Structural, surface and optical properties of nanoalumina produced by various ways

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Abstract. The compared study of the properties of liquid-phase and electric explosion alumina nanoparticles was made. The X-ray diffraction analysis demonstrated that these nanoparticles remain in amorphous and semi-amorphous states. The complete structural information of Al\(_2\)O\(_3\) nanoparticles was obtained as a result of the full-profile refinement of their model phase parameters. The parameters of the unit cells, spatial distribution of atoms, and occupancy of nodes were also determined. The data of IR spectra of surface OH groups and adsorbed CO revealed that the surface imperfection of an electric explosive sample is lower than that obtained using the liquid-phase method. Using photoluminescent spectroscopy, impurities of Cr\(^{3+}\), Mn\(^{4+}\) and Ti\(^{3+}\) in the octahedral oxygen coordination and Fe\(^{3+}\) in the tetrahedral oxygen coordination were detected. It was observed that the concentration of these impurities was significantly higher in the electric explosion sample. Using UV-Vis DR spectroscopy, it was found that the liquid-phase sample was amorphous, and the electric explosive sample was well crystallized and most probably consisted of 2D and 3D nanostructures.

1. Introduction
The synthesis modification of nanoparticle properties is an interesting and practically relevant task. Nanoparticles often do not have a crystalline structure (are X-ray amorphous) or the content of the crystalline phase is very low and can not be identified using conventional X-ray phase analysis methods. The properties of nanoparticle surfaces are the most important factors for determining the efficiency of their application. If the surface groups coincide, their heterogeneity becomes very important. For example, the ratio of the bridging to terminal –OH groups [1] and the number of Lewis acid sites [2] can vary. In addition, the synthesis method can introduce various impurities that also have a significant effect on the properties of nanoparticles. This leads to a variation of the catalytic activity, the intensity of the interaction of nanoparticles with the environment, particularly in ceramics [3], polymers [4, 5] etc. A similar effect was observed for alumina nanoparticles in [6], in which a similar comparative study of the structural state of nanoparticles obtained by electron beam evaporation and high-temperature hydrolysis was performed.
This work aims to identify and provide a model description of the structural state of Al\(_2\)O\(_3\) nanoparticles synthesised by electric explosion and liquid-phase methods; determination of the quantitative phase composition, structure parameters. Additionally, comparison of the surface characteristics of the samples and their relationship with the structural properties of the selected nanoparticles was performed.

2. Materials and methods

We used alumina nanoparticles synthesized by the liquid-phase method (LP) (China; mean size 25 nm) and the electric explosion method (mean size 55 nm) (EE) [7] in our study. The size of the initial nanoparticles was measured using TEM (JEOL-2010, Japan).

X-ray diffraction studies of Al\(_2\)O\(_3\) were carried out on DRON4-07. The surveys were performed on copper radiation (K\(_\alpha\)), according to the Bragg-Bretano scheme, with a step of 0.020. The exposure time at a point was 1 s in the angular range of 18–86°. The voltage on the X-ray tube was 30 kV and the beam current was 25 mA. A quantitative phase analysis (QPA) of Al\(_2\)O\(_3\) was carried out based on the Rietveld method [8]. As standards, we used lattices from the crystallographic bases COD and AMCSD [9, 10], (No. 96-120-0006, Corundum_0012922). The standards are symbolically called T and S, respectively. The X-ray diffraction analysis revealed that, as in [6, 8], alumina samples substantially had the same phases. Interestingly, the real states of the alumina samples were not strictly in the α phase, but all of them were in the X-ray amorphous state. Details of the X-ray studies of the corresponding “semi-amorphous” states can be found in [8].

The IR spectroscopy samples were pressed into tablets with a thickness (ratio of tablet weight to its geometric area) of 15 to 49 mg/cm\(^2\). The tablets were placed in a quartz IR cuvette and evaluated for 1 hour (vacuum of 10\(^{-5}\) Pa). After this, the samples, without coming in contact with the atmosphere, were transferred to a measuring chamber which allowed the recording of IR spectra at temperatures up to 77 K. Subsequently, we took the IR spectra of the samples before adsorption of CO at room temperature and then at 77–110 K. The IR spectra were taken from the Shimadzu IRTraser-100 spectrometer in the region of 600–6000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\). The IR spectra were accumulated through 100 scans which ensured a signal-to-noise ratio of at least 75000. The adsorption of CO was carried out at 77 K with doses that ensured pressure values in the cuvette as 0.1, 0.4, 0.9, 1.4 and 10 Torr.

The optical properties of the samples were studied using Ultraviolet-Visible Diffuse Reflection Spectroscopy (UV-Vis DRS) using a Shimadzu UV-2501 PC spectrophotometer with an ISR-240A diffuse reflection attachment. The samples in the form of a powder were placed in a quartz cuvette with an optical path length of 2 mm. The spectra were recorded relative to the reflection standard - BaSO\(_4\) in the range 190–900 nm (11000–54000 cm\(^{-1}\)) with a step of 2 nm. Reflection coefficients were converted to absorption coefficients using the Kubelka-Munk function \(F(R)=(1-R)^2/2R\), in which R is the diffuse reflection coefficient depending on the wave number expressed in cm\(^{-1}\). The obtained UV-Vis DRS data are presented in coordinates: the Kubelka–Munk function F(R) vs the wave number.

The photoluminescence (PL) spectra were measured using a Cary Eclipse (Varian) spectrofluorimeter in the wavelength range of 550-900 nm, with selective excitation of the wavelength region which is significant for the centre under study. Samples were placed in a quartz cuvette with an optical path length of 2 mm, and irradiation and collection of luminescence were carried out in the “reflection” mode. The measurements were performed under comparable conditions to compare the parameters of the observed PL. The PL excitation (PLE) spectra were recorded in the region of 200–600 nm. Processing of the PL spectra was performed in the OriginPro 15 program.

3. Results and discussion

3.1. X-ray modeling

Figure 1 shows the spatial distribution of atoms and the results of a full-profile refinement by the Rietveld method. Figure 2 shows the experimental diffraction patterns (a), b) curve 1), integrated
calculated intensities (curve 2), their difference (curve 3), and the calculated intensities of the individual phases in LP synthesis. For electric explosion synthesis, the refinement was carried out by the lattice T, whose contribution to the intensity turned out to be dominant (Fig. 1a).

Figure 1: Spatial distribution of atoms: lattice T (a); lattice S (b).

Figure 2: Diffraction patterns of the alumina nanoparticles. Synthesis: a) LP method; b) EE method. 1 - experimental, 2 - theoretical diffractograms, 3 - intensity difference. c) The calculated intensities of the phases: 1 - T; 2 - S.

Tables 1–4 show the structural parameters of lattices T and S in the initial state as well as after full-profile refinement. The tables also show the agreement criteria (R$_{wp}$) and fraction of the “explained” intensity of the experimental diffractograms. According to the results obtained (R$_{wp}$ criterion, intensity difference, Fig. 2), the theoretical intensities and quantitative phase contents are in accordance with the experimental ones. The acceptance criterion was found to be equal: R$_{wp}$ = 3.96, 7.37%, respectively. The structural parameters of the lattices of these phases are given in Tables 1. Tables 2, 3, and 4 show the relative coordinates of the atoms of the standards (initial) and the atoms after a full-profile refinement.

| Structure | a [nm] | b [nm] | c [nm] | $\alpha$ [deg.] | $\beta$ [deg.] | $\gamma$ [deg.] | Singony |
|-----------|--------|--------|--------|----------------|----------------|----------------|---------|
| T (LP)    |        |        |        |                |                |                |         |
| Initial   | 1.1795 | 0.2910 | 0.5621 | 90.00          | 103.79         | 90.00          | C2/m, monoclin. |
| Refinement| 1.20475| 0.27032| 0.6107 | 90.00          | 104.71         | 90.00          |         |
| T (EE)    |        |        |        |                |                |                |         |
| Initial   | 1.17950| 0.29100| 0.5621 | 90.00          | 103.79         | 90.00          | C2/m, monoclin. |
| Refinement| 1.19473| 0.28528| 0.5539 | 90.00          | 105.48         | 90.00          |         |
| S (EE)    |        |        |        |                |                |                |         |
| Initial   | 0.5120 | 0.5120 | 0.5120 | 55.28          | 55.28          | 55.28          | R-3C, trigon |
| Refinement| 0.51236| 0.51236| 0.51236| 55.03          | 55.03          | 55.03          |         |
Table 2. The relative coordinates of atoms in the lattice T (LP).

| Atoms | x      | y     | z      | Equval. | Occup. | Rwp | Part, [%] |
|-------|--------|-------|--------|---------|--------|-----|-----------|
| O     | Initial 0.16619 | 0 | 0.09877 | 0.01267 | 1.00  | 3.964 | 97.152    |
| O     | Refinement 0.163 | 0 | 0.123 | 0.01267 | 0.01267 |
| O     | Initial 0.56966 | 0 | 0.31235 | 0.01267 | 1.00  |
| O     | Refinement 0.489 | 0 | 0.261 | 0.01267 | 0.01267 |
| O     | Initial 0.91617 | 0 | 0.46845 | 0.01267 | 1.00  |
| O     | Refinement 0.83 | 0 | 0.439 | 0.01267 | 0.01267 |
| Al    | Initial 0.15117 | 0 | 0.83127 | 0.01267 | 1.00  |
| Al    | Refinement 0.101 | 0 | 0.794 | 0.01267 | 0.01267 |
| Al    | Initial 0.27202 | 0 | 0.64758 | 0.01267 | 1.00  |
| Al    | Refinement 0.352 | 0 | 0.687 | 0.01267 | 0.01267 |

Table 3. The relative coordinates of atoms in the lattice T (EE).

| Atoms | x      | y     | z      | Equval. | Occup. | Part, [%] |
|-------|--------|-------|--------|---------|--------|-----------|
| O     | Initial 0.163 | 0 | 0.123 | 0.01267 | 1     |
| O     | Refinement 0.05206 | 0 | 0.00074 | 0.01267 | 1     |
| O     | Initial 0.489 | 0 | 0.261 | 0.01267 | 1     |
| O     | Refinement 0.56517 | 0 | 0.27674 | 0.01267 | 1     |
| O     | Initial 0.83 | 0 | 0.439 | 0.01267 | 1     |
| O     | Refinement 0.94956 | 0 | 0.59524 | 0.01267 | 1     |
| Al    | Initial 0.101 | 0 | 0.794 | 0.01267 | 1     |
| Al    | Refinement 0.14416 | 0 | 0.81285 | 0.01267 | 1     |
| Al    | Initial 0.352 | 0 | 0.687 | 0.01267 | 1     |
| Al    | Refinement 0.26246 | 0 | 0.63903 | 0.01267 | 1     |

Table 4. The relative coordinates of atoms in the lattice S(EE).

| Atoms | x      | y     | z      | Equval. | Occup. | Rwp     | Part, [%] |
|-------|--------|-------|--------|---------|--------|---------|-----------|
| O     | 0.553 | -0.053 | 0.25 | 0 | 1 | 7.369 | 17.028 |
| Al    | 0.355 | 0.355 | 0.355 | 0 | 1 | 7.369 | 17.028 |

It can be assumed that

1) the main fraction of the LP particles was the amorphous phase (∼ 0.97 T, Table 2),
2) the main fraction of the EE particles was the superposition of the phases T and S (Table 3, 4),
the proportion of which was ∼ 0.79 and 0.17, respectively.

Figure 2 shows that the diffraction pattern of the alumina synthesised by the LP method corresponds to an amorphous state. In fact, the role of the main reflexes in the integrated intensity is insignificant (Fig. 2a. curve 1). The X-ray amorphous state is formed by 12 polyhedra with a central Al atom. Polyhedra can be of two types: angular and with edges [11]. The semi-amorphous state of electric explosion nanoparticles is characterised by six polyhedra (with edges). We estimated the mixing energy to analyse the stability of lattices with refined structural parameters. Details of the calculations are given in [12]. Modeling was carried out from the first principles by the formula $E_c = E_t - [x E_{Al} + y E_O]$, where $E_t$, $E_{Al}$, $E_O$ are the energy of the Al$_2$O$_3$ lattice and of pure Al and O elements, respectively. The $x$, $y$ values are the relative number of O and Al elements in Al$_2$O$_3$, which are equal for T and S lattices: $x = (\alpha / 4)$, $y = (\beta / 4)$. The numbers $(\alpha, \beta)$ are (8, 12) and (4, 6) for the lattices T and S, respectively.
The binding energy of atoms in the lattices is $|E_c|$. The results of the mixing energy calculations are given in Table 5, which also shows the energies of the lattices of pure elements. As follows from the above results, the alumina mixing energies in different states turn out to be substantially negative, i.e. model lattices are in highly stable atomic configurations [8].

Table 5. The mixing energy of Al$_2$O$_3$

| Method              | Phase | $E_b$ [eV]          | $E_c$ [eV] | $E_{Al}$ [eV] | $E_{O}$ [eV] |
|---------------------|-------|---------------------|-----------|---------------|---------------|
| Liquid phase        | T     | -5723.625753        | -356.89   |               |               |
| Electric explosion  | T     | -5649.928373        | -279.799  | -228.63489    | -3272.9775    |
|                     | S     | -2863.38232         | -184.906  |               |               |

Additionally, we calculated the elastic moduli of Al$_2$O$_3$ using GULP [13] for amorphous and semi-amorphous lattices T and S after preliminary geometric optimisation using the Streitz-Mintmire potential [14]. The calculation results are provided in Table 6. For comparison, Table 6 presents the experimental values of the elastic characteristics of crystalline phases [11]. The analysis showed that the elastic moduli of amorphous and semi-amorphous phases are lower than the corresponding values for crystalline phases.

Table 6. Elastic characteristics of Al$_2$O$_3$

| Method              | Phase | $B$ [GPa] | $G$ [GPa] | $E$ [GPa] |
|---------------------|-------|-----------|-----------|-----------|
| Liquid phase        | T     | 192.384   | 102.335   | 341.865   |
| Electric explosion  | T     | 192.384   | 102.335   | 340.952   |
|                     | S     | 241.174   | 137.823   | 358.564   |
| Solid               | $\gamma$ | 253      | 164       | 404.6     |
| Solid               | $\alpha$ | 192      | 102       | 342.0     |

3.2. IR spectroscopy

Fig. 3a presents the IR spectra for a sample obtained using LP synthesis. It consists of five bands of OH groups: 3795, 3780, 3732, 3695, and 3670 cm$^{-1}$. The first two bands are related to terminal OH groups associated with three- and five- coordinated (defective) aluminum ions. The remaining bands belong to OH bridging groups connected simultaneously with two aluminum ions in different coordination. Due to the broadening of the bands, it was very difficult to make a detailed interpretation of the spectra. According to the strength of the acid centres, the hydroxyl groups of 3795 cm$^{-1}$ were very weak, because their shift during CO adsorption was 30 cm$^{-1}$.

![Figure 3](image)

**Figure 3**: IR spectra of CO adsorbed on LP alumina (a) and EE alumina (b). 1 - IR spectrum of OH groups of the ignite sample (thickness 35 mg / cm$^2$), 2-6 IR spectra recorded after CO adsorption at pressures of 0.1; 0.4; 0.9; 1.4 and 10 Torr.
The bands related to bridging OH groups upon CO adsorption show the shift of 135–140 cm\(^{-1}\), which implies that these are weakly acidic OH groups. In the region of CO valence vibrations (2050-2250 cm\(^{-1}\)), bands 2197–2180 cm\(^{-1}\) are observed, which relate to complexes of CO with Lewis acid centres of medium strength. The 2164 cm\(^{-1}\) band belong to CO complexes with OH groups of medium acidity, but the corresponding OH groups, against the background of weaker complexes (band 2157 cm\(^{-1}\)) with bridging OH groups, cannot be detected. Probably the band 3690 cm\(^{-1}\) can be attributed to these OH groups.

The EE sample IR spectra of the OH groups (Fig. 3b) shows two bands 3783, 3721, and a shoulder of approximately 3680 cm\(^{-1}\). The first band refers to terminal OH groups associated with 3 and 5 coordinated (defective) aluminum ions; probably due to the broadening of the bands, 3780 cm\(^{-1}\) and 3795 cm\(^{-1}\) merge into one range. The remaining bands belong to OH bridging groups connected simultaneously with two aluminum ions in different coordination. The terminal OH groups, under CO adsorption (Fig. 3b), showed more than 30 cm\(^{-1}\) shift, which implies that these OH groups have stronger acidity. The bridging OH groups were weaker than for the LP sample, as the shift during CO adsorption was about 120 cm\(^{-1}\), instead of 135 cm\(^{-1}\). The strongest Lewis centres are characterized by a band of 2197 cm\(^{-1}\).

In the region of CO valence vibrations (2050–2250 cm\(^{-1}\)), EE sample cleared bands of 2198–2178 cm\(^{-1}\), which were related to complexes of CO with Lewis acid centres of medium strength. The strongest Lewis centres were found in the band 2189 cm\(^{-1}\). Additionally, in the IR spectrum upon adsorption of the first portion of CO, a band of 2112 cm\(^{-1}\) was cleared, which can be attributed to the adsorption of CO on Ti\(^{3+}\) clusters.

Therefore, it can be concluded that the LP sample was quite close to the well-crystallized \(\alpha\)-phase of alumina with a slightly pronounced increased defectiveness (the relative intensity of the band is 3780-3795 cm\(^{-1}\) compared to bands below 3735 cm\(^{-1}\)) than for well crystallized alumina. This is probably due to a higher ignition temperature. A similar result was obtained from the data on the properties of the Lewis centres. The EE sample probably contained a small amount of titanium oxide (concentrations about of 1-2 mkmol / g (0.006-0.01% wt.), due to the technological aspects of its synthesis way.

### 3.3. PL spectroscopy

It is known that, regardless of the synthesis method, defects in the form of anionic oxygen vacancies and 3d impurity elements are always present in Al\(_2\)O\(_3\) [15–18]. In the PL study, the focus was on the luminescence of 3d elements, due to their potential use as structurally sensitive probes. The most commonly analyzed impurities in Al\(_2\)O\(_3\) are Cr\(^{3+}\) ions. The studies demonstrated that upon selective excitation with \(\lambda = 532\) nm in the region characteristic of the 4A\(_2\) \(\rightarrow\) 4T\(_2\) electronic vibrational transition of Cr\(^{3+}\) ions, the PL of both samples appears in the region of 650-850 nm with a maximum at 693 nm (Fig. 4). This band results from the inhomogeneously broadened 2E \(\rightarrow\) 4A\(_2\) electronic transition in the octahedrally coordinated Cr\(^{3+}\)Oh ions. The FWHM value for the LP sample is larger which can be associated with the smaller size of nanoparticles. For both samples, the PL is represented as a complex curve. In addition to the main maximum, the PL spectra show shoulders with maxima at 676, 687 and 710 nm. The EE sample spectra show shoulders with peaks at \(\sim 750\) nm and \(\sim 800\) nm and also present bands with maxima of 705 and 713 nm.

The complex shape of the observed PL is due to the manifestation of various impurities of 3d elements, the luminescence of which can also occur at \(\lambda_{\text{ex}} = 532\) nm. The PL band with \(\lambda_{\text{max}} = 676\) nm is due to the inhomogeneously broadened electronic transition 2\(^2\)E \(\rightarrow\) 4A\(_2\) in octahedrally coordinated Mn\(^{3+}\)Oh ions. The wider bands with maxima at \(\sim 750\) and \(\sim 800\) nm results from luminescence by tetrahedrally coordinated Fe\(^{3+}\)Td ions (\(^4\)T\(_1\) \(\rightarrow\) \(^6\)A\(_1\) transition) and octahedrally coordinated Ti\(^{3+}\)Oh ions (transition \(^2\)E \(\rightarrow\) \(^2\)T\(_2\)), respectively [15-18].

In the case of Cr\(^{3+}\), its PL depends on the local environment; therefore, the observed bands with \(\lambda_{\text{max}} = 686\) nm, \(\lambda_{\text{max}} = 693\) nm, \(\lambda_{\text{max}} = 702\) nm and \(\lambda_{\text{max}} = 713\) nm can correspond to the emission of
Cr$^{3+}$ in the structure of alumina, whose local structure corresponds to various polymorphic modifications of Al$_2$O$_3$. The position of the band with $\lambda_{\text{max}} = 693$ nm was very close to the known value for Cr$^{3+}$ in high-temperature $\alpha$-Al$_2$O$_3$, with $\lambda_{\text{max}} = 687$ nm for Cr$^{3+}$ in $\theta$-Al$_2$O$_3$ and with $\lambda_{\text{max}} = 702$ nm for Cr$^{3+}$ in $\gamma$-Al$_2$O$_3$ and/or $\delta$-Al$_2$O$_3$ [15-19]. Moreover, the bands at 676, 705, and 714 nm correspond to vibronic sidebands in Cr$^{3+}$ ions which would then prove the presence of a local $\alpha$-Al$_2$O$_3$ structure in the EE sample (Fig. 4, curve 2).

![Figure 4: The PL spectra of samples obtained: 1 - by the LP method (dashed curve, signal intensity increased by 25 times); 2 - by EE method (solid curve), $\lambda_{\text{ex}} = 532$ nm.](image)

The PL decay kinetics for the band with $\lambda_{\text{max}} = 693$ nm ($^2E \rightarrow ^4A_2$ transition in Cr$^{3+}$) lied in the millisecond interval and is better described by a biexponential dependence with a fast $\tau_1 = 0.6$ ms and a slow component $\tau_2 = 4.2$ ms.

The PLE spectrum of Cr$^{3+}$ ions in Al$_2$O$_3$ ($\lambda_{\text{max}} = 693$ nm, $^2E \rightarrow ^4A_2$) recorded for the EE sample (Fig. 5) contained intense broad bands in the regions 350 - 475 nm and 500 - 625 nm. These bands with maxima at $\lambda_{\text{max}} = 405$ nm and $\lambda_{\text{max}} = 562$ nm correspond to transitions $^4T_1 \rightarrow ^4A_2$, $^4T_2 \rightarrow ^4A_2$, respectively.

![Figure 5: PLE spectrum of the EE sample, $\lambda_{\text{PL}} = 693$ nm.](image)

The maxima of these bands were very close to the known data for Cr$^{3+}$ in $\alpha$-Al$_2$O$_3$. In the UV region of the spectrum, there was a wide band in the region of 200-370 nm, which does not apply only to Cr$^{3+}$ in $\alpha$-Al$_2$O$_3$. Due to the considerable overlap of wide PL bands from different luminescence centres, the PLE spectra in the region of 200–370 nm recorded for the band $\lambda_{\text{max}} = 693$ nm, could contain luminescence centres other than Cr$^{3+}$. Of the most frequently encountered ions in Al$_2$O$_3$ that can produce a band in this region, we could distinguish Fe$^{3+}$ $^{T_d}$, Ti$^{3+}$ $^{T_d}$, and Mn$^{4+}$ $^{T_d}$ ions. The PLE bands in this region for them, as a rule, were due to the ligand-to-metal charge-transfer bands (LMCT). Excitation of an intense band in the UV spectral region with $\lambda_{\text{ex}} = 310$ nm made it possible to obtain intense emission bands in the wavelength range 650–875 nm, with a maximum near 750 nm and a shoulder with a maximum at ~ 800 nm (Fig. 6).
The bands with $\lambda_{\text{max}} \sim 747$ nm and $\lambda_{\text{max}} \sim 800$ nm were reproduced perfectly when the initial spectrum decomposed into two Gaussian components. Moreover, in the range 650–700 nm for a liquid-phase sample, under such excitation, a less intense band with a maximum at 676 nm appeared in the shoulder. Along with the analysis of the PL bands of these samples at $\lambda_{\text{ex}} = 532$ nm, the PL bands at $\sim 750$ nm and $\sim 800$ nm in Fig. 10 can be unambiguously attributed to the PL of tetrahedrally coordinated Fe$^{3+}$ Td ions and octahedrally coordinated Ti$^{3+}$ Oh ions and at $\sim 676$ nm to octahedrally coordinated Mn$^{4+}$ Oh ions. As in the case of Cr$^{3+}$ Oh ions, the intensity of the PL bands of Ti$^{3+}$ Oh and Fe$^{3+}$ Td in the electric explosion sample (curve 2) was significantly higher, which indicates a high concentration of these impurities in this sample; this is consistent with the DRS data.

The PL decay kinetics of an electroexplosive sample for a band with $\lambda_{\text{max}} = 750$ nm ($^4T_1 \rightarrow ^6A_1$ transition in Fe$^{3+}$ Td) at $\lambda_{\text{ex}} = 532$ nm, as in the case of Cr$^{3+}$ Oh ions, lies in the millisecond range and is better described by a biexponential dependence with fast $\tau_1 = 1.0$ ms and the slow component $\tau_2 = 4.7$ ms. The PLE spectrum for this band contains only an intense wide band in the UV region of the spectrum with a maximum at $\sim 300$ nm; this results from the O$^2-$ - Fe$^{3+}$ charge-transfer band and also through the partial contribution of O$^2-$ - Ti$^{3+}$ due to the strong overlap of the PL bands with $\sim 750$ nm and $\sim 800$ nm.

### 3.4. UV-Vis DRS results

UV-Vis DRS spectrum shows that the LP sample (Fig. 7a) clears three absorption regions: up to 20,000 cm$^{-1}$, 20,000–40,000 cm$^{-1}$ and a region above 40,000 cm$^{-1}$. The nature of the UV-Vis DRS spectrum of the EE sample (Fig. 7b) was completely different: absorption was observed below 25,000 cm$^{-1}$, a wide shoulder 30,000–42,000 cm$^{-1}$, and absorption in the region above 42,000 cm$^{-1}$.

It is known [20] that in the IR region a weak absorption band results from the d–d transition of Fe$^{2+}$ cations in octahedral oxygen coordination for which LMCT bands appear in the UV spectral region. In oxygen-containing matrices, such Fe$^{2+}$ Oh cations are isolated and embedded in the lattice of this matrix and produce FeAl$_2$O$_4$ type clusters. The reason is that the Al$_2$O$_3$ matrix can fix only Me$^{3+}$ Oh, such as Cr$^{3+}$, Fe$^{3+}$ and Ti$^{3+}$ cations due to an isomorphic substitution of Al$^{3+}$ cations in the lattice. Furthermore we discovered them in these samples using PL spectroscopy.

![Figure 6](image)

**Figure 6:** The PL spectra of 1 – the LP sample (dashed curve); 2 - the EE sample (solid curve, the signal intensity was reduced 93 times), $\lambda_{\text{ex}} = 310$ nm.

Based on the analysis of the UV-Vis DRS spectrum of a LP sample, it was observed that absorption of about 30,000 cm$^{-1}$ has a lower intensity than absorption in the region up to 20,000 cm$^{-1}$. This indicates that this sample contains impurity ions absorbing in the near IR region at a border with the visible region, such as Ti$^{3+}$ Oh and Fe$^{2+}$ Oh, almost twice as much as ions absorbing only in the visible region at the border of the UV region of the absorption spectrum such as Cr$^{3+}$ Oh and Mn$^{4+}$ Oh. In this case, the UV region of the UV-Vis DRS spectrum above 40,000 cm$^{-1}$ shows the LMCT bands of the mentioned d elements, which were earlier detected and uniquely identified by PL spectroscopy. EE sample (Fig. 7) presents a completely different picture of the UV-Vis DRS spectrum. The visible region shows up, as in the case of a LP sample, d-d transitions of impurity d elements, such as Ti$^{3+}$ Oh and Fe$^{2+}$ Oh, most likely contained in a feedstock wire.
Based on the analysis of absorption in the region above 30,000 cm\(^{-1}\) in the UV-Vis DRS spectrum, it can be suggested that the EE sample consisted of two parts. The first part is well crystallized (3D structure) which absorbed in the UV region of the UV-Vis DRS spectrum above 42,000 cm\(^{-1}\). The second part is 2D crystalline structures, similar to the alumina obtained by microwave activation of the initial gibbsite Al(OH)\(_3\) [21].

![UV-Vis DRS spectra](image)

Figure 7: UV-Vis DRS spectra of: a) the LP sample (dash, the intensity is increased 100 times); b) the EE sample (solid).

Moreover, the total absorption in the entire range for the LP sample was almost 100 times less than that for the EE sample. This indicates that the LP sample was amorphous, and the EE sample was well crystallized and probably consisted of 2D and 3D aluminum-containing structures, similar to the alumina samples obtained through microwave irradiation of the initial gibbsite Al(OH)\(_3\) [21]. In this case, the LP sample contained the main Fe\(^{2+}\)\(_{\text{OH}}\) cations. The content of Ti\(^{3+}\)\(_{\text{OH}}\) cations and other impurity cations (Mn\(^{4+}\)\(_{\text{OH}}\), Fe\(^{3+}\)\(_{\text{Td}}\) and Cr\(^{3+}\)\(_{\text{OH}}\)) was low, but was discovered using PL spectroscopy. However, the EE sample contained only Fe\(^{2+}\)\(_{\text{OH}}\) cations.

Thus, it was shown that the surface and optical properties of nanoparticles can unpredictably differ depending on the method of their synthesis, despite the proximity of their structure. A comparison with the results obtained in [6] confirms this conclusion and necessitates a more detailed study of the properties of nanoparticles before their practical use.

### 4. Conclusion

The structural state of alumina produced by the LP and EE methods was examined using the Rietveld and simulation methods. The Rietveld method demonstrated that an amorphous state was formed in the first case, with T phase being the main part phase. In the second case, alumina nanoparticles consisted of a mixture of phases based on the lattices T and S, with T being the dominant structure. The distribution of atoms in polyhedra and other types as well as a variation in the parameters of model lattices were demonstrated. The distinguishing features of the structural state were the differences in the total and binding energies. Due to the higher binding energy, the alumina synthesised by the LP method was more stable.

Using IR spectroscopy, it was demonstrated that the fraction of terminal OH groups and their strength on the surface of EE sample was lower than that of LP sample.

The PL of impurity 3d elements revealed that the concentration of impurities was significantly higher in the EE sample, which is associated with the features of the synthesis. The analysis of the PL, PLE spectra, and PL decay kinetics allowed the determination of the coordination of the detected impurity ions. The use of Cr\(^{3+}\)\(_{\text{OH}}\) ions as structurally sensitive probes allowed to reveal a local structure close to well crystallized \(\alpha\)-phase in both samples.

The UV-Vis DRS cleared that the EE sample contained well-crystallized, probably, 2D and 3D Al\(_2\)O\(_3\) nanostructures, and the LP sample was amorphous. Moreover, the LP sample contained significantly less impurity cations and had almost a 100-fold lower absorption compared to the EE sample.
Acknowledgments
The studies of UV-Vis DR, IR and PL spectroscopy of the Al_2O_3 samples are conducted using the equipment of the Center of Collective Use "National Center of Catalyst Research".
This work was supported by Ministry of Science and Higher Education of the Russian Federation (project No. AAAA-A17-117041110045-9 and project No. 0336-2019-0008).

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