. Therefore luminescence spectra were recorded using different settings (slit widths) in the excitation as well as in the detection channel, which introduces uncertainties in quantitative comparison of light yields of studied materials. The integrated intensity of broadband emissions (Al_2O_3 , KMgF_4) is higher than that of edge emission observed from MgO . The d-f emissions in LiGdF_4 and GdF_3 , however, produce less light compared to VUV luminescence of pure MgO . In addition, the selection of excitation energy plays a significant role because the location of inner-shell edges strongly influences absorption as well as relaxation processes in the scintillators. Nevertheless, taking into account above-mentioned limitations, such investigations provide useful information about relative light yields, since each XUV photon creates many electron-hole pairs in the crystal, similar to the processes of energy dissipation in the scintillator under irradiation by high-energy photons or particles.

The specific spectral and temporal behavior of VUV luminescence in different crystals is due to the features of energy transfer mechanisms for each kind of luminescence: CL, different kinds of excitonic emission, d-f luminescence of rare earth ions. In most scintillating crystals, the so-called recombination mechanism is responsible for the energy transfer from the host crystal to luminescence centers, which are usually some impurity ions. This mechanism suggests that one carrier (e.g., a hole) is first captured by the impurity ion and then the partner

(electron) recombines with this hole resulting in excitation of the ion to some excited level. Both processes are fast and do not lead to any increase of luminescence decay time. However, the processes of carrier trapping by some other traps (defect centers), in particular hole self-trapping, can compete with the capture of carriers by the luminescence centers. In this case some delay of the energy transfer to luminescence centers can occur resulting in slower decay of luminescence, sometimes with an initial rising part in the luminescence timing profile with a duration corresponding to characteristic time of the energy transfer process.

In the case of “conventional” scintillators based on luminescence of some impurity ions excited via the recombination mechanism, it is usually assumed that practically all electrons and holes created after the absorption of high-energy photon with energy $E\gamma$ will recombine eventually at the luminescence centers. If the intrinsic luminescence quantum efficiency of the luminescence centers is unity, the light yield of the scintillator η will be determined by the number of created electron–hole pairs n_{e-h} . This can be expressed as: $\eta \sim n_{e-h} = E\gamma/\beta \cdot E_g$, where β is the conversion efficiency for creating electron-hole pairs [21]–[23]. As was found both from experiments and theory, β is about 2–3 times higher than the band-gap energy E_g . However, it seems that the recombination mechanism and accordingly the above estimation of the light yield are not applicable to all crystals studied here, in particular because of rather high energies of the emitted photons.

A good approximation for the energy that can be transferred from the host to the luminescence center by the recombination mechanism is the photon energy of STE emission (if it exists). This value also limits the maximum energy of photons that can be emitted from the luminescence center. In all such crystals there is a rather large Stokes shift (several eV) between the energy of direct optical creation of (free) excitons (which is less by few tenths of eV than the value of the band-gap E_g) and the photon energy of STE emission. Accordingly, one cannot expect that the recombination mechanism works if the energy of emitted photons is close to the value of the band-gap.

The mechanism of the energy transfer for CL is obviously different and rather specific. CL is observed only if the hole is created in the (uppermost) core band. This leads to quite a moderate light yield in any CL scintillator (~ 1500 photons/MeV) since it is necessary to “spend” considerably more energy for the creation of one photon of luminescence than for the case of creation of the hole in the valence band. However, the main factors determining the low light yield of CL scintillators are fast electron thermalization and core hole Auger decay [24]. On the other hand, no delay of the energy transfer is possible for CL since the core hole disappears in any case after its creation either radiatively via CL or as a result of Auger decay. Therefore, scintillation will be always fast for CL scintillators. Some weak dependence on excitation energy of CL decay time is due to different quenching mechanisms of CL [3], which are rather weak for such high-penetration radiation as γ —rays. A detailed analysis of CL quenching mechanisms in BaF_2 under XUV excitation has been carried out in [25].

No self-trapping of excitons, electrons or holes has been detected in MgO crystals, i.e., no other types of intrinsic lumines-

cence are observed from pure MgO except for the narrow edge emission due to large radius excitons. Doping with iso-electronic Ca^{2+} and Be^{2+} ions introduces small radius states, which emit broadband luminescence with maxima at 7.0 and 6.3 eV, respectively [5]. Latter emissions have higher integrated intensity, but their decay time is considerably longer (in ns range) and the achievable time-resolution is not so good as for pure MgO scintillator.

The 166 nm emission from Al_2O_3 is due to luminescence of so-called self-shrunk excitons. This kind of immobile excitons can exist in a system where an electron and a hole do not separately undergo self-trapping while the sum of their deformation potentials is sufficient for the recombination formation of a localized exciton [18]. Under high-energy excitation, the prevailing mechanism of formation of such excitons is the recombination of free electron-hole pairs, which is not efficient for band-to-band excitation by low-energy photons creating single electron-hole pairs. However, under XUV excitation the local density of electron-hole pairs created after the absorption of each high-energy photon is strongly increased and the probability of electron-hole recombination becomes much higher, resulting in rather high light yield of excitonic luminescence. The process of electron-hole recombination can be delayed by the presence of existing defects/traps. As a result, the decay becomes non-exponential with considerable fraction of the slow emission component.

An interesting comparison can be made with the luminescence characteristics of free and self-trapped excitons in rare gas solids (RGS) under XUV excitation [26]. Due to the lack of optical phonons in these mono-atomic crystals, energy relaxation of conduction band electrons occurs on a nanosecond timescale. This allows the distinction between prompt exciton luminescence from primary excitons that are created directly during the excitation, and delayed secondary excitons from electron-hole recombination processes. Under XUV excitation, conduction electrons with high kinetic energies are created, which can create additional prompt secondary excitons, if their kinetic energy exceeds the energy of a free exciton [27]. The prompt creation of excitons occurs through an electron-electron scattering process, which is essentially the same impact mechanism as discussed below in more detail for excitation of 5d states of rare earth ions. The thresholds for this process can be clearly observed in time-resolved excitation spectra for the exciton luminescence in RGS in the region of valence and core excitations as summarized and analyzed in [28].

The mechanism of the energy transfer from the host crystal to $\text{Gd}^{3+}5d - 4f$ luminescence cannot be the recombinational one since too much energy (~ 10 eV, i.e., close to the band-gap value) should be transferred to the Gd^{3+} ion in order to excite it to the 5d level. This fact is confirmed by measurements of $\text{Gd}^{3+}5d - 4f$ luminescence excitation spectra in the region $h\nu > 12$ eV, corresponding to band-to-band transitions of the host crystals, where no $\text{Gd}^{3+}5d - 4f$ luminescence was detected [10]–[12]. The dominant mechanism of the energy transfer in these systems is so-called impact mechanism, when fast photoelectrons excite directly (by impact) the Gd^{3+} ions to the 5d level. For this process, the kinetic energy of such electrons must exceed the energy of 4f-5d excitation E_{fd} , i.e., the photon en-

ergy of exciting radiation needs to be above the value $E_g + E_{fd}$ which is ~ 22 eV for LiGdF_4 and GdF_3 . The presence of this mechanism can be clearly seen in excitation spectra of $\text{Gd}^{3+}5d - 4f$ luminescence measured in this region, where the threshold is observed for the Gd^{3+} luminescence excitation at photon energies $h\nu \sim 22$ eV [29]. The same impact mechanism has been demonstrated to occur for excitation of $\text{Er}^{3+}5d - 4f$ luminescence in fluoride crystals [30]. A comprehensive study of impact mechanism by methods of photoelectron and luminescence spectroscopy has been performed for Ti^{3+} impurity ions in alkali chlorides [31]. The efficiency of the impact mechanism of the energy transfer cannot be very high. However, for compounds with high concentration of Gd^{3+} ions, in particular for stoichiometric compounds, one can expect to obtain a light yield of the same order as for the well-known UV scintillator CeF_3 , in which the same impact mechanism is responsible for the scintillation emission due to $5d - 4f$ transitions of Ce^{3+} [32], [33]. Taking into account that the photon energy of Gd^{3+} VUV luminescence is roughly 2.5 times larger than the photon energy of CeF_3 emission, one can expect a light yield of stoichiometric Gd^{3+} compounds up to ~ 1600 photons/MeV. However our measurements have shown that the real light yield is much lower. The reason of this is most probably due to the fact that the efficiency of the impact mechanism decreases with the increase of the energy, which should be transferred to the excited ion by fast photoelectron.

The inverted behavior of the absorption spectrum and excitation spectrum of $\text{Gd}^{3+}5d - 4f$ luminescence can be explained by near-surface losses of (fast) photoelectrons. However, if the electron has excited (by impact) the Gd^{3+} ion into the $5d$ state, the energy will not be lost by the Gd^{3+} ion because of the localized type and short lifetime of the $5d$ excitation. Accordingly, the decay time of $\text{Gd}^{3+}5d - 4f$ luminescence under XUV excitation will be roughly the same as under $4f-5d$ excitation. However, some shortening of decay can appear due to quenching caused by interaction of neighbor excitations, the local density of which can be rather high under XUV excitation.

IV. CONCLUSION

Inorganic materials offer a variety of VUV scintillators, which have very different spectral and temporal properties. The Gd^{3+} -containing fluoride compounds show the shortest-wavelength emission, which overlaps spectrally with emission of liquid argon, but they have the lowest light yield among all studied VUV emitters. Al_2O_3 has a much higher light yield of VUV emission, but timing properties of this emission are not optimal, with a considerable contribution of the slow emission component. MgO excitonic emission has very fast decay and a high-intense narrow-line spectrum but its spectrally integrated emission intensity is not as high as that of broad-band emission from CL scintillators. CL crystals (KF-based) can be considered as the best VUV scintillator among those studied in this work, with relatively high light yield and fast (~ 1 ns) decay, but its emission spectrum does not fit well the spectral range of emission from liquid xenon and argon scintillators. The general recommendation is that according to the specific need of the particular application, VUV emitters with the required performance have to be selected.

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