Luminescence and ultraviolet excitation spectroscopy of SrI_2 and $SrI_2:Eu^{2+}$

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HIGHLIGHTS

► Luminescence properties of SrI_2 and SrI_2:Eu single crystals have been investigated.
► Excitation spectroscopy technique using synchrotron radiation was applied.
► Excitonic properties in nominally pure and europium doped crystals have been studied.

ARTICLE INFO

ABSTRACT

We report measurements of luminescence and its ultraviolet excitation spectra in SrI_2 and $SrI_2:Eu^{2+}$ at temperatures of 10 and 300 K. Attention is focused on determining the exciton energy and its temperature shift from features of the excitation spectra and limits placed by absorption spectroscopy on a 120 μm thin crystal, on observation of a broadened Eu emission band attributed to trace Eu associated with oxygen in nominally undoped crystals, and on adding observations concerning the 3.4 eV band at low temperature attributed by Pustovarov et al. to the self-trapped exciton.

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1. Introduction

$SrI_2:Eu^{2+}$ was first proposed and patented as a scintillator by Hofstadter (1968). In the renewed search for high resolution γ-ray scintillators within the last decade, improved SrI_2 crystals grown by the Bridgeman technique and measured in 2008 were found to have exceptional light yield of about 90,000 photons/MeV (Cherepy et al., 2008; Alekhin et al., 2011), near the "theoretical limit" based on βE_{gap} (Dorenbos, 2010), and to have γ resolution of 2.8% at 662 keV (Cherepy et al., 2009), the best up to that time and still one of the best resolutions among scintillators. In fact, $SrI_2:Eu^{2+}$ was the forerunner of similar excellent performance figures in Eu-doped complex halide crystals grown or re-examined since 2008, including $BaBrI:Eu^{2+}$ (Bourret-Courchesne et al., 2010) and $Ba_2CsI_5:Eu^{2+}$ (Bourret-Courchesne et al., 2009). A reason for the outstanding proportionality and light yield of complex heavier halide crystals (multivalent metal iodides, bromides, and chlorides) was suggested in (Li et al., 2012).

Despite the promising scintillator performance of $SrI_2:Eu^{2+}$, the fact remains that it is a very hygroscopic crystal and thus somewhat challenging to make certain physical measurements on. As a result, several of its important physical properties have not yet been measured or in some cases only recently measured for the first time. In this paper we report measurements of both undoped and 3% Eu-doped SrI_2 luminescence and ultraviolet excitation spectroscopy obtained using tunable ultraviolet synchrotron radiation at the SUPERLUMI station of DESY in Hamburg (Zimmerer, 2007).

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Pustovarov et al. (2012) have recently published luminescence and excitation spectroscopy of 3% Eu-doped SrI_2, also conducted at the SUPERLUMI station. Our data and associated interpretations are in agreement with most of the results and interpretations of Pustovarov et al. This publication focuses on four observations and associated analyses and interpretations contributing to the following: (1) Determination of the exciton energy and interband gap at $T = 10$ K and 300 K by combined analysis of excitation spectra and optical transmission of a very thin crystal, (2) Tentative identification of the spin-orbit splitting of the valence band as expressed in the exciton spectrum, (3) Observation that nominally undoped powder and single crystal SrI_2 samples have trace Eu which appears associated with a defect, perhaps oxygen, broadening the Eu 5d-4f luminescence band by a factor x3, and (4) Spectra relating to the afore-mentioned search for self-trapped exciton luminescence. Determining accurate exciton and bandgap energies is important for understanding the scintillator performance such as application of the βE_{gap} rule (Dorenbos, 2010), and for modeling SrI_2 proportionality (Grim et al., 2012).

2. Experiment

The SrI_2 and SrI_2:Eu crystals were grown from 99.99+% purity Sigma–Aldrich beads of SrI_2 and admixed EuI_2 beads for dopant. We take additional precaution to remove all residual water before crystal growth by vacuum pumping (10^{-5} torr for 6 h) the starting materials under moderate heating (below 150 °C). The purity of the reagents used is 99.999% (for metal content) but, after the crystal growth process which by itself has a purifying effect, most impurities accumulate at top of the crystal boule which is cut and discarded in the process of sample preparation. The source materials were loaded into a taper-ended fused silica ampoule under glove box dry inert gas atmosphere, then pumped to high vacuum and sealed. Vertical Bridgman growth from the melt was conducted in a two-zone oven with a temperature gradient of approximately 5 °C/cm in the solidification region of the oven at 535 °C and pulling rates of 0.5–1 cm/day. The oven allows real time in-situ observation of the seeding and growth processes. Crystals were cut and polished initially using mineral oil as lubricant, then cleaned of oil with trichloroethylene in the glove box and dry polished using fine polishing pads (12.6 μm and 8.4 μm). They were encapsulated between sapphire windows cemented to a fused silica cylinder.

The SUPERLUMI experiment station (Zimmerer, 2007) of HASYLAB was used for the measurements of emission and excitation spectra. This experimental set-up is unique tool for investigations of wide band gap materials as well as nanocrystalline semiconductors (Pankratov et al., 2011a, 2011b). Excitation spectra were recorded in the 330–125 nm (3.7–10 eV) spectral range with a spectral resolution of 0.3 nm. Sodium salicylate was used to normalize excitation intensity. Luminescence spectra in the ultraviolet and visible/infrared range were recorded with a SpectraPro-308i monochromator (Acton Research Corporation) and a HAMAMATSU R6358P photomultiplier, achieving 11 nm resolution. Emission spectra were corrected for the spectral response of the detection system. The sealed sample cells were cemented onto the sample holder of a flow-type liquid helium cryostat that allows temperature manipulation in 10–300 K range.

3. Results and discussion

3.1. Exciton and band gap energies

Fig. 1 shows luminescence spectra in SrI_2:Eu(3%) at $T = 10$ K excited at four wavelengths. Excitation at 4.60 eV (270 nm) is in the transparency gap of the host crystal and excites the 4f-5d
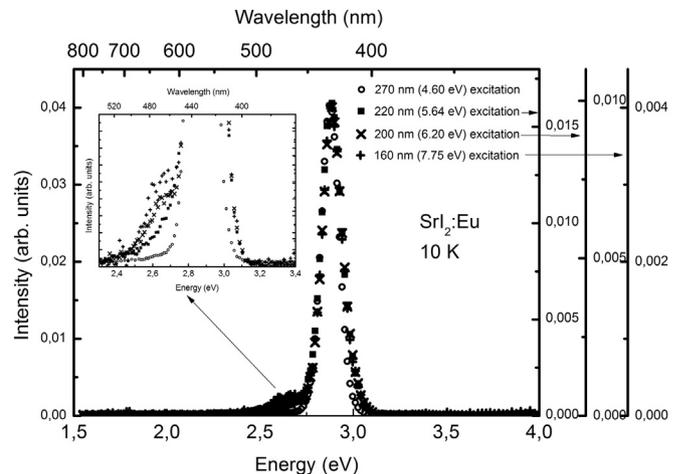

Fig. 1. Luminescence spectra in SrI_2:Eu (3%) at $T = 10$ K excited at photon energies as labeled. Inset shows detail of the shoulder.

absorption bands of Eu^{2+} dopant directly, producing the narrow and symmetric luminescence band with peak at 432 nm. The other three excitation energies of 5.60, 6.20, and 7.25 eV lie within the exciton or interband absorption spectrum of the host SrI_2 (see data and discussion below). Most of the luminescence they excite in this Eu-doped crystal is also within the 432 nm Eu^{2+} emission band, but it includes a low energy shoulder associated probably with host lattice defects-based emission center. The 470 nm wavelength within the shoulder will be monitored along with the 432-nm peak in the following analysis of excitation spectroscopy of SrI_2:Eu to estimate exciton and band-gap energies.

The excitation spectra for SrI_2:Eu(3%) at $T = 10$ K are shown in Fig. 2(a). The 432-nm Eu luminescence is directly excited with high efficiency below about 5.1 eV. In the region that we suggest is the exciton band tail and impurity-perturbed edge from about 5 eV to 5.4 eV, the excitation of defect luminescence such as that monitored at 470 nm increases in competition with the Eu dopant. The spectral position of the competition near and somewhat above 5 eV might suggest that excitons transfer to one center and free carriers to the other. This competition can also be seen in the anticorrelated broad dip (for 432 nm) and peak (for 470 nm) around 4.4 eV excitation. It is commonly found and interpreted in ultraviolet excitation spectroscopy of luminescence that strong intrinsic absorption resonances such as exciton peaks are seen as a dip in luminescence yield. There are two reasons. First, as the absorption coefficient approaches values of order 5×10^5 cm^{-1} at an exciton peak, the excitation is deposited within about 20 nm of the surface and so is subject to surface quenching. Second, the reflectivity peak at such a strong intrinsic resonance rejects some of the excitation photons. The sharp dip at 5.45 eV for 432 nm luminescence and 5.49 eV for 470 nm luminescence could be associated with the lowest 1s exciton peak in SrI_2 at $T = 10$ K. A second dip at about 0.25 eV higher energy can also be seen.

Excitation spectra of the nominally undoped SrI_2 sample shown in Fig. 3 give resolved spectral dips at $T = 300$ K. The excitation spectra are plotted for luminescence at 430 nm (believed due to trace Eu) and 570 nm. The 570 nm band is associated with oxygen impurity in SrI_2. Pustovarov et al. have shown that its intensity increases with exposure to the vacuum ambient, presumably reacting with residual water vapor content. They concluded that a significant part of the oxygen contamination comes from surface hydrate reactions. As seen in Fig. 3, there is a well-resolved dip in the room temperature excitation spectrum at 5.02 eV (430 nm) and 5.16 eV (570 nm) [average 5.09 eV]. To assign a single approximate
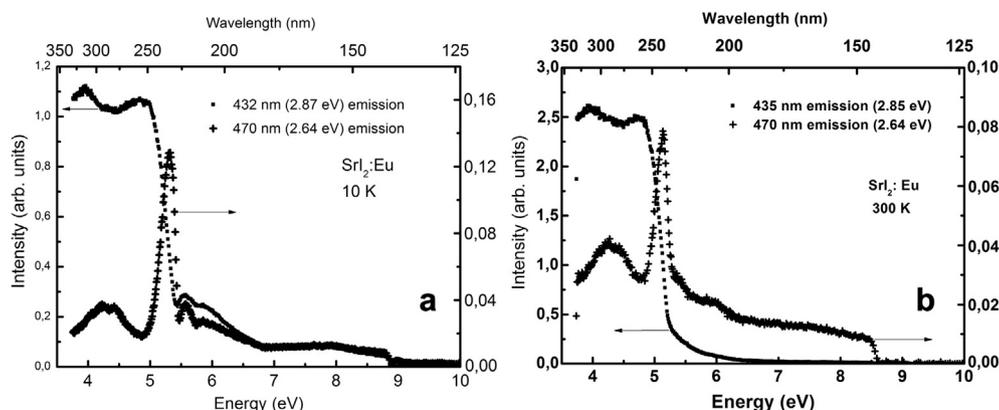
Fig. 2. Excitation spectra of the indicated luminescence wavelengths in SrI$_2$:Eu (3%) at $T = 10$ K (a) and $T = 300$ K (b).

energy for the room-temperature exciton peak, we suggest 5.12 eV ± 0.1 eV. Thus the thermal peak shift of the 1s exciton in SrI$_2$ from 10 K to 300 K seems on this basis to be about 0.35 eV.

In both excitation spectra of Fig. 3, there is a broad dip near 6 eV, about 0.9 eV above the dip suggested to mark the *1s* exciton. We can speculate that the upper broad dip might be the upper member of the exciton doublet associated with the spin-orbit splitting of the valence band edge. The spin-orbit splitting energy of the lowest exciton doublet in the alkali iodides NaI, KI, RbI, CsI has a typical value of about 1.2 eV, similar to spin-orbit splitting in xenon (Teegarden and Baldini, 1967).

An independent measurement that places at least a lower limit on the 1s exciton energy is absorbance spectroscopy of a 120 μm thin crystal. A thin crystal of SrI$_2$ was prepared by polishing and its thickness was measured by stylus profilometer. The absorbance spectra [$\log_{10}(I_0/I)$] at temperatures from 10 to 300 K are shown in Fig. 4. The absorbance data indicate that the exciton peak is at an energy not less than 5.1 eV at 300 K and not less than 5.25 eV at 10 K. This is a smaller thermal shift than was deduced above from the presumed exciton peak dips in excitation spectra.

The exciton Rydberg for SrI$_2$ can be roughly estimated with static $\varepsilon = 3.86$ (www.chemicaldictionary.org), $m^* = 0.288\ m_e$ (Setyawan et al., 2009) to be 0.26 eV. Fröhlich and Staginnus (1967)

and Fröhlich et al. (1970) made experimental band gap assignments in CsI and RbI based on two-photon spectroscopy at 20 K. Comparing to the one-photon 10 K exciton absorption spectra of Teegarden and Baldini (1967), they deduced exciton Rydberg of 0.25 eV in CsI and 0.52 eV in RbI. The static dielectric constants of the latter two crystals are 5.65 and about 4.8 respectively. Considering the spread of values from CsI to RbI and the relatively lower dielectric constant in SrI$_2$, we suggest that the SrI$_2$ exciton binding energy is about 0.38 eV ± 0.12 eV. Adding this to the *1s* exciton energy estimated from the above data at about 5.12 eV, one obtains $E_{gap} \approx 5.5$ eV (band-to-band) in SrI$_2$ at $T = 300$ K and 5.85 eV ± 0.12 eV at $T = 10$ K. This effectively agrees with the SrI$_2$ band gap estimate of 5.7–5.8 eV at 90 K by Pustovarov et al. (2012). Åberg et al. (2012) calculated a band gap of about 5.5 eV in SrI$_2$ (effectively $T = 0$ K) using several techniques ranging from hybrid Density Functional Theory + exact exchange to self-consistent GW and Bethe Salpeter approaches. Since the exciton binding energy is estimated at 0.38 eV in SrI$_2$, we look again at Fig. 2(a) where a second dip in the excitation spectrum occurred 0.25 eV above the feature suggested to be the 1s exciton. The alkali iodide absorption spectra at 10 K (Teegarden and Baldini, 1967) exhibit a distinct step at the interband edge. The second dip in Fig. 2(a) might be an analogous interband step in the absorption (ε_2) spectrum of SrI$_2$.
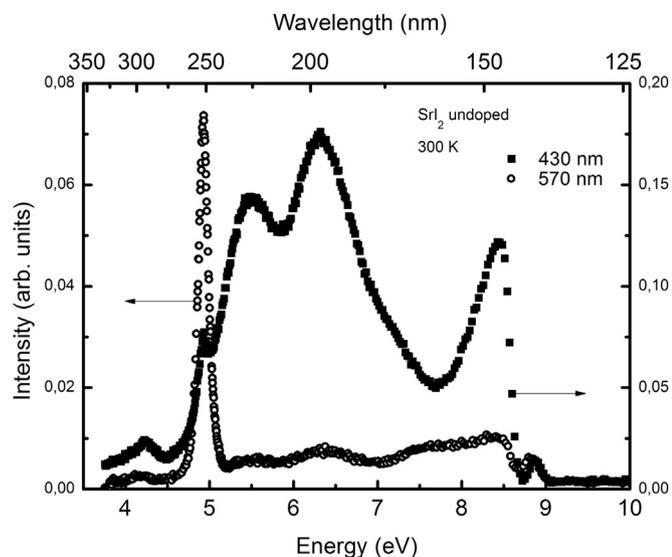

Fig. 3. Excitation spectra of 430 and 570 nm luminescence in undoped SrI$_2$ at $T = 300$ K.

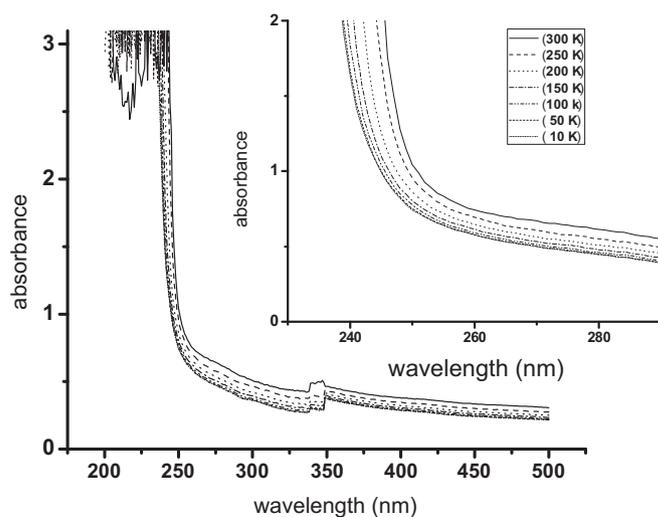**Fig. 4.** Spectra of absorbance in 120 μm SrI$_2$ crystal from 10 to 300 K, showing that the exciton peak at $T = 300$ K is ≥ 5.1 eV.
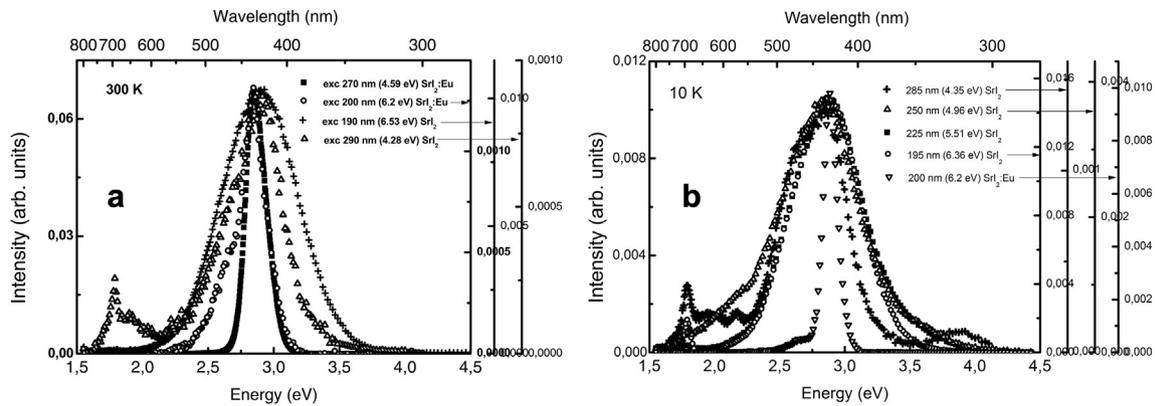
Fig. 5. Luminescence spectra of nominally undoped and 3% Eu-doped SrI$_2$ at 300 K (a) and 10 K (b), excited at the indicated photon energies.

3.2. Broadened spectrum of trace Eu^{2+} in undoped SrI$_2$

The luminescence spectra excited by several photon energies in nominally pure and 3% Eu-doped SrI$_2$ are compared in Fig. 5(a) for $T = 300$ K. Excitation at 4.59 eV and 4.28 eV is directly in the 4f-5d absorption transitions of Eu^{2+}. The resulting luminescence in SrI$_2$:Eu is the relatively narrow and symmetric Eu^{2+} band plotted by the solid square points in Figs. 5(a,b). In undoped SrI$_2$, the band shown by triangles is significantly broader. When the excitation is above the host band gap, 3% Eu-doped SrI$_2$ develops a low energy shoulder near 470 nm as we saw in Fig. 1, but the main Eu band remains narrow. However, above-gap excitation in undoped SrI$_2$ containing trace Eu produces a luminescence band centered at 430 nm, which is 3x broader than the luminescence of Eu intentionally doped at higher concentration. We have observed broadened luminescence of trace Eu both in undoped single crystals and in x-ray luminescence of SrI$_2$ powder. We hypothesize that trace Eu in the starting materials is likely to be an oxide impurity such as Eu$_2$O$_3$, and thus may be incorporated in the crystal still closely associated with oxygen in forms of EuO or dissolved O^{2-}. In contrast, intentional doping of crystals is done with europium iodide, less likely to bring in oxygen. This oxygen related emitting center has also been identified and further discussed in other alkali earth metal halides, such as BaFCl and BaFBr (see, e.g., Radzhabov and Otroshok, 1995).

3.3. Self-trapped exciton luminescence

Self-trapped excitons have been identified in the alkali halides including the alkali iodides and the alkaline earth fluorides (Song and Williams, 1993). It seems reasonable therefore to expect self-trapped exciton luminescence in SrI$_2$. Aberg et al. have calculated the electronic structure and lattice configuration anticipated for the STE in SrI$_2$, predicting a luminescence energy of about 4.2 eV (Åberg et al., 2012). Luminescence bands seen at room temperature in undoped SrI$_2$ at 560 nm (2.21 eV) (Cherepy et al., 2009) and 400 nm (3.1 eV) (Sturm et al., 2011) have been previously suggested to be STE luminescence. Pustovarov et al. (2012) recently suggested that a band observed at low temperature at 365 nm (3.4 eV) in SrI$_2$:Eu(3%) excited by synchrotron radiation is the STE luminescence. We have observed a band fitting the description by Pustovarov et al. (2012) in x-ray excited luminescence of undoped SrI$_2$ powder at low temperature. However, it is not observable even at 7 K in 1% Eu-doped SrI$_2$ powder. Except for temporary puzzlement over this difference of observation on 3% and 1% Eu-doped samples, we agree with the reasoning of Pustovarov et al. (2012)

in assigning the low-temperature 3.4 eV band to the STE luminescence. Fig. 5(b) shows the luminescence spectra of an undoped SrI$_2$ single crystal at $T = 10$ K excited by synchrotron radiation in the present work. The 3.4 eV band is not resolved, but it could be buried under the wing of the broadened trace-Eu band discussed above.

Acknowledgments

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