X-ray diffraction study of structure of CaO—Al₂O₃—SiO₂ ternary compounds in molten and crystalline states

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Abstract

Anorthite and gehlenite crystalline structure and short-range order of anorthite melt have been studied by X-ray diffraction in the temperature range from room temperature up to ~ 1923 K. The corresponding anorthite and gehlenite phases were identified as well as amorphous component for anorthite samples having identical shape to XRD pattern of the anorthite melt. The structure factor and the radial distribution function of atoms of the anorthite melt were calculated from the X-ray high-temperature experimental data. The partial structural parameters of the short-range order of the melt were reconstructed using Reverse Monte Carlo simulations.

Keywords: gehlenite, anorthite, mullite, high-temperature X-Ray diffraction, RMC simulations

Abbreviations
IC is the intensity curve of X-Ray diffraction
SF - the structure factor
RDF - the radial distribution function
RMC -the reverse Monte-Carlo method
CN - the average coordination number of atoms
ASNG - the alumina silicate nanogrouping
CAS - CaO—Al₂O₃—SiO₂ system
Rₐ(i-j) the most probable nearest interatomic distances between atoms of i- and j-type

1. Introduction

Materials based on the CaO—Al₂O₃—SiO₂ (CAS) and MgO—Al₂O₃—SiO₂ ternary diagrams are crucial for the Ukrainian national economy and other countries due to numerous applications. For example, slags based on these systems are applied in blast furnace production. Many welding fluxes and fluxes for surfacing are also known [1]. Gehlenite, anorthite, mullite, sillimanite and other synthetic compounds of the CAS system have been used at ZAO “Technohim” (Zaporizhia, Ukraine).

It should be noted that the number of publications about properties and structure of main minerals of this system in liquid and crystalline states are relatively limited [2-6]. We performed investigation of the melts of three eutectic CAS oxide system samples [6] by high-temperature X-ray diffraction. The study of the ceramic welding flux based on the MgO-Al₂O₃-SiO₂ system with CaF₂ additives are presented in [7]. In according to [6] the eutectics exist at the anorthite region boundaries.

Our previous high-temperature study [6] allows to conclude that the anorthite is present in all solid samples of the eutectics. The present work is devoted to investigation anorthite and gehlenite compositions which are only known ternary compounds of the CAS system. The study of anorthite and gehlenite both in solid and molten states is necessary to understand the nature of
interaction in the CAS system, since the minerals that are formed are very important for physical chemistry, metallurgy and materials science.

2. Experimental procedure

At the initial stage, powders of $\text{Al}_2\text{O}_3$, $\text{SiO}_2$, and $\text{CaCO}_3$ reagents having especially pure grade were mixed in required ratios and were grounded by “Retsch PM 400” ball mill. The ternary compounds were synthesized by heat treatment in platinum-iridium alloy crucibles at 1750°C for 2 h using the Tamman furnace in the flow of high purity argon with further cooling to room temperature (RT). The cores of the samples were separated from the crucibles without touching the crucibles walls using diamond-coated drill. The resulting product was ground again in the same mill and then was further purified in a laboratory scale magnetic separator. Composition, melting points, experimental temperature and phase composition before melting according to XRD analysis are shown in Table 1.

Table 1. Composition, melting points, investigated temperatures and phase composition of investigated samples

| №  | Composition, atomic fraction | Melting point, K | Temperatures of investigation, K | Phase composition before melting |
|----|----------------------------|------------------|---------------------------------|--------------------------------|
| 1  | CaO 0.25, Al$_2$O$_3$ 0.25, SiO$_2$ 0.50 | 1820 [8] 1873 [our data] | 293 (RT), 1073, 1273, 1373, 1473, 1673, 1773, 1823 (melt) | CaAl$_2$Si$_2$O$_8$ |
| 2  | CaO 0.50, Al$_2$O$_3$ 0.25, SiO$_2$ 0.25 | 1863 [8] | 293 (RT), 773, 1073, 1273, 1473, 1673 | Ca$_2$Al$_2$SiO$_7$ |

The powdered sample was placed in special molybdenum (Mo) crucible with the carefully smoothed out and polished inner surface to reduce interaction with investigated melts. The XRD study was performed by high-temperature X-ray θ-θ diffractometer using monochromatic MoK$_\alpha$ radiation in a vacuum chamber filled with high-purity helium X-ray diffractometer. The design and experimental procedure of the diffractometer were described in [2,6,9,10]. The XRD pattern of anorthite at room temperature is shown in Fig. 1. The amorphous backgrounds of the XRD patterns of the anorthite at all investigated temperatures are shown in Fig. 2. The crystalline part of the XRD patterns of anorthite at different temperatures in comparison with the XRD of the anorthite melts are given in Fig 3. After amorphous background subtraction the all XRD patterns were normalized to maximum intensity of 1000 n.u.

![Figure 1. XRD pattern of anorthite at room temperature](image1)

![Figure 2. Normalized background of anorthite sample in liquid and solid states at different temperatures](image2)
temperatures. There are two curves at RT: before (1) and after remelting (2).

Figure 3. XRD patterns of crystalline anorthite at different temperatures (a) and anorthite melts (above); XRD patterns of anorthite at room temperature (b) before (1) and after remelting (2)

The XRD patterns of gehlenite at various temperatures are shown in Fig. 4, 5. The subtraction of the amorphous background and normalization of the XRD patterns of gehlenite were performed in the same way like in the anorthite case. The following software was applied to analyze crystalline diffraction patterns: PCW, Match, X’Pert HighScore Plus, Diamond 3.2.

Figure 4. X-Ray patterns of gehlenite samples at different temperatures
Figure 5. XRD patterns of gehlenite samples at room temperature before (1) and after remelting (2).

The phase diagram of CAS system is shown in Fig. 6. The red circles indicate the location of the ternary compounds that are studied in this work. The gray circles show the compositions (1,2,3) investigated in [6]. It should be noted that the anorthite position on CAS phase diagram is in the immediate vicinity of the mullite field, and gehlenite is much further. Therefore, the composition of the sample studied in [4] (green circle) even more enriched with calcium oxide and having structure in the molten state that may differ significantly.

The XRD-pattern of molten anorthite at 1923 K was obtained by high-temperature 0-0 diffractometer (MoKα radiation). It should be noted that the anorthite melting point is in accordance with [8]. However, the XRD pattern of anorthite sample at 1820 K contains unstable crystalline peaks which does not match with mullite phase. The completely molten sample was
obtained at 1873 K only. Nevertheless, the experimental temperature was increased up to 1923 K to avoid mentioned unstable effects observed near the melting point.

The structure factor (SF) and radial distribution function (RDF) curves were calculated by self-developed software [6, 7]. The structure models were reconstructed from experimental data (experimental SF) using Reverse Monte Carlo (RMC) simulations [11,12,13]. There are no experimental densities of the CAS melts therefore required melt density values at the investigated temperature was evaluated using the approach proposed in [14]. This method is based on the analysis of the RDF region before the first (main) peak. It allows estimating adequate density values of the investigated melts. Fig. 7, 8 show the SF and RDF curves for the anorthite melt. The dotted line in Fig. 7a is the SF curve obtained by RMC simulations, the solid line – experimental data. The experimental and simulated structure factor curves are consistent and complement each other within the experimental error.

Figure 6. Phase diagram of the CAS system. The investigated ternary compound (red circle), the eutectic samples (1,2,3) studied in [6] (gray circles).

Figure 7. Experimental (solid line) and simulated (dotted line) SF (a) and experimental IC (b) for anorthite melt.

Figure 8. Radial distribution curve for the anorthite melt.

3. Results

3.1 Crystalline samples

The XRD pattern of anorthite samples at RT and annealed at different temperatures contain reflections identified as crystalline anorthite phase as well as the rather strong background of amorphous component. An example of such XRD pattern at RT is shown in Fig.1. The amorphous contributions at all experimental temperatures are presented in Fig.2. These patterns have a certain similarity with each other and resemble a scattering curve from the
melt. Therefore, it might lead to the preliminary conclusion that the crystalline and amorphous components have identical composition in samples. The reflexes of different XRD patterns of crystalline anorthite sample (up to 1773 K) were identified as the anorthite phase. The good agreement with peaks positions with minor difference in the peaks relative intensities were observed. There were no changes up to melting point with exception of an enlargement of the anorthite phase lattice parameters with temperature rise and the characteristic intensive amorphous background of anorthite XRD patterns. During solidification of remelted sample in the furnace cooling mode there is no enough time to form crystalline phases therefore an amorphous phase is also formed (Fig. 1). It should be noted that both crystalline and non-crystalline scattering components have no changes even during long isothermal treatment. The anorthite sample XRD pattern was changed significantly (Fig. 3b) after melting and heat treatment for two hours at 1923 K and following fast cooling in accordance with the furnace cooling mode. It may be noted that after remelting the XRD of the solid sample has weak peaks of the anorthite phase and more intense peaks of the unidentified phase (phases) that was absent before melting. The non-crystalline component of scattering is very high and reminds practically the same after melting (Fig. 2).

The amorphous background is practically absent on the XRD patterns of gehlenite (Fig. 4) (unlike the XRD patterns of anorthite). The temperatures of this study are indicated in Table 1 and Fig. 4. The melting point of gehlenite is 1866 K [8]. Unfortunately, our attempts to register a typical liquid curve were failed up to temperatures about 1700°C (the limiting operating of high temperature diffractometer). The XRD patterns of the gehlenite samples were interpreted as gehlenite phase below the melting point (up to 1773 K). The background amorphous component is practically absent before and after melting on the diffractograms. Like anorthite, the crystalline component undergoes significant changes after remelting. To interpret successfully obtained data we should assume that the gehlenite (and probably anorthite) partial decomposition into simple oxides and more complex CaSiO$_3$ type double oxides have place. The absence of amorphous background on XRD pattern of the gehlenite can be explained by difference of their melt viscosity (2.5 Pa×s for anorthite and 0.27 Pa×s for gehlenite melts) [17]. In case of the anorthite the crystallization is complicated by higher viscosity of corresponding melt therefore the amorphous phase is formed.

3.2. RDF analysis of the anorthite melt

The first maximum on the experimental RDF has position at 0.167 nm. According to our data, it can be the superposition of Si-O (0.164 nm) and Al-O (0.169 nm) coordination contributions. Silicon and aluminum coordination numbers by oxygen were calculated by the formula:

$$A_{Si(O)} = 2n_{Si}K_{Si}K_{O}Z_{Si(O)} \quad A_{Al(O)} = 2n_{Al}K_{Al}K_{O}Z_{Al(O)}$$  \hspace{1cm} (1)

where $A_{Al(O)}$, $A_{Si(O)}$ are the areas of Gaussian curves (coordination contributions) calculated from experimental RDF, $n_{Me}$ is the atomic fraction of the corresponding oxide component; $K_{Me}$, $K_{O}$ are the atomic scattering factors of elements averaged out at scattering angles and composition, $Z_{Me(O)}$ is the coordination number (CN) of silicon or aluminum by oxygen. The Equation (1) describes the case of central cationic polyhedron surrounded by polyhedrons of the same type. So far as the atomic fractions and scattering factors ($K_{Me}$) are slightly different they give very similar results. The oxygen polyhedrons with silicon and aluminum atoms inside (mostly tetrahedra) form joint nanogroupings. These alumosilicate nanogrouping (ASNG) based on close packed structure of oxygen atoms with Al$^{3+}$ occupying both octahedral and tetrahedral sites, Si$^{4+}$ occupying tetrahedral ones that forms in the molten and amorphous states.

Calcium atoms are probably not a part of such groupings. The coordination contribution of Ca-O is observed at 0.223 nm (the position of the peak R$_1$(Ca-O) = 0.223 nm) and the calcium coordination number by oxygen is quite large (about 9.5). This value of coordination number is undoubtedly too large to support joint Si—Al—Ca—O nanogroupings since the octahedral cavities formed in close packed ASNG will be small to accommodate Ca$^{2+}$ cations. According to
obtained data the melt consists of Si-Al-O nanogroupings with calcium captions concentrated on the surface of the ASNG and followed by the outer layer of oxygen atoms.

### 3.3 RMC simulations of the anorthite melt

The simulated SF is in good agreement with experimental one (Fig7). It may be noted that unlike to most oxide melts the first maximum on SF is lower than the second one. The structural parameters obtained by both RDF and RMC methods correlate well with each other. For example, according to RDF analysis the $R_1$(Si-O) is 0.164 nm and $R_1$(Al-O) is 0.169 nm. The closest interatomic $R_1$(Si-O) and $R_1$(Al-O) distances obtained from partial pair correlations functions (RMC data) are equal to 0.163 and 0.171 nm, respectively (Fig. 9, a1). The corresponding CNs for both cases are close to 4 (Fig. 9, a2). Therefore, four oxygens are coordinated predominantly around the silicon or aluminum atom. The distance of $R_1$(Ca-O) is equal to 0.219 nm (Fig.9, a1), CN = 8.7 (Fig.9, a2). This value is slightly lower than the one calculated from the RDF (9.5 atoms) but it is still high. Fig. 9, a2 shows also the partial pair correlation functions ($g_{ij}(r)$) for Al-Al and Si-Si bonds that are very similar to each other although expressed not clearly. In both cases the position of the first peak is close to 0.314 nm ($R_1$(Al-Al) and $R_1$(Si-Si) are 0.314 nm). Partial $g_{AlSi}(R)$ resembles $g_{AlAl}(R)$ and $g_{SiSi}(R)$, however, the $R_1$(Al-Si) is somewhat larger (~ 0.318 nm). The similarity of $g_{AlSi}(R)$, $g_{AlAl}(R)$ and $g_{SiSi}(R)$ is probable due to occupation of Al$^{3+}$, Si$^{4+}$ ions the same positions in the ASNG. According to the results of [6] the eutectic melts are characterized by the CN of aluminum by oxygen is between 4.3 and 5.3 [6], confirming 5—6 oxygen atoms surrounding aluminum. In the present work, the RDF calculation estimates $Z_{Al(O)}$ as ~ 4.05, and RMC provides ~ 3.9. Therefore, both methods indicate that almost all aluminum cations (like silicon) are in the oxygen tetrahedron centre.

![Figure 9. Partial pair correlation functions $g_{ij}(r)$ and coordination number distributions $P(Z)$ calculated from RMC-model of the anorthite melt: $g_{SiO}(R)$, $g_{SiO}(R)$ $(a1)$, $g_{SiSi}(R)$ $(b1)$, $Z_{Al(Ca)}$ coordination distribution $(c1)$, $Z_{Ca(O)}$, $Z_{Si(O)}$, $Z_{Al(O)}$ and $Z_{Al(Si)}$ coordination distribution $(a2)$, $Z_{Si(Si)}$, $Z_{Al(Al)}$, and $Z_{Al(Si)}$ $(a2)$, $Z_{O(O)}$ coordination distribution $(c2)$.

Aluminum (or silicon) atoms are surrounded by ≈2 atoms of the same kind and ≈2 atoms of the different kind (Si or Al, consequently). We assume that the low value of CN is caused by bonds of non-bridge oxygen with the Ca$^{2+}$ on the surface of the ASNG as a part of oxygen surroundings of silicon and aluminum cations. If aluminum and silicon cations were in oxygen tetrahedral microregions (which may occur in some crystals), $Z_{Al(Al)}$ and $Z_{Si(Si)}$ CNs would be
close to 4, and \(Z_{Ca(Al)}\) and \(Z_{Ca(Si)}\) would be about zero (\(\sim 1\) according to RMC method). Figure 9, c1 shows that aluminum cation surrounding includes approximately one \(Ca^{2+}\), and less than one \(Ca^{2+}\) is coordinated around silicon (not shown in the figure). Obtained results support suggestion about the presence of the ASNG in the melt.

The \(g_{oo} (R)\) has main maximum at 0.275 nm, which is characteristic of \(R_1(O-O)\) distance in the grid of silicon-oxygen tetrahedrons, but it is somewhat shorter than in the aluminum—oxygen tetrahedron. Obviously, a slightly longer distance is also characteristic for \(AlO_4\) tetrahedron. In our opinion, a small influx \(g_{oo}(R)\) in the region of 0.32 nm is typical for \(R_1(O-O)\) in calcium polyhedrons (not shown in the figures). The \(Z_{O(O)}\) coordination distribution is broad (Fig. 9, c2) and demonstrates a significant contribution of large coordinations. The small \(Z_{O(O)}\) contribution could be from the ASNG, while the large one forms the nearest oxygen surroundings of \(Ca^{2+}\).

The obtained \(Z_{Ca(O)}\) values (between 8 and 12) is overestimated in contrary to \(Z_{Ca(O)}\) values close to 6 in slag melts [6-7]. The model of multicomponent silicate melt structure based on close packed shell of oxygen atoms, with all cations of the melt occupying existing tetrahedral and octahedral cavities, was also proposed in [9]. Smaller cations are located closer to the center of this grouping, whereas larger cations are closer to the periphery. However, such a model is unsuitable for the investigated melt and the eutectic melts [6]. In this study, the melt structure model of the same system is proposed in close to the mullite existence region. We have assumed that thermally stable ASNG are formed in the melt. However, these nanogroups are different than mullite-sillimanite type nanogroupings. As shown in [6], the negative surface charge of oxygen layer on the boundary of the nanogrouping is neutralized by \(Ca^{2+}\) cations. These cations form a positively charged surface layer around the ASNG, which in turn is surrounded by oxygen atoms in the melt.

The mullite-sillimanite type ASNG (close spherical shape) are based on the close packed oxygen atoms, whose tetrahedral cavities (according to our data) can be occupied with silicon or aluminum atoms, with some octahedral cavities filled by aluminum atoms. In anorthite type melts, the low CN of aluminum cations (\(\sim 4\)) and other data indicate that aluminum cations are predominantly tetrahedrally surrounded by oxygen. By the way, the sample 1 in [6] (see Fig.6), whose composition is the most distant from the phase mullite region, is characterized by the smallest CN \(Z_{Al(O)} \sim 4.1-4.5\). In melt 2 (see Fig.6) \(Z_{Al(O)} \sim 4.4-5.3\), and \(Z_{Al(O)} \sim 4.9-5.1\). In our opinion, six oxygen-coordinated \(Al^{3+}\), in the melt of anorthite, can only be in a disordered quasi-gas matrix, in which the ASNG are also located. This matrix is highly disordered and makes an insignificant contribution to scattering is highly. Therefore, groupings based on \(AlO_4^3-\) are not observed. The expansion of nanogrouping size with temperature increasing can lead to diffusion of aluminum atoms into the expanding octahedral vacant positions. Calcium cations with significantly larger size compare aluminum and silicon will be forced to occupy positions outside of the ASNG.

4. Discussion

Crystalline anorthite can be attributed to framework aluminosilicates (Fig. 10, a1). Alternating layers of pure aluminosilicate tetrahedra and layers that have cavities saturated with calcium cations exists in the crystalline structure anorthite. Figure 10, b1 shows fragment of the the anorthite unit cell in the form of coordination polyhedrons. As can be seen in Fig. 10, b1, all Si (yellow) and Al (green) polyhedrons are tetrahedral, and calcium polyhedrons consist of irregular polyhedrons of complex shape with CN of about 8-9. Tetrahedrons are linked by vertices, but calcium cation polyhedrons have no bonds with one another. The part of SiO4 and AlO4 tetrahedrons are connected with Ca2+ polyhedrons even by faces. Mullite also belongs to framework aluminosilicates, forming infinite 3D-grid of aluminum-silicon-oxygen tetrahedrons in crystalline state. However, it contains aluminum-oxygen octahedron groupings, with aluminum atoms playing the role of cations. The fragment of mullite structure is shown in Fig. 10, c2 (all atoms outside polyhedrons were removed). The SiO4 and AlO4 tetrahedrons and AlO6 octahedrons are highlighted here in orange and green,
respectively. Crystalline mullite reflections (hardly distinguishable from the liquid melt curve) were observed for all melts investigated in [6]. Therefore, it can be suggested that mullite type ASNG are formed in samples near the melting point present work. However, this suggestion was not confirmed by subsequent analysis. The predominant tetrahedral oxygen cations of aluminum and the presence of calcium cations around the ASNG significantly distinguish the structure of the anorthite melt from the mullite one. Calcium cations were present in all eutectic compositions in [6], however, the ASNG in the anorthite and mullite melts significant differences. In anorthite and, possibly, in melt 1 from ref.6[6] (Fig.6), the silicon and aluminum cations occupy mainly positions inside the tetrahedron of oxygen atoms, and in melts close to mullite region, aluminum cations partially occupy octahedral positions.

Assuming that the substance will retain some similarity with its high-temperature crystal structure after melting we should expect that remaining of the some specific features of the crystal in the melt. Obtained data allow suggesting that the ASNG have the anorthite type in case of investigated melt and the melt 1 from ref. [6]. The mullite type of nanogrouping has place for sample 2 and 3 [6] (Fig.6). In contrary to [6], the crystalline mullite peaks were not observed in the investigated melts in anorthite type melt before and after melting, although probably some peaks (at least two in Fig. 3b) can be interpreted as mullite after remelting. Like [6] this paper supports suggestion about the presence of the ASNG, with their negative surface charge neutralised by calcium cations. Nevertheless, the ASNG of the investigated melts have some differences from the ASNG of the melts investigated in [6]. The ASN in the anorthite melt have practically empty octahedral cavities. On the other hand, a significant part of the octahedral cavities contains aluminum atoms in the melts close to the mullite phase region.

According to [8] the complex aluminosilicate particle existence transferred to an anode and Ca\(^{2+}\) ions migrating to a cathode in the anorthite melt. Johnson et al [15] indicated that there are two types of oxygen ions in supercooled silicate melts (bridging and non-bridging). Bridging oxygens form bonds with two grid-forming cations, whereas non-bridging oxygens are associated with only one grid-forming cation. In accordance with [6], the contributions of non-crystalline and crystalline components should be established from the diffraction data obtained for anorthite before melting in the investigated temperature range. The non-crystalline component is represented by strongly disordered ASNG resembling the melt structure. The crystalline part consists of anorthite polycrystals. In general, after melt solidification crystals of the same type as before melting are usually obtained. The ASNGs formed during melting mainly retain other microgroupings in the nearest surroundings. They rapidly restore bond distances with one another and build a long-range order during solidification. However, in high viscosity melts, some particles that pass significant diffusion distances have no time to occupy their crystal lattice positions during fast cooling. They can interact with one another forming more simple compounds. Therefore, anorthite and gehlenite can decompose, and, as a result, their decomposition products are observed. Applying the high-temperature microscopy method, Welch et al [16] observed the appearance of corundum crystals and pseudovollastonite CaSiO\(_3\) upon cooling the anorthite melt from 1873 to 1673 K, although the remaining part of cooled sample consisted of various modifications of anorthite. Berezhnoi [8] suggested partial decomposition of anorthite during melting but appearance of corundum was explained by non-equilibrium (fast) crystallization of the melt.

In our opinion, the crystalline part of anorthite is completely transformed into a melt structure upon melting. The non-crystalline part is also reconstructed but insignificantly since the non-crystalline SRO in many respects resembles a liquid one. At least at the initial stage, a homogeneous liquid structure of the anorthite melt is formed. Although crystalline peaks are still observed in the anorthite melt, but they are unstable and not close to mullite as shown in [6]. These peaks disappear after overheating and long exposures at high temperatures. Unfortunately, these peaks could not be interpreted since their instability during XRD experiment.

In accordance with proposed model, the ASNG are formed inside of a disordered (quasi-gas) matrix in the anorthite type melt. The molten matrix consists of atoms and small atomic clusters, which have weak interaction and diffusion equilibrium with each other. The molten
Matrix interaction forces with the ASNG are significantly lower than forces inside of the ASNGs. They are close to Van der Waals forces by nature and depend on temperature significantly. In contrary to the bulk material, nanogrouping surface atoms fraction commensurates with their fraction inside. The presence of non-bridging surface oxygen atoms will lead to a negative microgroup charge. There are only calcium cations freely migrating in the molten matrix that can compensate this negative charge. Cations of calcium near the ASNGs surface will completely or at least partially compensate its negative surface charge. An oxygen layer of the melt matrix behind the calcium cations compensates the positive Ca$^{2+}$ surface layer charge. Therefore, the oxygen surroundings of Ca$^{2+}$ will consist partially of the ASNG non-bridging oxygens, and also the molten matrix that provides large CN value of calcium by oxygen. Some anorthite crystal images from well-known collection of CIF-files for crystals and processed using Diamond 3-2 are shown in Fig. 10.

![Figure 10](image_url)

Figure 10. Crystalline structure of the anorthite: a1) silicon (yellow), aluminium (green), calcium atoms (red) in the anorthite lattice, b1, c1, d1, a2) - polyhedrons junction in the anorthite unit cell. Crystalline structure of the mullite: c2) silicon-oxygen and alumina-oxygen tetrahedra surrounded by Ca$^{2+}$ (gray), d2) aluminium-oxygen tetrahedral network of one of the anorthite structures (calcium octahedrons are not shown).

As mentioned above, the short-range order in the melts retains some features of the short-range order of crystalline anorthite or mullite. During melting the formation of nanogroupings close to the regular polyhedrons of cluster type (for example, the Mackay cluster take places). The regular polyhedron of cations and anions is formed under the action of powerful surface and electrostatic forces. These forces are responsible for spherically symmetric nanoclusters at the atomic grouping of small size. The cluster has oxygen close packed structure. Octahedral and tetrahedral cavities are occupied with Si$^{4+}$ and Al$^{3+}$ cations with practically identical ionic radii. Slightly large cations (for example, Al$^{3+}$) can also fill octahedral cavities.

A simplified model of the structure of anorthite or mullite melt is shown in Fig. 11. The figure shows only oxygen (yellow) and (red) calcium atoms. The ASNG is constructed on the principle of the Mackay cluster by cations Al$^{3+}$ and Si$^{4+}$. In the case of anorthite, only tetrahedral cavities are occupied, and in the case of mullite, part of the octahedral cavities is occupied. Clusters of the smallest possible size can be present in disordered (quasi-gas) matrix. The cations Si$^{4+}$, Al$^{3+}$ are not shown, because the pattern is difficult to perceive.
5. Conclusions

Anorthite and gehlenite demonstrated the absence of phase transitions in the temperature range between RT and melting point. The slight enlargement of lattice parameters with temperature rise was only detected. The features of aluminum-silicon-oxygen grid structure observed in anorthite crystals differ from the crystalline structure of eutectic samples studied in [6] that cause the difference in the aluminum-silicon-oxygen nanogroupings of the corresponding melts.

Silicon and aluminum are predominantly tetrahedrally coordinated by oxygen in the investigated melt. The interatomic Si — O and Al — O distances in melts are consistent with those in crystals and melts of other oxide systems. Oxygen atoms form the nearest surroundings of Ca\(^{2+}\) at the distance of 0.223 nm with coordination number in the range between 8 and 10. It is evident that some distinctive structure elements of crystalline anorthite are retained in the anorthite melt.

Negatively charged ASNG are formed in investigated melts. This negative charge is compensated by Ca\(^{2+}\) cations that saturate the disordered (quasi-gas) matrix. The matrix consists of ions and small atomic clusters. The randomly distributed aluminum-silicon-oxygen nanogroups in the matrix resemble nanocrystals.

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