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**LOCAL CHEMICAL ACTIVITY AND
MICROSTRUCTURAL HETEROGENEITY OF THE
NEAR-SURFACE LAYER IN THE SI-EU SYSTEM: A
COMPREHENSIVE ASSESSMENT BY XRD, FTIR,
AND SEM/EDS**

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Abstract. *This paper evaluates the local chemical activity and microstructural heterogeneity of the near-surface layer in the Si-Eu system through a correlated interpretation of XRD, FTIR, SEM, and EDS data. XRD and WPPF processing showed that the crystal-phase basis of the sample is cubic Si with a mass fraction of $99.37 \pm 0.07\%$. A very weak secondary component at the level of $0.63 \pm 0.07\%$ was not interpreted as a reliably established independent phase because no additional independent confirmation was available. In the FTIR spectrum, broad bands at 3428 and 3324 cm^{-1} were associated with adsorbed moisture and hydroxyl-related states, whereas the 2113 cm^{-1} signal was assigned to Si-H bonds. The 1980-1463 cm^{-1} range was considered a cautious spectral indicator of the chemically complex state of the near-surface layer. SEM images revealed uneven relief, local clustering, and partly agglomerated areas. Point EDS analysis detected C, P, and Eu signals; however, these data characterize only the selected local region and do not represent the average composition of the whole sample. The combined results indicate that, in a Si-matrix-dominated system, the near-surface layer is chemically active and morphologically nonuniform.*

Keywords: *Si-Eu system, near-surface layer, local chemical activity, microstructural heterogeneity, XRD, FTIR, SEM, EDS, Si-H bonds, surface morphology.*

1. Introduction

In silicon-based materials, the chemical and microstructural state of the near-surface layer has a significant effect on the physical properties of the entire system. In particular, for Si systems modified with rare-earth elements, the results can be interpreted correctly only when the main crystal matrix, surface bonding states, and local elemental distribution are evaluated simultaneously. Therefore, XRD, FTIR, SEM, and EDS should be used not as isolated techniques but as a complementary set of data [1-8].

XRD is the main method for identifying crystal phases and lattice parameters, whereas the WPPF approach allows quantitative evaluation of strong and weak components in a diffractogram [1, 2]. At the same time, a very small fraction of secondary signals cannot be accepted as an independent phase on the basis of WPPF alone; confirmation by FTIR, SEM/EDS, or other independent methods is required. FTIR analysis is important for identifying hydroxyl states, adsorbed moisture, Si-H bonds, and other local bonding states in the near-surface layer [3-7]. SEM reveals surface relief and microrelief, whereas EDS shows the elemental composition of a selected local region [8].

Studies of Eu-containing silicon nitride, porous silicon, SiO₂, and silicate systems show that europium is often manifested not as a homogeneous bulk dopant, but through local coordination centers, near-surface chemical regions, or separate phase environments [9-20]. In such materials, optical activity, luminescence, and functional properties are often related precisely to the chemical state and defect-morphological structure of the near-surface layer.

Recent review articles emphasize the need for joint evaluation of structural, spectral, and morphological results in materials modified with rare-earth elements [21-24]. However, within a single Si-Eu sample, the issue of combining the dominance of the Si matrix, surface-specific Si-H/OH states, and local EDS signals within a cautious methodological interpretation has not been sufficiently addressed.

The aim of this work is to comprehensively evaluate the local chemical activity and microstructural heterogeneity of the near-surface layer in the Si-Eu system on the basis of XRD, FTIR, SEM, and EDS results. The scientific novelty of the work is that Eu-related local signals are not automatically generalized to the entire sample composition. Instead, the capabilities and limitations of each method are taken into account, and the Si matrix, surface chemistry, and local morphological heterogeneity are considered within a unified cautious interpretation.

2. Materials and research methodology

The near-surface layer of the Si-Eu system was chosen as the research object. XRD, FTIR, SEM, and EDS methods were used to determine the phase basis of the sample, the surface chemical state, and local microstructural heterogeneity. These methods do not duplicate one another; rather, they reveal different physicochemical features: XRD characterizes the crystalline phase, FTIR characterizes surface bonds, SEM characterizes surface relief, and EDS characterizes the elemental composition of a selected local region [1-8].

X-ray diffraction measurements were performed on a MiniFlex 300/600 diffractometer using Cu radiation. The measurement conditions were 40 kV voltage and 15 mA current over a 3-90° (2 θ) range with a step of 0.01° and a scanning speed of 10.00°/min. The diffractogram was processed using the WPPF approach, and the main phase, possible weak components, lattice parameter, and microstrain indices were evaluated [1, 2].

The FTIR spectrum was recorded in the range of 4000-450 cm⁻¹. The main minima in the spectrum were interpreted in terms of adsorbed moisture, hydroxyl states, and Si-H bonds. For the 1980-1463 cm⁻¹ range, where several vibrations may overlap, no strict molecular identification was given; this region was evaluated as a general spectral feature reflecting the complex chemical state of the near-surface layer [3-7].

SEM images were obtained on a JEOL JSM-IT210 electron microscope using an SED detector at an accelerating voltage of 3.0 kV, a working distance of 15.2 mm, and high-vacuum mode, with magnifications from 60x to 2700x. EDS point analysis was performed at an accelerating voltage of 15 kV, 45x magnification, a signal acquisition time of 30 s, and a count rate of 222 CPS. EDS results were interpreted not as the average composition of the sample, but as information specific to the selected local point [8].

Three methodological limitations were considered separately. First, a secondary XRD component with a very small fraction was not accepted as a definite phase without additional independent confirmation. Second, ambiguous regions in FTIR were left at the level of cautious spectral description. Third, because EDS represents a single local point, it was not used to draw a firm conclusion about the distribution of Eu over the entire surface or bulk of the sample.

3. Results and discussion

3.1. XRD analysis: dominance of the Si matrix and a weak secondary signal

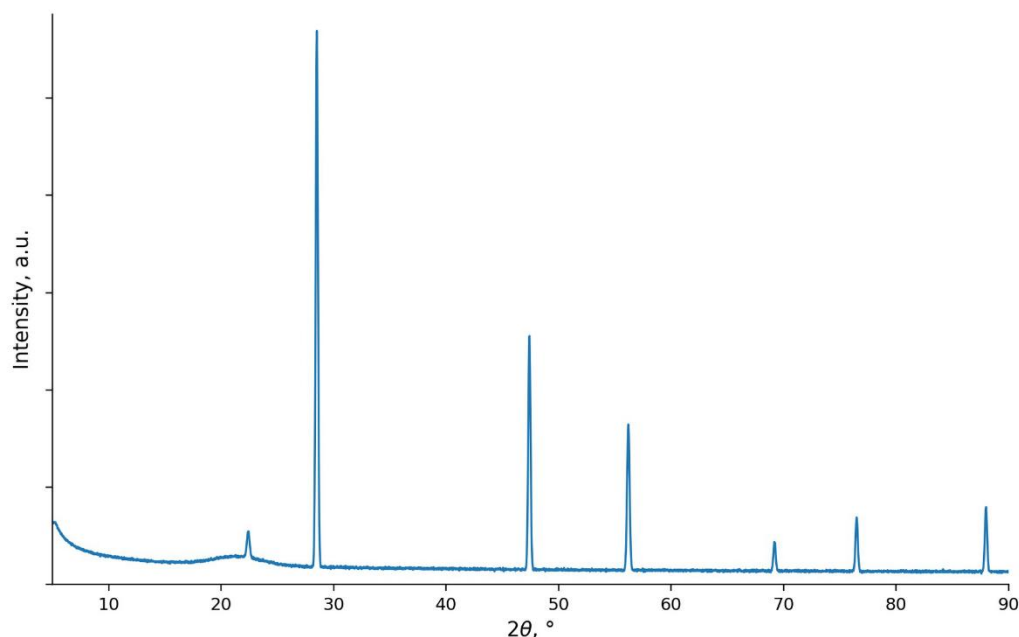
Processing of the XRD data by the WPPF approach showed that the crystal-phase basis of the sample is almost completely cubic Si. The mass fraction of the main phase was $99.37 \pm 0.07\%$, and the lattice parameter was $a = b = c = 5.43158 \text{ \AA}$. The WPPF report also separated a very small secondary component with a fraction of $0.63 \pm 0.07\%$. However, because its fraction is extremely low and no additional independent confirming evidence is available, this component was treated in the article only as an unconfirmed weak secondary signal.

Table 1. Phase composition and lattice parameters determined by XRD

Phase	Mass fraction, %	a=b=c, Å	Crystal system	Microstrain, %
Si	99.37 ± 0.07	5.43158	Cubic	0.0119(9)
Unconfirmed secondary component (automatically)	0.63 ± 0.07	7.98942	Cubic	0.0230(10)

separated according to the WPPF report)				
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Figure 1. XRD diffractogram of the Si-Eu system.



The most intense maximum in the diffractogram is observed at $2\theta \approx 28.44^\circ$, corresponding to the Si(111) plane. Maxima around 47.30° , 56.11° , 69.12° , 76.37° , and 88.02° also correspond to the main reflections of the cubic Si phase. A very weak line near 31.65° may be related to the unconfirmed secondary component separated by WPPF; however, it is not methodologically sufficient to accept such a weak signal as a final phase identification [1, 2].

Table 2. Selected main maxima in the XRD spectrum

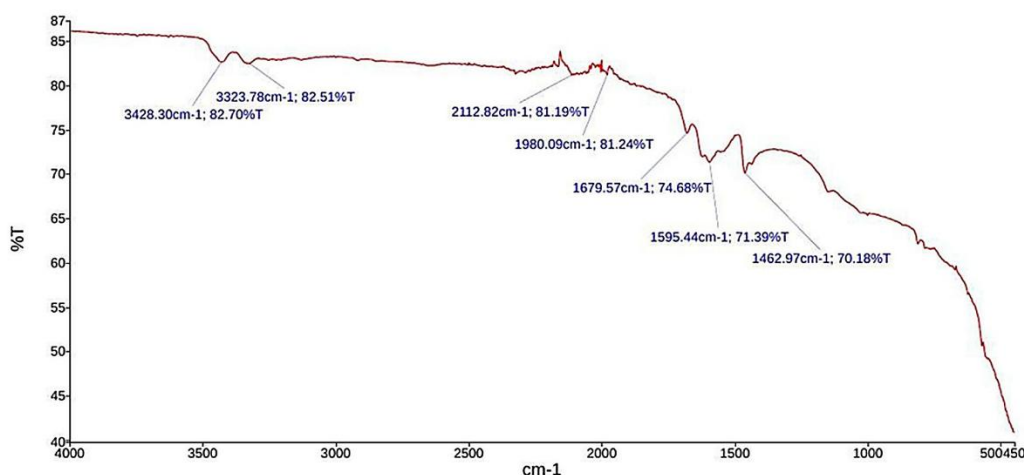
$2\theta, ^\circ$	$d, \text{\AA}$	(hkl)	Assignment
28.43886	3.13593	111	Main maximum of the Si phase
47.29669	1.92035	220	Strong reflection for Si
56.11499	1.63768	311	Line corresponding to the Si crystal lattice
31.65016	2.82469	220	Weak maximum related to an unconfirmed secondary component

Thus, the most reliable conclusion from XRD is the dominance of the Si matrix. The obtained data do not directly confirm large-scale homogeneous incorporation of Eu into the silicon lattice. On the contrary, possible Eu-related features may be associated with local near-surface regions or chemically distinct microdomains [9, 10].

3.2. FTIR analysis: chemical activity of the near-surface layer

In the FTIR spectrum, the broad bands observed at 3428 and 3324 cm⁻¹ were assigned to adsorbed moisture and hydroxyl states. The relatively distinct signal at 2113 cm⁻¹ corresponds to the spectral region typical of Si-H bonds [3, 5, 6]. These features indicate that the near-surface layer in the Si-Eu system is not chemically passive; rather, it is activated by moisture, hydroxyl states, and hydrogenated silicon bonds.

Figure 2. FTIR spectrum of the Si-Eu system.



The signals near 1980, 1679, 1595, and 1463 cm⁻¹ were not strictly assigned to a single compound. In this region, moisture deformation vibrations, combination vibrations, or overlapping surface-specific signals may appear. Therefore, in this article the range was interpreted as a general spectral feature reflecting the complex chemical state of the near-surface layer [4, 7].

Table 3. Main minima in the FTIR spectrum and their cautious interpretation

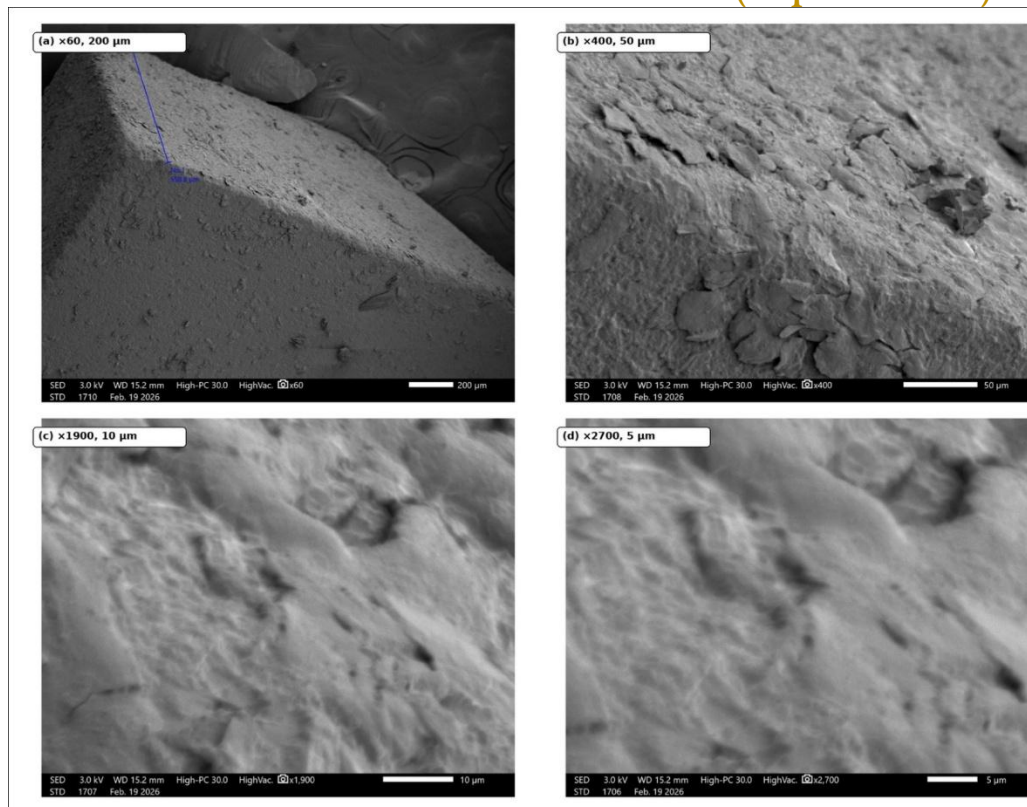
ν , cm ⁻¹	Signal description	Corresponding range in the literature	Comment
3428; 3324	Broad bands	Region of adsorbed moisture and/or surface hydroxyl groups	Consistent with surface moisture or hydroxyl-type groups
2113	Relatively distinct signal	Region typical of Si-H stretching vibrations	Consistent with the presence of Si-H bonds
1980	Weak signal	Region where combination or overlapping signals may be observed	No final identification was given
1679; 1595	Medium signal	Moisture deformation region and overlapping signals	Exact molecular attribution was not determined by FTIR alone
1463	Weak-to-medium signal	Region where ambiguous surface signals may be observed	Interpreted cautiously; no final identification was given

The FTIR results show that, although the Si matrix is dominant, chemically active bonding states are present in the near-surface layer. When considered together with the subsequent SEM/EDS results, this indicates that the surface is not homogeneous not only geometrically, but also chemically.

3.3. SEM/EDS analysis: microrelief and local elemental features

The SEM images showed surface heterogeneity, uneven relief, and partially clustered and agglomerated areas. At low magnification, the overall surface relief of the sample appears uneven, whereas at higher magnifications fine fragmentation, roughness, and local accumulations in the near-surface layer become more pronounced. This appearance indicates that surface formation processes did not proceed uniformly over the entire surface.

Figure 3. SEM images of the Si-Eu sample obtained at different magnifications.



Point EDS analysis detected C, P, and Eu signals, whereas the Si signal was observed at very low intensity. The calculated mass fractions were $91.85 \pm 2.04\%$ C, $0.01 \pm 0.16\%$ Si, $4.16 \pm 0.61\%$ P, and $3.97 \pm 1.84\%$ Eu. These ratios reflect the chemical characteristics of the selected local point rather than the average composition of the whole sample.

Figure 4. EDS point analysis: optical view, selected local region, and EDS spectrum.

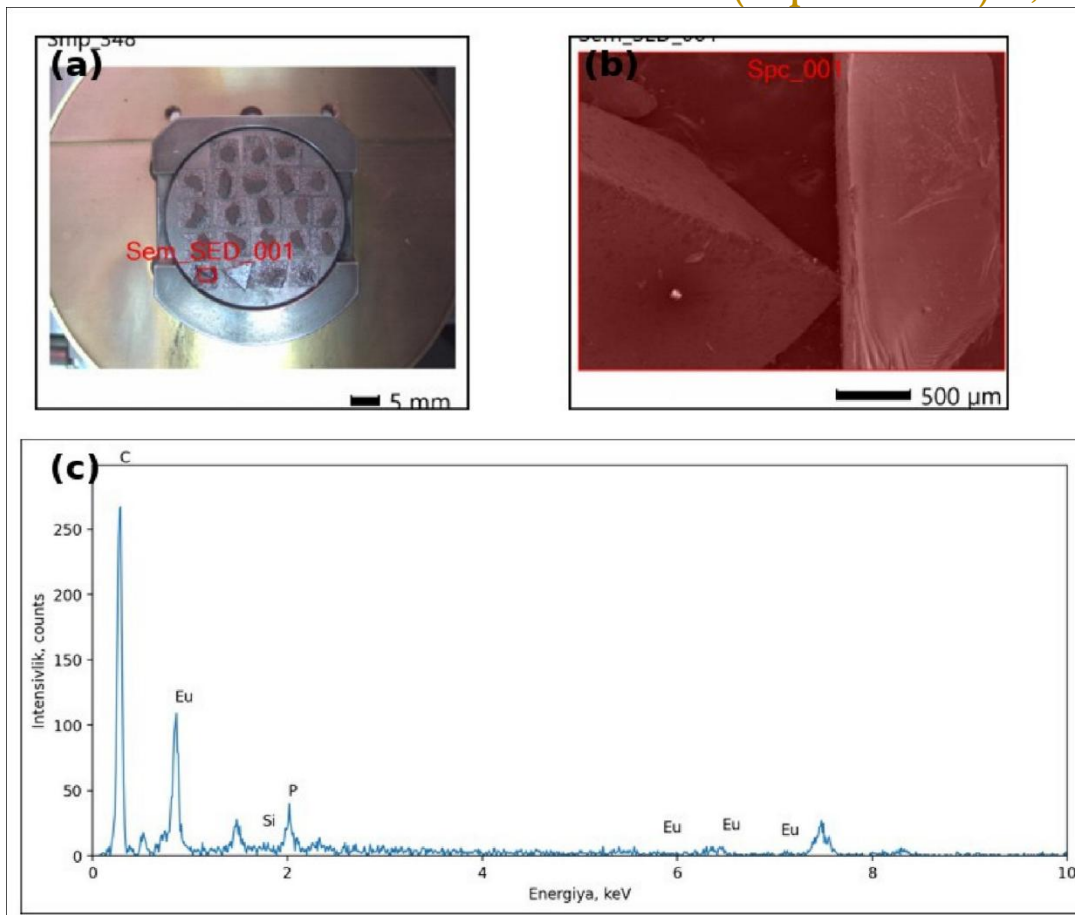


Table 4. Elemental composition at the selected EDS point

Element	Spectral line	Mass fraction, %	Atomic fraction, %
C	K	91.85 ± 2.04	97.94 ± 2.18
Si	K	0.01 ± 0.16	0.00 ± 0.07
P	K	4.16 ± 0.61	1.72 ± 0.25
Eu	L	3.97 ± 1.84	0.33 ± 0.15

Note: the values in the table refer only to the selected local point and are not interpreted as the average elemental composition of the entire sample volume.

3.4. Integrated interpretation of the results

When the XRD, FTIR, SEM, and EDS results are considered together, it becomes clear that the main crystalline basis of the Si-Eu system is the Si matrix, whereas the near-surface layer is chemically and morphologically nonuniform. XRD shows the dominance of the Si phase for the whole sample, FTIR reveals Si-H/OH states specifically in the near-surface layer, SEM shows the uneven surface relief, and EDS indicates that C, P, and Eu signals are detected at certain local points.

These results are not contradictory; rather, they represent information obtained at different depths and spatial scales. XRD provides information on the bulk crystalline basis, FTIR on surface bonds, SEM on surface topography, and EDS on the local elemental composition of a selected point. Therefore, it is not correct to generalize the Eu signal detected at a single EDS point as the distribution of Eu throughout the entire sample. The most cautious and scientifically justified conclusion is that, in a system dominated by the Si matrix, the near-surface layer is characterized by local chemical activity and microstructural heterogeneity.

This approach defines the main methodological advantage of the article: the results are not overgeneralized, and the strengths and limitations of each experimental method are taken into account. This makes it possible to cautiously interpret local signals in complex systems such as Si-Eu and correctly evaluate the real physicochemical state of the near-surface layer.

4. Conclusion

The local chemical activity and microstructural heterogeneity of the near-surface layer in the Si-Eu system were comprehensively evaluated using XRD, FTIR, SEM, and EDS methods. According to XRD and WPPF results, the crystal-phase basis of the sample is cubic Si, with a mass fraction of $99.37 \pm 0.07\%$. The very small secondary component recorded by WPPF at the level of $0.63 \pm 0.07\%$ was not interpreted as an independent phase without additional evidence.

In the FTIR spectrum, the broad bands at 3428 and 3324 cm^{-1} were shown to correspond to adsorbed moisture and hydroxyl states, while the signal at 2113 cm^{-1} was associated with Si-H bonds. The 1980-1463 cm^{-1} range was evaluated, without final molecular identification, as a cautious spectral feature reflecting the complex chemical state of the near-surface layer. SEM images showed uneven surface relief, local clustering, and partly agglomerated areas. EDS point analysis recorded C, P, and Eu signals; however, these results do not represent the average composition of the sample or the distribution of Eu over the entire surface.

Thus, the main scientific result of the work is the substantiation, through cautious comprehensive analysis, that in the Si-Eu system dominated by the Si matrix, the near-surface layer is chemically active and microstructurally nonuniform. This interpretation indicates the need to use additional mapping methods in future studies, including EDS mapping, XPS, or depth-profile analysis, to determine the real local distribution of Eu and its influence on optical and electronic properties.

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