

Research Article

Sol-Gel Synthesis, X-Ray Diffraction Studies, and Electric Conductivity of Sodium Europium Silicate

Ekaterina V. Borisova,¹ Alexey V. Ignatov,¹ Eugeni I. Get'man,¹ Stanislav N. Loboda,¹ Lyudmyla I. Ardanova,² Lyudmila V. Pasechnik,¹ and Vitaly S. Ponurovsky¹

¹ Department of Inorganic Chemistry, Donetsk National University, 24 Universitetskaya, Donetsk 83001, Ukraine

² Department of Chemistry and Geology, Minnesota State University, Mankato, 241 Ford Hall, Mankato, MN 56001, USA

Correspondence should be addressed to Lyudmyla I. Ardanova; lyudmyla.stackpool@mnsu.edu

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Sodium europium silicate, $\text{NaEu}_9(\text{SiO}_4)_6\text{O}_2$, with apatite structure has been obtained and studied using X-ray diffraction and SEM. It has been shown that sodium sublimation does not take place upon synthesis by the sol-gel method. Rietveld refinement has revealed that sodium atoms are ordered and occupy the 4f position. O(4) atoms not related to silicate ions are placed at the centers of Eu(2) triangles. DC and AC electric conductivity and activation energy have been determined for the compound studied.

1. Introduction

Compounds with apatite-type structure are widely investigated because they can be used as biomaterials [1], catalysts [2], ionic conductors [3], and luminescent materials [4]. Studies on electrical conductivity of these compounds have been motivated by research in which high ionic conductivity of $\text{La}_{9,33}(\text{SiO}_4)_6\text{O}_2$ has been previously determined [5]. Subsequently, similar results have been obtained for germanates, which also exhibit high ionic conductivity [6]. Rare earth silicates with apatite structure are of great interest as a new class of oxygen ionic conductors. The characteristics of their structure provide high oxygen conductivity at a medium temperature range, low activation energy of conductivity, stability in reducing media, and a possibility for isomorphous substitution by different elements to modify their transport properties [7]. Lanthanide silicates have been synthesized in a single crystal as well as in polycrystalline form. polycrystalline lanthanide silicates with apatite structure were synthesized by solid phase methods, including mechanochemical synthesis [8] and the sol-gel method [9]. Single crystals were obtained by a hydrothermal method [10]. The compounds of $\text{Ln}_{9,33}(\text{SiO}_4)_6\text{O}_2$, $\text{NaLn}_9(\text{SiO}_4)_6\text{O}_2$, and $\text{LiLn}_9(\text{SiO}_4)_6\text{O}_2$ have been obtained by the solid phase

method utilizing all of the rare earths. Mixtures containing corresponding oxides and salts have been pressed into pellets with a pressure of 200 kg/cm^2 and sintered at the temperature ranging from 1000 to 1900°C for 24 hours. The lattice parameters of the compounds have been obtained [11], but the crystalline structure was not studied in detail. The compounds of $\text{Eu}_{8,18}\text{Na}_{1,08}(\text{SiO}_4)_6(\text{OH})_{1,62-2\gamma}\text{O}_\gamma$ and $\text{Eu}_{3,96}\text{Gd}_{3,96}\text{Na}_{1,2}(\text{SiO}_4)_6(\text{OH})_{1,86-2\gamma}\text{O}_\gamma$ have been obtained by hydrothermal synthesis and their crystalline structures have been studied [12]. Indeed, the accuracy of the suggested formulae is not quite clear, considering fractional coefficients and presence of vacancies at the cation sites and in the structural channels. the electrophysical properties of these compounds have not been studied.

2. Experimental Procedure

In the current study, $\text{NaEu}_9(\text{SiO}_4)_6\text{O}_2$, as an example of alkali and rare earth element apatite, has been synthesized using the sol-gel method. The crystalline structure and electrophysical properties of this compound have been investigated in detail.

Highly pure Na_2CO_3 (>99.99% purity), tetraethoxysilane (TEOS) $\text{Si}(\text{OC}_2\text{H}_5)_4$ (>98% purity), and Eu_2O_3 (>99.99%

TABLE 1: Results of elemental analysis for $\text{NaEu}_9(\text{SiO}_4)_6\text{O}_2$ (% by weight).

Section #	Number of points (regions)	O	Na	Si	Eu
1	7	21.18	1.14	8.67	69.01
2	12	21.43	1.12	8.97	68.48
3	7	21.84	1.13	9.46	67.57
4	7	21.41	1.13	8.95	68.51
5	7	21.40	1.19	8.92	68.49
6	9	21.63	1.10	9.21	68.06
7	7	21.34	1.15	8.92	68.59
8	4	21.02	1.06	8.50	69.42
Determined		21.44	1.13	8.98	68.45
Calculated		21.06	1.16	8.53	69.25

urity) were used as precursors in the synthesis by the sol-gel method. To measured quantities of Eu_2O_3 and Na_2CO_3 in 100 mL beakers, the concentrated nitric acid and distilled water were added drop by drop. Then 12 mL of ethyl alcohol and a precalculated volume of TEOS were added to each beaker to prevent hydrolysis. The solution was left for 12 hours and then evaporated until the formation of solid residue at 80°C . This residue was transferred into alumina crucibles and calcined at temperatures ranging from 550°C to 1100°C as follows: 550°C for 6 h, 700°C for 15 h, 800°C for 20 h, 900°C for 43 h, 1000°C for 55 h, and 1100°C for 30 h. The density of the synthesized ceramics was about 60% of the theoretical value, due to the low sintering temperature (1100°C) compared to the sintering temperature of apatite-like rare earth silicates containing no alkali metals ($1600\text{--}1750^\circ\text{C}$) [3]. Pellets were pressed from the powder, calcined at 900°C , and sintered at 1100°C for 30 hours.

A 5% solution of polyvinyl alcohol was used as a binder for the production of ceramic pellets. The pressed pellets were dried at temperatures of $75\text{--}120^\circ\text{C}$ to evaporate the alcohol, calcined for 3 hours at 500°C , and sintered at 1100°C for 30 hours. The sintering temperature was not raised above 1100°C to avoid the possibility of sodium oxide sublimation [11]. Calcination was carried out until a consistent phase composition was attained. Preparation of the pellets for the measurements of electrical properties included polishing, washing with alcohol, and then annealing them in a muffle furnace after the deposition of the silver paste. The annealing was carried out at the following temperature conditions: rapid heating to 200°C , then annealing from 200°C to 370°C at a heating rate of $3\text{--}3.5^\circ\text{C}/\text{min}$; from 370°C to 510°C at a rate of $4^\circ/\text{min}$, and from 510°C to 850°C at a rate of $5^\circ/\text{min}$ with the maximum temperature held for 10–15 minutes.

The electric conductivity measurements were carried out using a complex impedance meter (RLC E7–15 and E7–12) at a frequency of 1000 Hz while increasing the temperature from 320 to 750°C at 10°C increments in an electric resistance furnace with a chromel-alumel thermocouple.

Powder diffraction analysis was performed on X-ray diffractometers DRON-3 (Russia) using CuK_α radiation and a

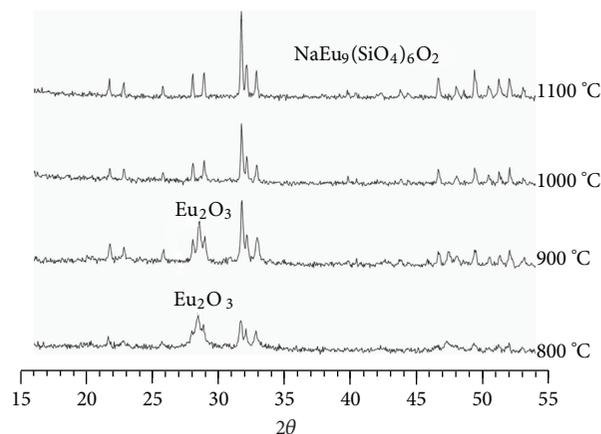


FIGURE 1: X-ray diffraction spectra for $\text{NaEu}_9(\text{SiO}_4)_6\text{O}_2$ samples after calcination at 800 , 900 , 1000 , and 1100°C .

Ni filter. The angular scan rate to determine the composition of the samples was $1\text{--}2^\circ$ per minute (2θ). Rietveld refinement was then used to determine the crystalline structure by powder diffraction data. The angular range chosen for calculations was from 15 to 95° (2θ). The angle increment and exposure times were 0.05° and 3 seconds, respectively. The refinement was carried out using the FULLPROF2k (version 3.40) software [17] with WinPLOTR graphic interface [18].

The semiquantitative elemental analysis has been performed using JEOL JSM-6490LV SEM with INCA Penta FETx3 (OXFORD Instruments) energy dispersion spectrometer. The precision was within 1%. The micrographs and element distribution maps over the surface of the samples were also obtained using this instrument.

3. Results and Discussion

Powder diffraction has revealed that the apatite structures appear in the samples after calcination at 800°C , but the phase composition is not yet uniform, as the lines corresponding to Eu_2O_3 phase still are quite visible. Figure 1 shows phase compositions for the samples sintered at temperatures ranging from 800 to 1100°C .

The intensity of europium oxide lines during the synthesis of $\text{NaEu}_9(\text{SiO}_4)_6\text{O}_2$ decreases considerably only after calcination at 1000°C . The single phase $\text{NaEu}_9(\text{SiO}_4)_6\text{O}_2$ has been obtained after calcination at 1100°C .

The elemental composition in $\text{NaEu}_9(\text{SiO}_4)_6\text{O}_2$, determined over 60 points (surface regions) on 8 thin sections, is in satisfactory consistency with the calculated data (see Table 1). This indicates that Na_2O has not undergone sublimation during the apatite synthesis.

Electron microscopy reveals (see Figure 2) that the elements are distributed over the particle surface almost uniformly, which indicates the formation of a homogeneous sample. The residual nonuniformity is due to the surface pattern.

A fine powder was obtained from the synthesis; the size of aggregates was less than $10\ \mu\text{m}$, and the grains' size was about several hundred nanometers (Figure 3).

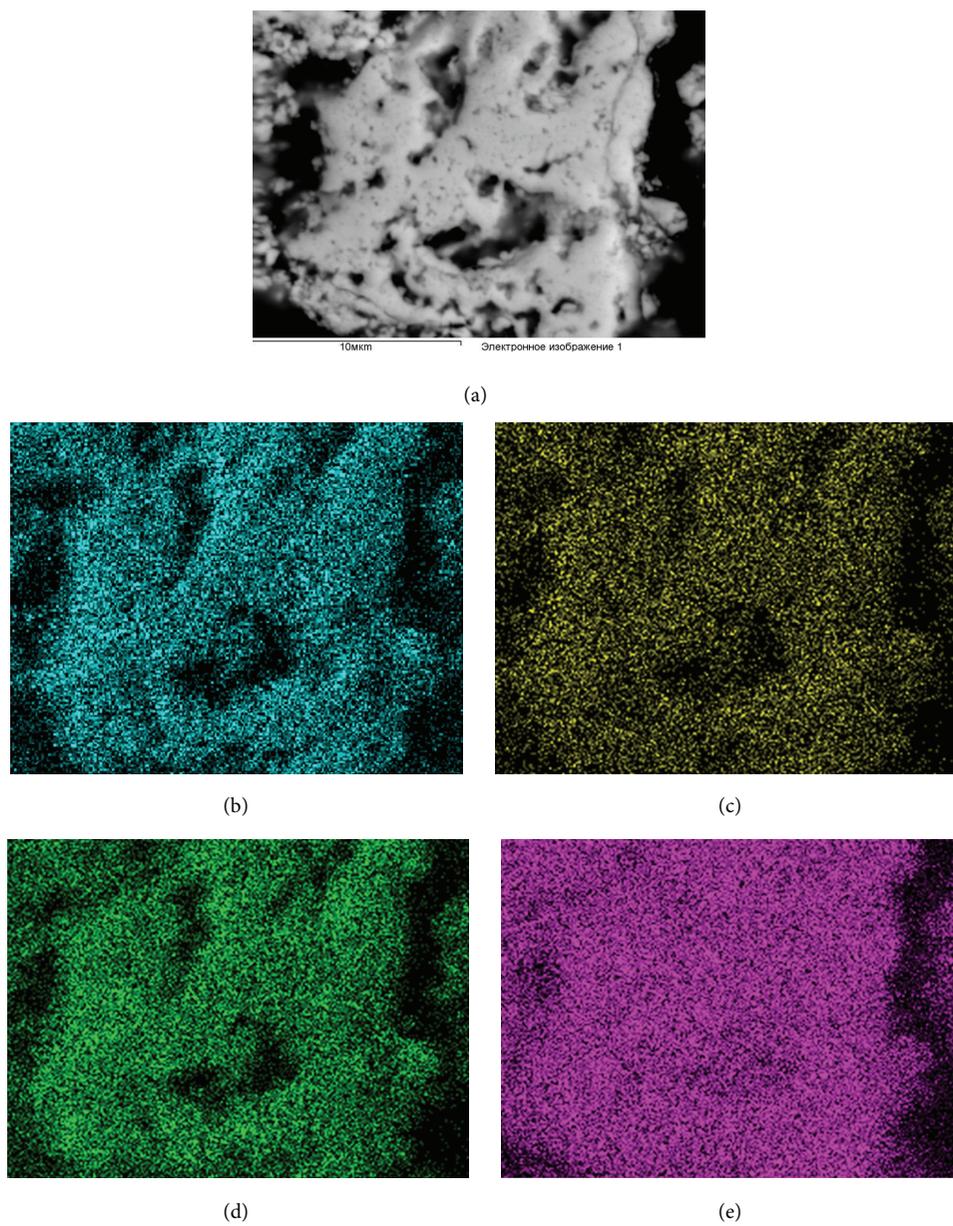


FIGURE 2: Distribution of elements in $\text{NaEu}_9(\text{SiO}_4)_6\text{O}_2$: (a) sample surface SEM scan, (b) O, (c) Na, (d) Si, (e) Eu.

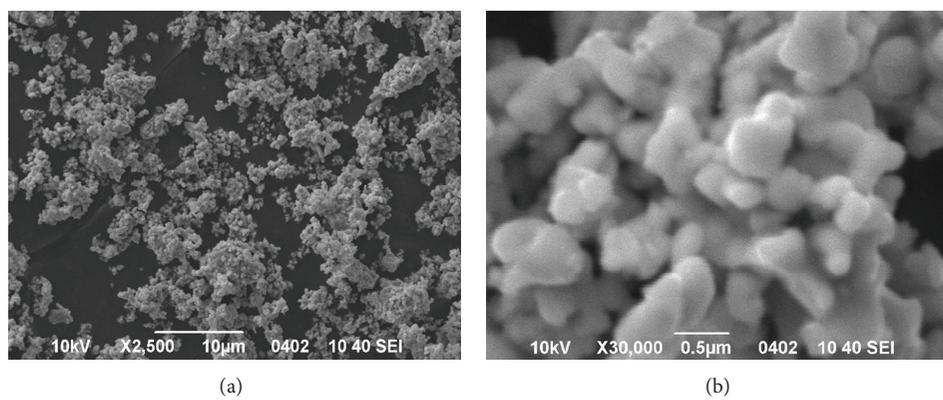


FIGURE 3: SEM scans of the sample surface with magnifications: (a) 2,500, (b) 30,000.

TABLE 2: Coordinates, isotropic thermal parameters of atoms B_{iso} and occupancies G (space group $P6_3/m$, $a = 9.4425(7)$, $c = 6.9119(5)$, Å).

Atom	Position	x	y	Z	$B_{\text{iso}}, \text{Å}^2$	G
Eu(1)	4f	2/3	1/3	0.00217	0.512	0.745(8)
Na(1)	4f	2/3	1/3	0.00217	0.512	0.255(8)
Eu(2)	6h	0.2320(5)	0.9907	1/4	0.198	1.003(5)
Na(2)	6h	0.2320(5)	0.9907	1/4	0.198	-0.003(5)
Si	6h	0.3998(6)	0.374(2)	1/4	1.005	1
O(1)	6h	0.3320(3)	0.493(8)	1/4	1.693	1
O(2)	6h	0.3320	0.473(4)	1/4	1.693	1
O(3)	12i	0	0.247(8)	0.056(5)	1.693	1
O(4)	2a	0	0	1/4	1.693	1

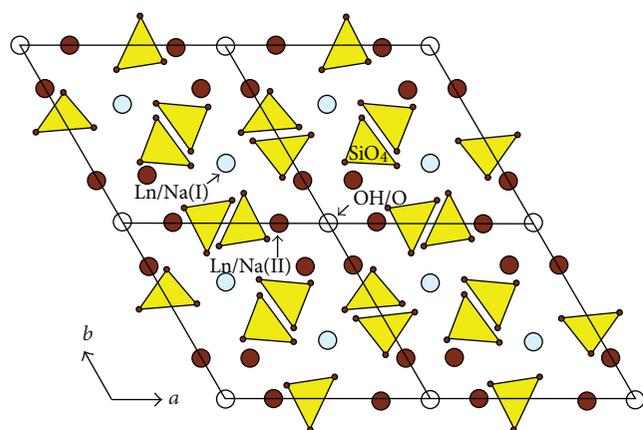


FIGURE 4: View of the refined crystal structure of the apatites [12].

Reitvelt refinement shows that the apatite structure (Figure 4) features two structurally nonequivalent positions in the cation sublattice, marked herein as Ln(1) and Ln(2) [12].

The Ln(1) position lies inside a ninefold coordination polyhedron. The coordination of the Ln(2) position is sevenfold, with six oxygen atoms of SiO_4 tetrahedra and one O(4) placed in the channels of the structure (see Figure 4). It is also important to note that the cavity in the Ln(1) polyhedron is somewhat larger than that in the Ln(2) case. The O(4) atoms are placed at the centers of the equilateral triangles formed by the Ln(2) sublattice [12, 19].

The crystalline structure refinement was based on calcium hydroxyapatite as an initial data model [20]. The coordinates of atoms, isotropic thermal parameters B_{iso} , and occupancies G are given in Table 2. The reliability factors are the following: $R_p = 0.0437$; $R_F = 0.0849$; $R_{\text{wp}} = 0.0635$; Bragg's R -factor = 0.0625; $\chi^2 = 1.17$.

The above data show that the Eu atoms occupy all positions in sevenfold polyhedra (occupancy of 6h position is 1.003). The ninefold sites are only partly occupied; Eu occupancy is only 0.745 for 4f position. The sodium atoms, due to their larger size compared to Eu atoms, occupy only some positions in larger ninefold polyhedra ($G = 0.255$ for the 4f position). In contrast to the phosphate with apatite structure, the oxygen atoms O(4) are located at the

TABLE 3: Selected interatomic distances, (Å).

Atoms	Distances
Si-O(1)	1.56(9)
Si-O(2)	1.69(7)
Si-O(3) $\times 2$	1.69(4)
$\langle \text{Si-O} \rangle$	1.66(3)
Eu, Na(1)-O(1) $\times 3$	2.38(5)
Eu, Na(1)-O(2) $\times 3$	2.40(6)
Eu, Na(1)-O(3) $\times 3$	2.87(4)
$\langle \text{Eu, Na(1)-O(1,2,3)} \rangle$	2.55(4)
Eu(2)-O(1)	2.77(7)
Eu(2)-O(2)	2.40(7)
Eu(2)-O(3) $\times 2$	2.51(3)
Eu(2)-O(3) $\times 2$	2.26(3)
$\langle \text{Eu(2)-O(1,2,3)} \rangle$	2.452(9)
Eu(2)-O(4)	2.275(7)
Eu(2)-Eu(2)	3.874(19)

centers of the triangles formed by Eu(2) atoms, apparently due to the larger radius of silicon atoms compared to phosphorus atoms. Similar results were reported earlier for $\text{Eu}_{8.18}\text{Na}_{1.08}(\text{SiO}_4)_6(\text{OH})_{1.62-2y}\text{O}_y$ [12], as well as $\text{NaLa}_9\text{Ge}_6\text{O}_{26}$ [21], $\text{NaPr}_9\text{Ge}_6\text{O}_{26}$, and $\text{NaNd}_9\text{Ge}_6\text{O}_{26}$ [22].

The interatomic distances determined for the crystalline structure studied are given in Table 3.

Dimensions of the coordination polyhedron for the Eu(1) atoms are also larger than those for the Eu(2) one (mean Eu-O distances are 2.55(2) and 2.452 Å, resp.; see Table 3). This is for two reasons: first, different coordination numbers, 9 and 7; second, the preferential localization of larger Na^+ compared to Eu^{3+} ions in the Eu(1) position. The small distance of Eu(2)-O(4) is specific for oxygen atoms located in the structural channels, not related to silicate ions and interacting with three europium atoms.

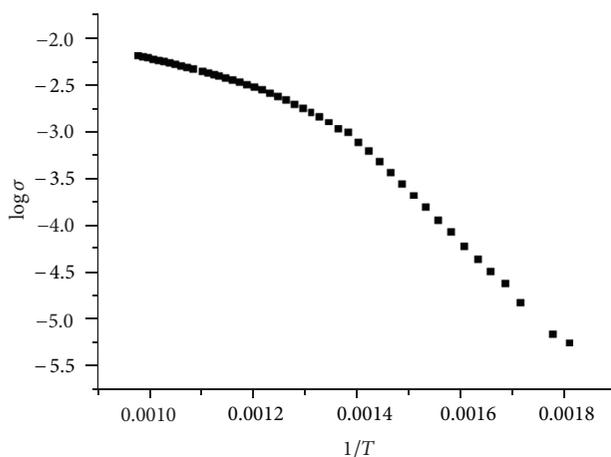
To evaluate electrical conductivity, graphs of $\log \sigma$ against $1/T$ were plotted to facilitate the data processing. The conductivity activation energy was calculated for different temperature ranges using the slopes of quasi-linear portions of the curve (see Figure 5). The lower temperature range was 300–440°C, while the higher one was 450–750°C.

TABLE 4: DC and AC conductivity and activation energy for the samples.

Composition	σ (500°C), mScm ⁻¹	σ (600°C), mScm ⁻¹	σ (700°C), mScm ⁻¹	E_A , eV
NaEu ₉ (SiO ₄) ₆ O ₂ (direct current)	0.547	1.887	3.120	0.62
NaEu ₉ (SiO ₄) ₆ O ₂ (1000 Hz)	1.257	2.681	4.059	0.77
La _{9.33} Si ₆ O ₂₆ [3]	0.023	—	0.26	0.84
La ₉ Mg _{0.5} Si ₆ O ₂₆ [3]	0.021	—	—	0.98
La _{8.67} SrSi ₆ O ₂₆ [3]	0.083	—	—	0.87
La _{8.67} CaSi ₆ O ₂₆ [3]	0.058	—	—	0.87

TABLE 5: Selected interatomic distances, (Å).

Composition	Si–O(1)	Si–O(2)	Si–O(3)	Max. difference	Reference
NaEu ₉ (SiO ₄) ₆ O ₂	1.56	1.69	1.69 × 2	0.13	Current work
Eu _{8.18} Na _{1.08} (SiO ₄) ₆ (OH) _{1.62-2γ} O _γ	1.668	1.567	1.616 × 2	0.101	[12]
La _{9.33} (SiO ₄) ₆ O ₂	1.618	1.630	1.623 × 2	0.012	[13]
La _{9.67} Si ₆ O _{26.5}	1.622	1.633	1.631 × 2	0.011	[14]
La _{9.55} (SiO ₄) ₆ O _{2.32}	1.621	1.631	1.617 × 2	0.014	[15]
La _{9.33} (SiO ₄) ₆ O ₂	1.65	1.60	1.63 × 2	0.05	[16]
Nd _{9.33} (SiO ₄) ₆ O ₂	1.63	1.64	1.61 × 2	0.03	[16]

FIGURE 5: Logarithm of conductivity, σ (mScm⁻¹) as a function of $1/T$ (K⁻¹) for NaEu₉(SiO₄)₆O₂.

The inflection point on the Arrhenius plot is due to a transition from extrinsic to intrinsic conductivity as the temperature increases. The values of DC and AC electric conductivity as well as activation energy were measured for this compound and given in Table 4.

As can be seen from the data, the conductivity values measured at the alternating current are higher than the values measured at the direct current, because both active and reactive components of the conductivity are measured at the alternating current (capacitive and/or inductive), and only the active component is measured at the direct current.

NaEu₉(SiO₄)₆O₂ has greater electrical conductivity, and in most cases slightly lower activation energy compared to

lanthanum silicates La_{9.33}Si₆O₂₆ as well as some silicates of lanthanum doped with magnesium and alkaline earth metals La₉Mg_{0.5}Si₆O₂₆, La_{8.67}SrSi₆O₂₆, and La_{8.67}CaSi₆O₂₆ [3]. An increase in electrical conductivity in compounds containing excess oxygen atoms, such as La₁₀Si₆O₂₇, was established previously [3]. A greater electrical conductivity of NaEu₉(SiO₄)₆O₂ can be explained by local distortion of the crystal structure since it does not have excess of oxygen. The alkali metal replacing europium has a much smaller charge and larger size. Some oxygen atoms of each SiO₄ tetrahedron surround both Eu(1) and Eu(2). This leads to a weaker electrostatic interaction of oxygen with the Eu(1) and a stronger electrostatic interaction with Eu(2), respectively, and as a result distorts the geometry of SiO₄, which is confirmed by the results presented in Table 5.

As shown in Table 5, the maximum Si–O distance differences in the SiO₄ tetrahedra containing no alkali metals are in the range of 0.01–0.05 Å, while they are significantly larger (0.10–0.13 Å) in NaEu₉(SiO₄)₆O₂ and double silicates containing sodium [12]. This can affect the mobility of the oxygen ions in the structure, and thus the electrical conductivity.

4. Conclusions

The sol-gel method has been used to obtain a sodium europium silicate with apatite structure, NaEu₉(SiO₄)₆O₂. Elemental composition determined by X-ray energy dispersion spectra is in good agreement with computational data (analysis error is under 1%). The crystalline structure of NaEu₉(SiO₄)₆O₂ has been refined using the Rietveld method. It has been found that Eu atoms occupy all 6 h positions in sevenfold polyhedra, while the ninefold ones (4f position) are

occupied by Eu and Na atoms. The electric conductivity has been measured at the temperature range of 320–750°C and found to be the same or higher than that for some lanthanum silicates without sodium.

Acknowledgments

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