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Orange Emitting SrS: Eu^{2+}, Dy^{3+} Afterglow Phosphor: Structural and Luminescence Properties

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ABSTRACT

SrS:Eu is known as an attractive material for imaging, scintillator, or persistent phosphor applications, thanks to its effective photoluminescence (PL) and thermoluminescence (TL) capabilities, but there are still great mysteries of persistent phosphors and attract great interest. Hence, this work investigated the luminescence properties of well-known persistent phosphor based on SrS using various spectroscopic techniques for detailed characterization. Measurements using X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) were used to analyze the phase and elements of the phosphor. Belongs to the XRD data the microcrystalline phosphor is cubic, and the diameters ranged from 1 to 100 µm. The morphology of the phosphor was examined by scanning electron microscope (SEM). A time-resolved PL system recorded PL properties, namely the emission and excitation spectra of the phosphor. SrS emits around 626 nm with a broad excitation band peaking around 466 nm. A TLD reader system measured the TL glow curve of the phosphors after UVB radiation. The TL glow curve exhibited a broad peak around 160°C. The dose-response of this peak was obtained up to 600 seconds of exposure to UVB radiation, and it was observed that the dose-response curve exhibits a saturating exponential behavior.

Keywords: Persistent phosphor, Thermoluminescence, Time-resolved photoluminescence, Long afterglow phosphors, XPS

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Introduction

Persistent phosphors are phosphors that emit light even after stopping the excitation. In those phosphors, electrons are liberated by daylight and stored in impurities. Then they are spontaneously released during the nighttime to produce luminescence. The phenomenon is also called afterglow. These phosphor materials are feasible for various uses. For instance, they are used as 'glow in the dark' phosphors in luminous paints or plastics, such as signs that show escape routes in buildings, safety clothing, traffic signs, and road markings, in hospitals and dentistry, such materials, in which X-rays move the electrons to deep capture centers, have now almost entirely replaced traditional X-ray films. Nonetheless, there are not enough effective red-emitting materials. Since the strong nephelauxetic impact of an alkaline earth sulfide phosphor SrS: Eu2+ shifts Eu2+4f65d1→4f7 to red and the weak connection between strontium and sulfide, resulting from the soft base-hard acid character, generates a significant number of intrinsic defects, it remains a promising choice [1].

Alkaline earth sulfide phosphors [1] are used in a wide variety of display applications and lighting [2-5]. They are employed especially in inorganic electroluminescent devices, field emission displays, and wavelength converters in light-emitting diodes (LEDs) for solid-state lighting [2-5]. The alkaline earth sulfides, especially SrS: Eu, have been studied as an inorganic luminescence material for some time [1]. Recently, the presence of up-conversion and optical storage in SrS: Eu has taken a new interest in these phosphors [6,7].

Now one of the most successful practical photoluminescent phosphors is SrS: Eu2+, Dy3+ however, there are still strong background radiations from afterglows [8]. Since both the formation and crystallinity have a substantial impact on the luminescence curves, the first step of our investigation consists of a comprehensive analysis encompassing structural phase analysis, elemental analyses, structure morphology, and particle size. It has long been known that the crystalline phase, which is mainly caused by temperature and pressure, is responsible for all the characteristics of the luminescence phenomenon, including lifetime, efficiency, and emission spectra. Furthermore, the current study intends to achieve the following primary contributions, which are summarized as follows:

- This, in our opinion, is the first time a commercial SrS: Eu2+, Dy3+ phosphor has been thoroughly examined.
- The PL emission and excitation spectrums were studied.
- The PL emission's decay nature was measured.
- Dose response to UV radiation and fading of the glow peak studied by TL measurements.

Material and Method

The samples used in these experiments (SrS: Eu^{2+}, Dy^{3+}) were commercial persistent phosphor. To guarantee the accuracy of the data, three aliquots were utilized in each experiment rather than just one. Each aliquot is 4×10^{-2} g powder.

The samples' phases and crystal structures were identified. through a Thermo Scientific ARL- Kα X-ray diffractometer (XRD). Radiation has been produced using Cu-Kα. For qualitative testing, XRD diagrams were obtained at intervals of $20^o\leq2\theta\leq60^o$ [9,10].

XPS (Thermo-Scientific) was used to investigate the surface chemistry of all samples. It used a monochromatic Al-Kα (1486.7 eV) X-ray source with a 400 nm diameter beam. The gadget was calibrated using $4f^{7/2}$, the gold standard. The pressure was maintained during the collection of spectral data below $5x10^{-10}$ mbar. With a precision of 1 eV and a pass energy of 150 eV, the XPS data were collected between 0 and 700 eV. A single point's ten scans were recorded. The morphology was studied using a COXEM E30 [10].

The microstructures of the particles were examined with a high voltage (30 kV) accelerator and an electron microscope (COXEM EM-30+). The samples were directly attached to sample holders and coated with carbon. There was no surface polishing.

The optical characteristics were investigated using the PL method. The PL studies were performed in a Time-Correlated Single Photon Counting (TCSPC) system with a red-sensitive photomultiplier tube and a spectrofluorometer kit. For steady-state and lifespan measurements, the device was fitted with a normal 15W Xenon light and a microsecond flash bulb, respectively. Throughout the experiment, a non-fluorescing silica aerogel combination (LU-DOX 30%, Sigma Aldrich) in water was utilized to determine the Instrument Response Function (IRF).

All TL measurements were carried out using a Harshaw 3500 TLD Reader. The irradiations were applied via a UVB lamp (310 nm). All measurements were performed in a nitrogen atmosphere with a low constant heating rate of $2^oC/s$, to avoid significant temperature lag, and the samples were heated up to the maximum temperature of 350^oC. To determine the UVB dose response of the material, the following dose-response protocol was applied:

Step 0: Zero dose TL signal (ZDTL) recording

Step 1: Test Dose (TD), immediately recording the TL sensitivity up to 350^oC.

Step 2. Exposure to UVB Radiation with various periods (2-600 s.)

Step 3. TL up to 350^oC

Step 4. Repeat steps 0-4 for a new phosphor.

Result and Discussion

Both the obtained results and their description are provided below.

Using XRD, the phase purity and crystallinity of SrS: Eu^{2+}, Dy^{3+} phosphor were investigated. Figure 1 displays the XRD pattern of the SrS: Eu^{2+}, Dy^{3+} phosphor. The peaks were indexed by the International Centre for Diffraction Data (ICSD) and matched precisely with standard data.

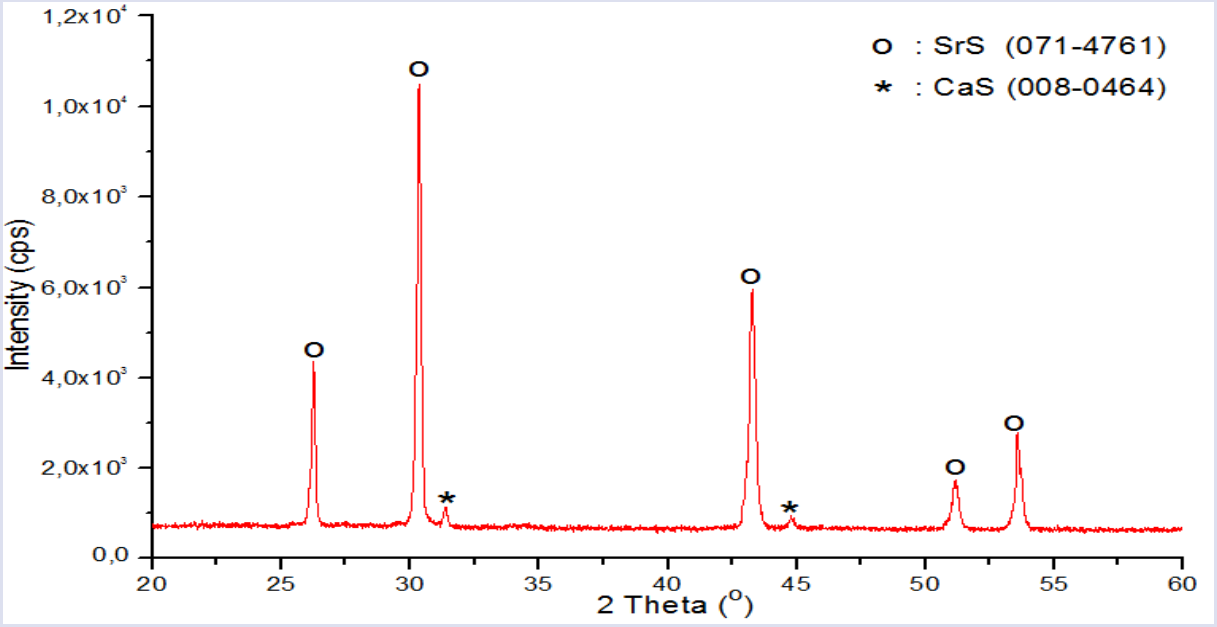


Figure 1. XRD pattern of SrS: Eu^{2+}, Dy^{3+} phosphor.

XRD Patterns are found to be characterized by peaks at 2θ values of 25°, 30°, 42°, 50.5°, and 53° corresponding to the planes (111), (200), (220), (311) and (222) (PDF card No.01-071-4761). These results are verified with already published reports [9-12]. Besides SrS, very little CaS (PDF card No.00-008-0464) phase has been identified in the structure (Figure 1). The structure is cubic.

The valence states, chemical nature, and oxidation of numerous elements in the SrS: Eu^{2+}, Dy^{3+} phosphor aliquots were characterized using XPS, as marked in Figure 2. It is a representation of the findings from the analysis and high-resolution elemental detects of the aliquot.

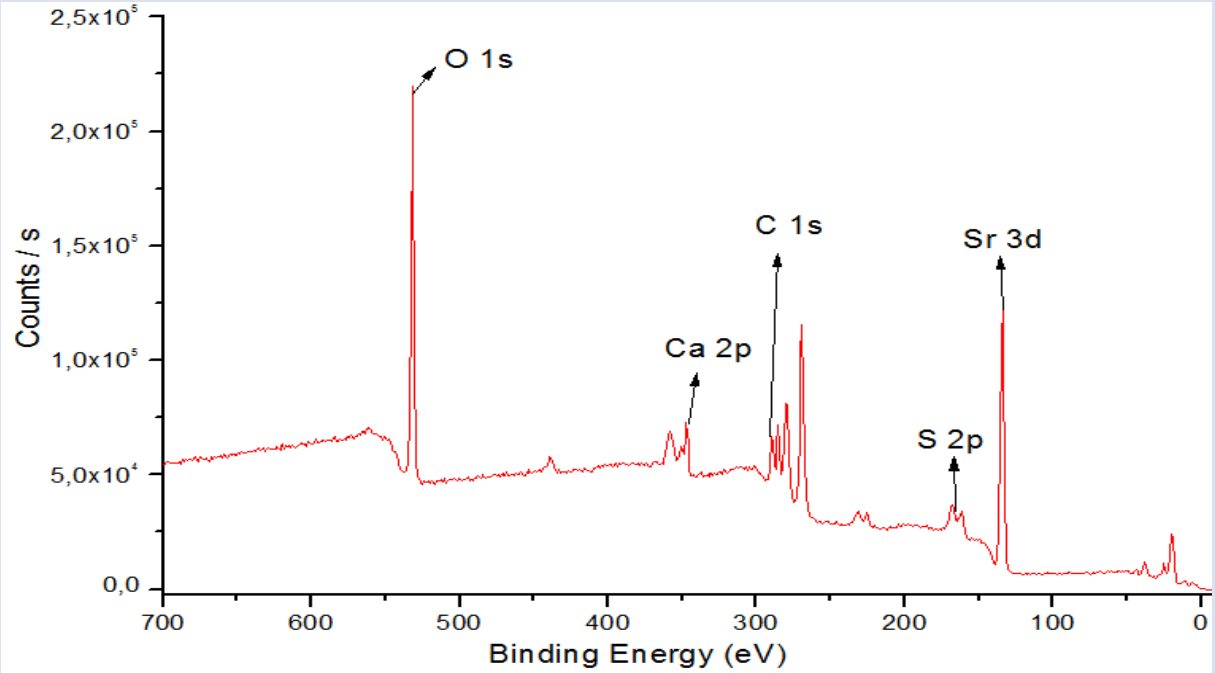


Figure 2. XPS survey spectra of SrS: Eu^{2+}, Dy^{3+} phosphor.

Figure 2 remarks on the regular XPS scanning of the aliquot. Here are the base elements of Sr, Ca, S, O, and C in material structure. The photoelectron peak of Sr 3d becomes evident at the binding energy of 134 eV. Likewise, photoelectron peaks of Ca2p, S2p, O1s, and C1s appear at 347, 167, 531, and 285 eV respectively. The XPS peaks for C1s and O1s (performing as internal standards) were observed because of the contamination from the particles and the accidental hydrocarbon from the XPS equipment. The peak positions line up with the values given in the literature [9].

The peaks obtained at the high-resolution elemental scans, the binding energies, and the weight % values of elements are given in Table 2.

Table 2: XPS outcomes of natural amazonite aliquots

Elements	*Survey Binding Energy (eV)*	*FWHM (eV)*	*Area (Peak) CPS.(eV)*	*Survey Weight (%)*
O1s	531.43	1.683	386805.76	25.21
Sr3d	134.12	3.497	298520.77	50.18
Ca2p	347.09	2.711	59128.21	5.02
S2p	167.78	4.327	63157.26	11.93
C1s	285.16	1.445	61268.59	7.65

Since the crystal structure, particle size, and morphology are important for luminescence properties

Figure 3 shows the SEM images of SrS: Eu^{2+}, Dy^{3+} phosphor powder aliquots.

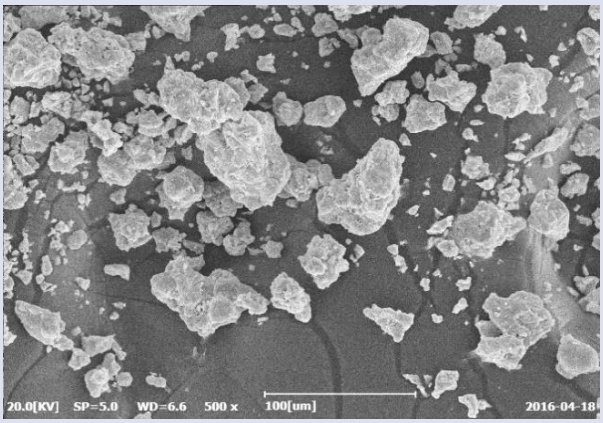
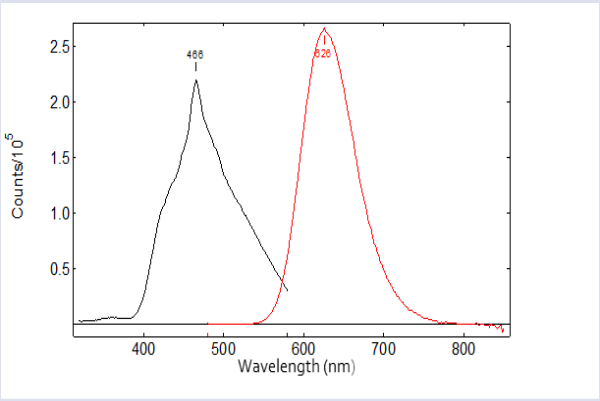
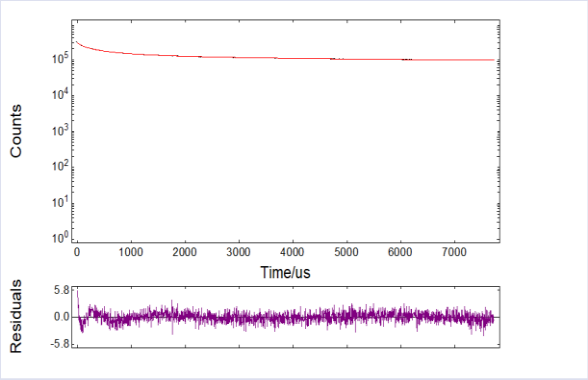


Figure 3. SEM micrograph of SrS: Eu^{2+}, Dy^{3+} phosphor with 500 magnification.

SEM patterns were used to evaluate the surface morphology (Figure 3). SEM images show that the crystal structure is not visible, most of the small particles aggregated together, and the blocky particles of phosphors had irregular morphologies with diameters ranging from 1 µm to 100 µm. These results constrict with the results of J. E. Van Haecke et al [12]



(a) Emission and excitation



b) 8000µs 1000 channel decaying

Figure 4: (a) PL emission spectrum of SrS: Eu^{2+}, Dy^{3} phosphors. **(b)** Decay curve of SrS: Eu^{2+}, Dy^{3} phosphors

The SrS: Eu2+, Dy3+ phosphors' excitation-emission bands and the PL decay curves at room temperature are shown in Figure 4. The excitation spectrum of emission has a wide band (400- 600 nm) making a peak around 466 nm, corresponding to the host lattice transition. The electromagnetic spectrum's visible area contains the excitation range (Figure 4(a)). When excited, the emission peak appears at 550 nm giving broadband that lasts until about 750 nm. The peak of the emission was found at approximately 626 nm, in the orange portion of the visible spectrum. Both the ground state 8S7/2 of the 4f7 configuration and the excited state T2g of the 4f6 5d1 configuration are where the permitted transitions between them are responsible for the emission of Eu2+ (Laporte's Rule) [1,12]. This allowing transition of Eu2+ is different from the transitions of other activators (f-f and d-d transitions). Furthermore, this transition is due to the strong nephelauxetic effect, and the low stoke shift leading to an excitation band in the blue-green region observed. So, this phosphor is important for several applications like white LEDs [1]. No Dy3+ emission was observed because, Dy3+ does not behave as an emission centre, but supports long afterglow [13]. A long afterglow is observed. The allowed transition period of Eu2+ was determined as around 2.4 ms (Figure 4(b)). The luminescent characteristics of the powder SrS: Eu2+, Dy3+ are comparable with those of crystal aliquots [10-12]. Moreover, since the excitation peak of SrS: Eu2+, Dy3+ phosphors overlaps with the excitation peak of Hg, this phosphor has a great potential to be used for lumination.

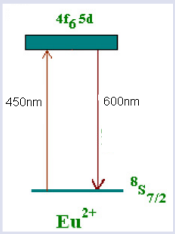


Figure 5. Energy level diagrams for a possible transition of Eu^{2+} ions for Excitation and Emissions.

In Table 3 there are three decaying durations: τ1, τ2, and τ3. The phosphor aliquots of SrS:Eu^{2+},Dy^{3+} exhibited three exponential decaying periods. Three components were identified: the long lifetime (3754.54 µs), the medium lifetime (562.99 µs), and the short lifetime (133.86 µs).

Table 3. Excitation and emission wavelength and decay time measurement outcomes of SrS: Eu2+, Dy3+ phosphor aliquots with standard deviation and percentage allocation.

Sample	Excitation wavelength (nm)	Emission wavelength (nm)	X^2		Decay Period (µs)	Standard Deviation	Rel.%
SrS: Eu^{2+}, Dy^{3+}	426	678	1.187	ζ_1	133.86	1.49459	3.56
				ζ_2	562.99	5.61877	17.41
				ζ_3	3754.54	39.49525	79.03

As a result of radiation, electrons, and holes are trapped in the band gap at local energy levels known as vacancies, interstitials, or contaminants. TL is created when they are liberated from the thermal stimulus and recombined with carriers of the opposite sign. The TL peaks' maximum and shape represent the trap's characteristics. For instance, deeper traps can be empty at higher temperatures (~200 °C), whereas shallow traps can be empty at lower temperatures (~100 °C).

The dose response to UV radiation of SrS: Eu^{2+}, Dy^{3+} is given in Figure 6. Irradiation was performed launching from very short durations and ended at 5 minutes. By increasing the irradiation duration, the height of the glow peak is increased while the speed of increasing decreases

(Figure 7). As seen in Figure 7 there is a saturation at high doses. Up to 75 seconds a linear increase was observed, but especially after 175 seconds, saturation was observed. This observed situation is reasonable. While irradiating the sample radiation affects the traps. Moreover, a shift to high temperatures was observed because of the filling of low-temperature traps with irradiation.

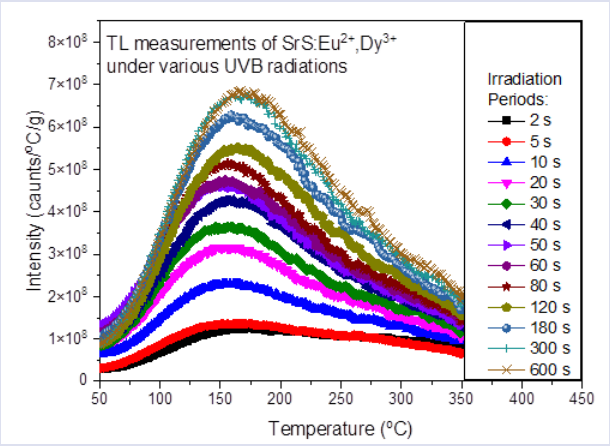


Figure 6. TL glow curves of SrS: Eu^{2+}, Dy^{3+} phosphor immediately after exposure to various UVB radiation.

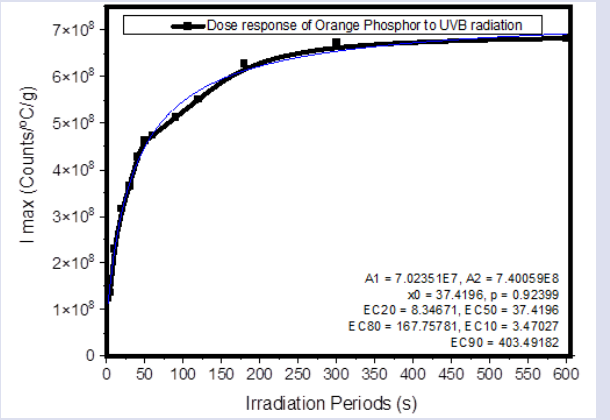


Figure 7. Dose-response curve of SrS: Eu^{2+}, Dy^{3+} phosphor to UVB radiation

To examine the fading of the phosphor, the aliquot was irradiated with 2 min UV radiation and stored in the dark for 5 days, and the TL glow peaks were recorded. As seen in Figure 8 after storing 5 days there is a great luminescence. This low fading property belongs to the cooping of Dy^{3+}

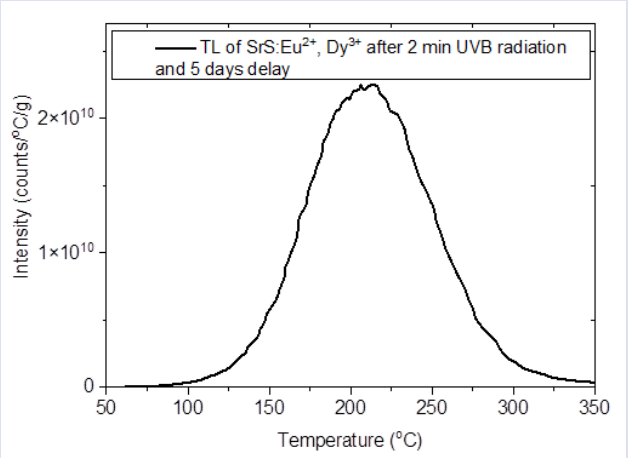


Figure 8. TL Glow curve of SrS: Eu2+, Dy3+ phosphor after 5 days storing at dark atmosphere.

Conclusions

The current conclusions can be summed up as the following:

- A comprehensive overlook of the persistent luminescence behavior of SrS: Eu^{2+}, Dy^{3+} is analyzed.
- XRD patterns indicate that peaks signify the cubic structure of SrS.
- The XPS survey spectra are in good agreement with XRD patterns, the basic elements in the material structure are Sr, Ca, S, O, and C.
- The crystal structure has block particles that bring irregular morphology with diameters ranging from 1 µm to 100 µm.
- SrS phosphors show efficient orange broad-band emission around 626 nm, which originates from the 4f–5d transitions of Eu^{2+} transitions. The co-dopant, Dy^{3+} ions, lengthened the duration of luminescence by behaving as a trapping state. They do not make any emissions. The result is well-matched with literature.
- This phosphor has storage properties, and this is because of Dy^{3+} dopants.
- The allowed transition period of Eu^{2+} was determined as around 2.4 ms.
- The dose-response of this peak was obtained up to 600 seconds of exposure to UVB radiation, and it was observed that the dose-response curve exhibits a saturating exponential behavior.
- These SrS phosphors can be used as a blue phosphor for white or full color. Thin film electroluminescent (TFEL) displays. (Surface Science 454–456 (2000) 529–533)

Conflicts of interest

There are no conflicts of interest in this work.

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