INVESTIGATION OF HALOGEN SODALITES BY ELECTRON MICROSCOPY

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Abstract. The aim of the paper is to study the applicability of electron microscopy to elicit optimal technological processes for getting optically transparent ceramics with non-stoichiometric structure. Both bromide and iodide sodalite powders, and ceramics pressed from powders were investigated. Methods of the preparation of samples for transmission and scanning electron microscopy have been elaborated and image analysis has been applied. The influence of the variations in different technological parameters on synthesizing the powder and hotpressing ceramics were determined. The influence of milling on the structure and granulometry of the sodalite powder was also studied. Comparative electron microscopy and X-ray diffraction measurements have been carried out to determine the size of the powder crystallites. As a result of the study the three-step hierarchical structure of sodalite powders was established. The structure of sodalite ceramics was found to be dependent on the kind of the recrystallization process.

Key words: electron microscopy, sodalite powder, sodalite ceramics, recrystallization, image analysis.

1. INTRODUCTION

Sodalite powders and ceramics are, due to their distinguished structure, intriguing objects of investigation for materials scientists. They are also perspective materials for practical applications as sodalite has the best cathodochromic properties. Sodalite is one of the best photochromic materials as well [1]. Bolyasnikova et al. [2] have found out that by low-temperature ($\leq 100\,^\circ$C) hydrothermal method the phase structure and chemical composition of the synthesized iodide sodalite powders (ISP) depend strongly on the composition of the starting reaction. In paper [3], the structure of the ISP and of the bromide sodalite powder (BSP) was investigated by electron microscopy and X-ray powder diffraction (XRPD) methods. Depending on the composition of

the starting mixture and on the chemical reaction and synthesizing conditions the following composition of the initial material was used [1,3]:

$(4.0–4.4)$ Na_2O + 1.0 Al_2O_3 + 1.7 SiO_2 + 3.0 NaBr (ISP 2.0 NaI) + $(13–84)$ H_2O.

Morphology of the powders was determined by scanning electron microscopy (SEM) and size of the powder crystallites was obtained by XRPD method in X-ray diffractometer DRON-2. The latter method showed the occurrence of powder crystallites 9–90 nm in size. Investigations by SEM showed an occurrence of grains of the polycrystal powder (agglomerates) and of big particles – conglomerates (joined agglomerates). The dependence of the powder structure on the water concentration and Si/Al ratio has been explained in paper [3]. In [4,5] the ball milled BSP samples were studied. To determine the crystallite and grain size in nanometer range, the XRPD results were compared with electron microscopy measurements.

In comparison with powders, the sodalite ceramics have many advantages due to their mechanical and optical properties [6]. Using recrystallization processes [7] in formation of sodalite ceramics the transparent non-stoichiometric ceramics are obtained [1]. Recrystallized ceramics possess, similarly to the initial powders, good reversible photo- and cathodochromic properties. Practical manufacturing of sodalite ceramics is complicated and expensive. Structure of the sodalite ceramics depends on the properties of the initial powder as well as on the hotpressing conditions. That field of materials science requires further ivestigations.

The aim of the present paper is to study the dependence of the structure of the sodalite powders on synthesizing parameters and milling, and to explain the influence of the properties of the initial powder and hotpressing conditions on the structure of the sodalite ceramics.

2. MATERIALS AND METHODS

Initial BSP and ISP samples were synthesized in National Optical Institute of St. Petersburg (GOI) by low-temperature ($\leq 100\,°C$) hydrothermal method from composition of initial materials as described in [3]. Initial BSP (sample 888) for mechanical milling was synthesized from the composition $3.5\,Na_2O$ + $1.0\,Al_2O_3$ + $2.0\,SiO_2$ + 3.0 NaBr + $13.6\,H_2O$ + 24 NaOH. Powder 888 was milled in a horizontally vibrating micro-mill with a vial and one ball ($\varnothing\,9$ mm) from tungsten carbide in Tartu University.

Ceramics used in this study were made by the hotpressing method. Standard parameters used in the process were: pressing temperature $T_{pr} = 1200\,°C$, pressure $p = 200$ MPa, pressing time $t = 40$ min. For explanation of the influence of different parameters on the structure of the ceramics, series of the objects, where only one parameter was mutable, were made.

Sodalite powders were studied by scanning electron microscopes TESLA BS-300 and JEOL JSM-840A ($U = 15$ kV, $I = 1$ nA) and transmission electron microscope (TEM) EMV-100BR at accelerating voltage 100 kV. In SEM, the secondary electron method was used. In TEM, mostly the replicas method was applied. To investigate the crystal structure of the powders, the bright and dark field diffraction methods were used. The porosity of obtained ceramics was estimated with the SEM method.

In the case of the sodalite powders the wet method of preparation was used in SEM investigations. The surfaces of the ceramics were first etched in 50% NaOH solution. The best results were obtained after 30 s etching of bromide sodalite ceramics and 60–100 s etching of iodide sodalite ceramics. In SEM investigation both powders and ceramics were covered with thin cold film by the method of ion sputtering.

For TEM investigation in ultrasound dispergator UZDN-2T, dispergated sodalite powder suspension was dried and covered with C (Pt, Pd) replica by the method of thermal spraying (Fig. 1a). Usually the powder was etched from replica in 1% HCl solution (Fig. 1b). In TEM investigation of sodalite ceramics the etched surfaces were covered with C (Pt, Pd) replicas in the same way as powders.

To measure the dimensions of the grains of the ceramics, the image processing system VIDEOLAB-2 was used.
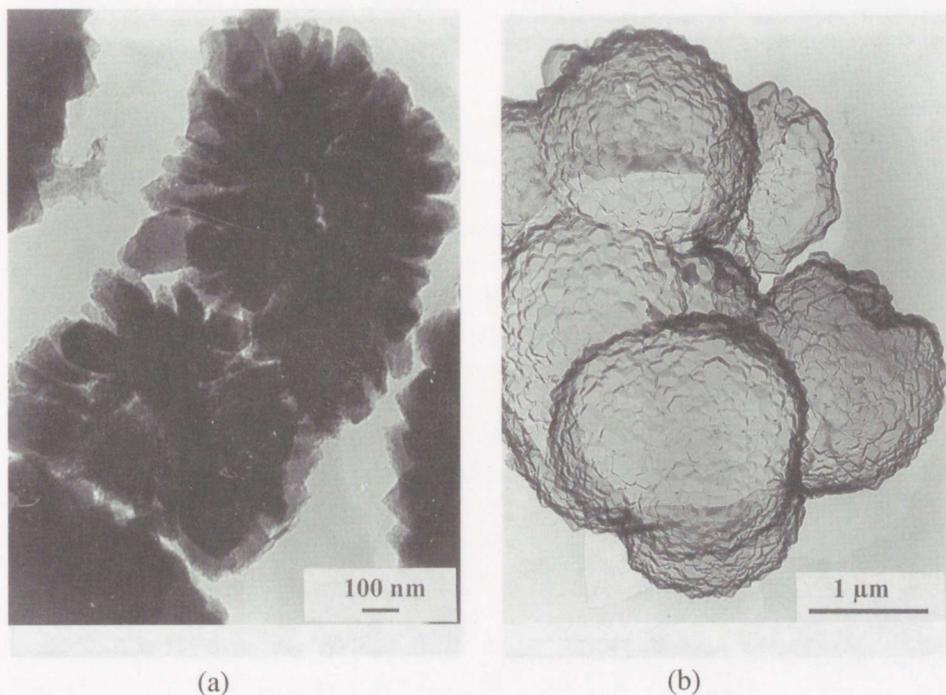

(a)   (b)

Fig. 1. TEM photos of BSP ($x > 0.8$): (a) carbon replica with powder, $T_s = 100\,°C$; (b) carbon replica without powder, $T_s = 80\,°C$.

3. RESULTS AND DISCUSSION

3.1. Sodalite powders

To determine the influence of the synthesizing temperature (T_s) on sodalite powder structure a series of samples of BSP was made at $T_s = 20–100\,°C$.

As seen in SEM photo (Fig. 2a), single phase BSP, synthesized at the temperature $20\,°C$, had a number of conglomerates (~15 μm) and small (0.1–0.6 μm) particles (agglomerates). Rise of the synthesizing temperature caused unification of the powders. At $T_s = 80\,°C$, the obtained powders were more homogeneous in particles size, but there were still some conglomerates and agglomerates. Powders made at $T_s = 100\,°C$ consisted mostly of agglomerates of 0.9–1.4 μm (Fig. 2b). At the same time, the rise of T_s from 20 to $100\,°C$ caused an increase in the average size of the powder agglomerates (from 0.5 to 1.2 μm).

In the TEM photo (Fig. 1b) it is clearly seen that agglomerates are built up of microcrystals (~0.1 μm) and agglomerates are joined onto conglomerates. Using diffraction TEM method (Fig. 1a), the shape of particular microcrystals can be seen. Above described hierarchical structure represents crystallization of silicates [8]. Similar results are also obtained for ISP [3] and it is typical by synthesizing zeolite powders [8].
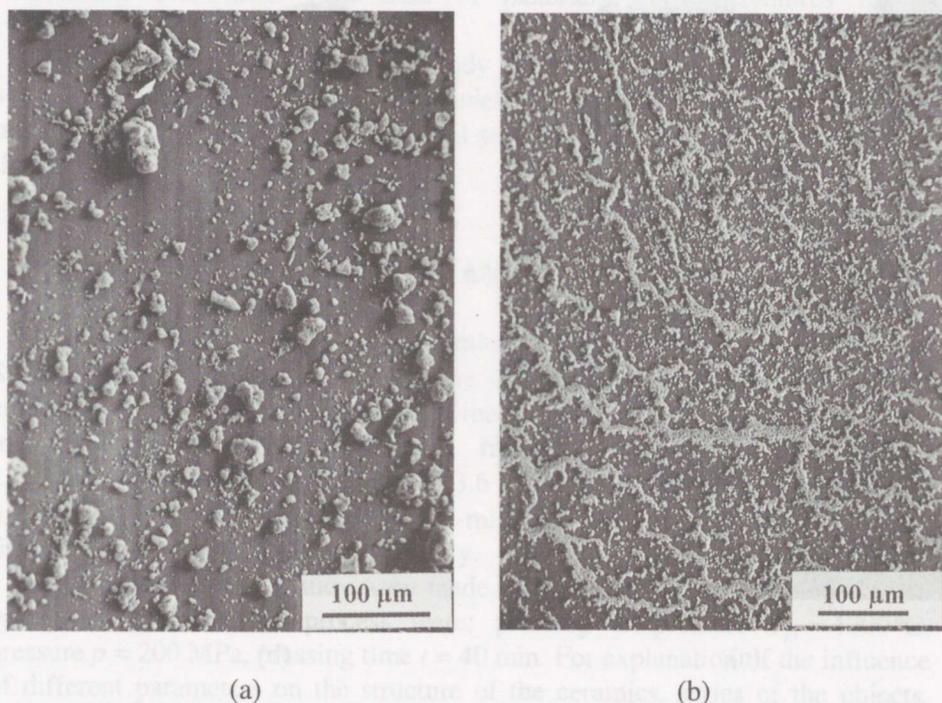

(a)   (b)

Fig. 2. SEM photos of BSP: (a) $T_s = 20\,°C$; (b) $T_s = 100\,°C$.

Investigation of the dependence of the structure of the sodalite powder at filling stage with halogen (x) is studied for ISP, synthesized at 80°C. The filling stages with halogen was measured in GOI using the method of potentiometric titration [2] and varied from 0.28 to 0.9. At lower filling stages ($x = 0.2$–0.4) a powder with uneven structure was obtained. The powder consists of conglomerates of the size 10–60 µm and of agglomerates of the size 0.2–0.8 µm. Increasing the filling stage caused unification of the size of the particles. At $x = 0.8$, a homogeneous powder, containing agglomerates of the size 0.6–0.7 µm, was obtained. The TEM investigation pointed at the same powder structure as in BSP.

Using the SEM method, the influence of the time of synthesis (t_s) on the sodalite powder was investigated. The time of synthesis was varied from 0.5 to 150 h. In the case of $t_s = 0.5$ h, the irregularly shaped powder with different form of conglomerates was formed and the quantity of distinguishable microcrystals in SEM was small (Fig. 3a). At $t_s = 5$ h, more regular powder was obtained, but still a number of conglomerates occurred and the agglomerates had mostly irregular form. Increase of the synthesizing time to 150 h caused the formation of a uniform powder with agglomerates of the size 0.3–1.0 µm (Fig. 3b). The microcrystals were also easily distinguishable.
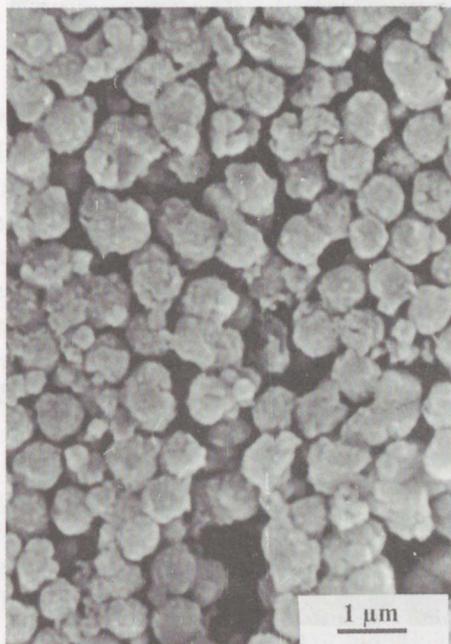
(a)   (b)

Fig. 3. SEM photos of BSP: (a) $t_s = 0.5$ h; (b) $t_s = 150$ h.

To study the influence of milling on the granulometry and structure of the sodalite powder, the BSP (sample 888) was milled in a micro-mill for 2 to 25 h. Both TEM and SEM methods were used. As seen in Fig. 4, milling had a strong influence on the granulometry and structure of the sodalite powder. After 2 h milling the majority of the conglomerates and many agglomerates were shattered. Agglomerates were rounded and became smaller, and some microcrystals appeared. Continuous milling caused fining of the powder, agglomerates became smaller and more round (outer microcrystals separated from agglomerates), and the number of microcrystals in the sodalite powder increased. After long-time (15 h or more) milling some agglomerates were joined onto conglomerates again that is probably caused by activation of particles of the powder. At the same time agglomerates became smaller and more round.

To compare the results of XRPD and electron microscopy for determination of crystallite and grain size in nanometric range, milled samples 888 were used. It was not possible to reduce the size of the initially large crystallites below 50 nm by milling. Therefore interruption of the synthesis was used to cover the range 20–50 nm (samples $1122.t_s$). Crystallite size of BSP was measured by XRPD line shape analysis and TEM and SEM methods [4,5]. The XRPD data were collected on the diffractometer DRON-2 and processed using Voigt analysis
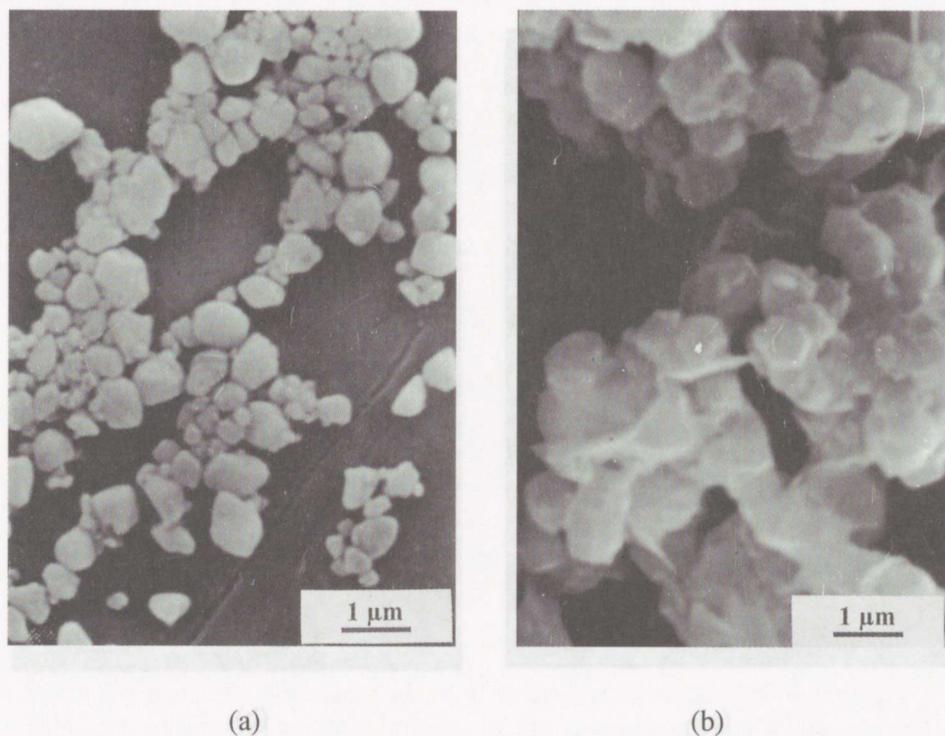

(a)   (b)

Fig. 4. SEM photos of milled BSP: (a) initial powder; (b) after 8 h milling.

of peak shapes, and volume-weighted crystallite size D_v was calculated from linear fit of the Williamson–Hall plot. From TEM photos the average size of powder crystallites (D_{cr}) was measured with image analysis system VIDEOLAB. Identification of a single crystallite in VIDEOLAB in the case of milled samples was difficult because the sharp edges of the crystallites in agglomerates of the initial powder were rounded. In this case, using SEM and TEM photos estimation of the interval of the crystallite size was used. In Table 1 the values of $<D_v>$ are taken from [5], and D_{cr} are measured directly on the TEM and SEM photos.

Table 1. Comparison of crystallite and grain sizes determined by XRPD (Voigt analysis + Williamson–Hall plot) and TEM/SEM methods

Sample No	XRPD method D_v, nm	TEM/SEM method D_{cr}, nm
888.0	109.8	147
888.2	99.5	50–200
888.4	97.8	50–200
888.8	93.0	50–200
888.15	74.3	50–150
888.25	53.6	40–100
1122.150	68.7	~100
1122.5	32.0	45
1122.0.5	20.8	34

From the results of the present study and [3–5] it is possible to state that TEM and SEM methods enable direct investigation of the structure of powdered materials and, consequently, to show the influence of technological processes on their structure. Using SEM it is possible to determine the form and size, and study the agglomeration of sodalite powder particles. Investigation of sodalite powders shows in most cases that particles are made up of microcrystals but the determination of the form and size of them is not possible with the SEM method. To investigate the form and size of microcrystals, TEM method is used.

In the study of sodalite powders with SEM and TEM methods the three-step hierarchical structure is obtained (Fig. 1). The first step consists of smallest distinguishable particles – microcrystals with a diameter of 20–200 nm. The microcrystals are joined onto spherical agglomerates with diameter 0.3–2.0 µm. The third step is formed from joined agglomerates – conglomerates which have an irregular form and a size 10 µm or more.

The optimal T_s for synthesizing the BSP by low-temperature hydrothermal method is 80–100 °C. At 80 and 100 °C, synthesized powders have spherical agglomerates and sharp-edged microcrystals. Temperature rise from 80 to 100 °C causes some unification effect of the powder particles: agglomerates grow bigger and conglomerates appear less.

Increasing x over 0.6, the obtained sodalite powder is significantly more uniform and the powder is in the form of agglomerates. The minimal size of agglomerates is obtained in the case $x = 0.55–0.6$ when distinguished changes in the powder structure have taken place.

Increasing the synthesizing time, the obtained powder is more homogeneous and microcrystals grow bigger. The relations of the growth parameters for ISP and BSP are generally the same. But powder microcrystals and agglomerates grow bigger in BSP in comparison with ISP at the same conditions.

Table 1 shows that average size of the particles D_v, measured with XRPD, is 1.3–1.6 times smaller than D_{cr} obtained with the TEM/SEM method. Besides, the difference in the average size is bigger in the case of smaller microcrystals. There can be many reasons for the differences in the average size: 1) the smallest particles may be invisible in TEM investigations, 2) particles, seen in TEM as single microcrystals, could look in XRPD investigations as multiple micro-crystals.

Electron microscopes enable to study crystallites, agglomerates, and conglomerates separately, and X-ray diffraction method gives the average size of the microcrystals.

3.2. Sodalite ceramics

The dependence of the structure of the iodide (ISC) and bromide (BSC) sodalite ceramics on the following parameters was investigated: pressing temperature (T_{pr}), pressure (p), pressing time (t), filling stage with halogen (x), impurities, and starting powder.

To study the influence of T_{pr} on BSC structure, a series of ceramics ($p = 200$ MPa, $t = 40$ min) in temperature interval 900–1250 °C from the same initial powder ($x > 0.8$) was prepared. To clarify the influence of the pressure on the structure of the BSC, a second series ($T_{pr} = 1000–1250$ °C) was made at lower pressure ($p = 25$ MPa).

At $T_{pr} = 900$ and 950 °C, the BSC had the same structure as the initial powder (Fig. 5a). No recrystallization was observed. Powder agglomerates were joined to ceramics with weak forces. Many agglomerates were broken up to powder crystallites and formed the intergrain bond material. After 30 s etching of this ceramics with 50% NaOH, it fell into pieces of the starting powder. In temperature interval 950–1000 °C, the ceramics became thicker and turned into recrystallized substance. At these temperatures, the primary recrystallization (PRC) processes started. The melting temperature (T_{ml}) of sodalite was approximately 1450 °C [9]. Thereby at pressure $p = 200$ MPa the PRC processes began approximately at $0.7\ T_{ml}$. At $T_{pr} = 1000$ °C the PRC processes ceased (Fig. 5b). From 1000 to 1150 °C, the BSC grains increased and the structure became thicker under the influence of collecting recrystallization (CRC) (Fig. 5c). At 1250 °C, the
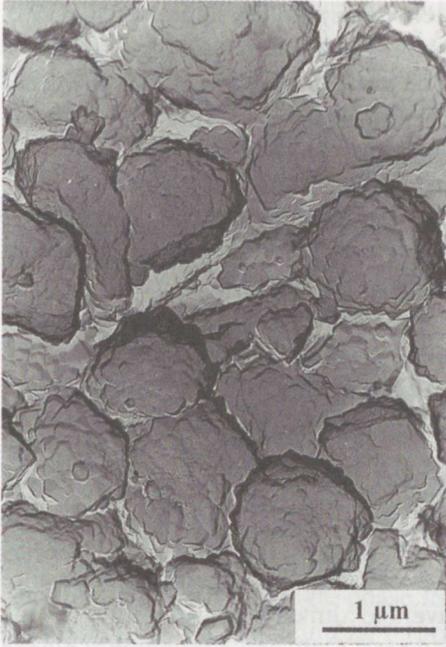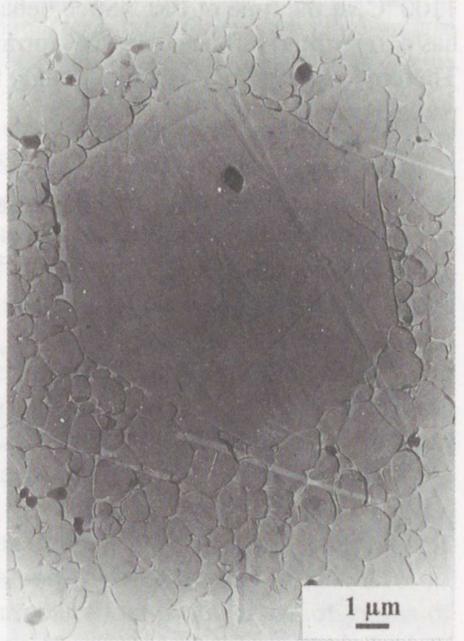
(a)
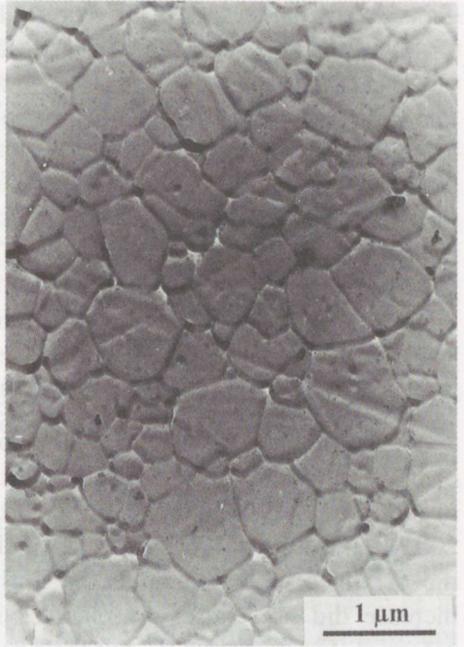
(b)
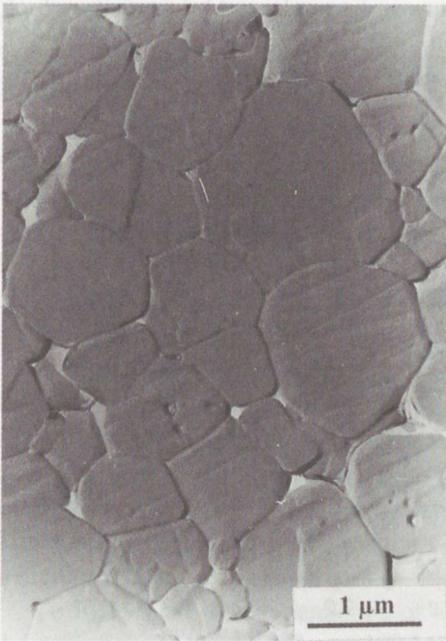
(c)

(d)

Fig. 5. Structure of the BSC at different temperatures of pressure: (a) 950 °C; (b) 1000 °C; (c) 1150 °C; (d) 1250 °C.

anomalously large secondary recrystallization (SRC) grains appeared (Fig. 5d). Rising of the pressing temperature caused increase of the dimensions of the grains of the ceramics. As seen in Fig. 6 (points A), at $p = 200$ MPa, $t = 40$ min, BSC has linear dependence on T_{pr} in Arrhenius co-ordinates. Using equation

$$D_g = D_0 \exp[-E_a/kT],$$

where D_g is average size of grains, D_0 is constant, k is the Boltzman constant, T is absolute temperature, and E_a is the activating energy of the process, we can calculate E_a:

$$E_a = -k \tan \alpha.$$

The activating energy of the above described BSC is 0.92 ± 0.28 eV.

At the pressure 25 MPa, BSC has pores. Influence of CRC on the formation of the structure of the ceramics is weak and after PRC, SRC will start. The PRC began in BSC at 1050 °C. It is 100 °C higher than in the case of BSC pressed at 200 MPa. Between 1050–1100 °C, thickness of the BSC raised and the grains of the ceramics increased under the influence of CRC. Continuous temperature increase did not cause any changes in average dimensions of grains of the ceramics (Fig. 6, points B), but their porosity rose. Only some favourably placed particles grew into big SRC grains. As is seen in Fig. 6, in the at $p = 25$ MPa pressed ceramics the average size of grains reached their maximum value at 1100 °C, at the time of PRC. Such behaviour can be explained by porosity which has a retarding influence on the formation of the recrystallized structure [7]. Thereby $p = 25$ MPa is not enough for getting a homogeneous and thickly packed ceramics.
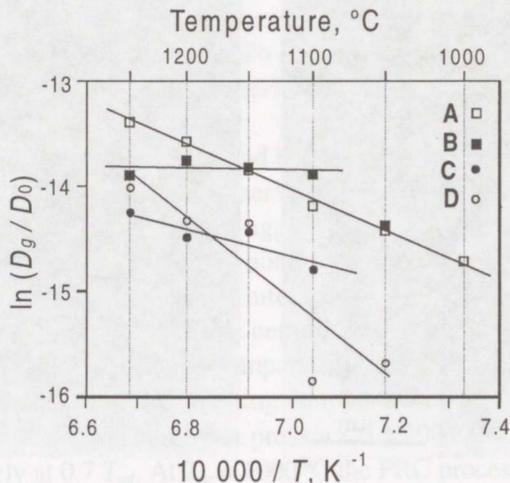

Fig. 6. Dependence of D_g on the pressure temperature: A – BSC pressed at $p = 200$ MPa; B – BSC ($p = 25$ MPa); C – single-phase ISC ($p = 200$ MPa); D – two-phase ISC ($p = 200$ MPa).

In case of ISC, both single- and two-phase (containing nepheline) ceramics were investigated. The same pressing parameters ($p = 200$ MPa, $t = 40$ min) were used. In single-phase ISC ($x > 0.8$) T_{pr} was in the interval 1000–1250 °C, and in the case of two-phase ISC ($x = 0.5$–0.6) $T_{pr} = 1050$–1250 °C.

With single-phase ISC the recrystallization processes began at $T_{pr} = 1050$ to 1100 °C, that was 100 °C higher than in case of BSC, pressed in the same conditions. The reason of higher temperature of recrystallization of ISC is bigger radius of Γ-ions in comparison with Br^--ions, and that their diffusion through ISC Al–Si lattice is prevented. At $T_{pr} = 1100$ °C, the PRC processes take place. Development of CRC processes are inhibited with pores in the ISC structure. From 1100 to 1200 °C, the ISC grains are increased under the influence of PRC and CRC, but the ceramics obtained is still porous. At $T_{pr} = 1200$ °C, the SRC processes start, but the extent of SRC is not so big as in the case of BSC.

In nephelin containing two-phase ISC, the recrystallization processes begin at $T_{pr} = 1050$–1100 °C on the basis of PRC. At higher temperatures the increase of the grains of the ceramics is caused by PRC and SRC processes. The role of the CRC process in formation of the structure is small due to the big porosity of the ceramics. Similarly to single-phase ISC, the extent of SRC is not so large as in the case of BSC. As seen in Fig. 6 (points C, D), rise of the pressure temperature causes an increase of the average size of the grains of the ceramics. At 1200 °C, both single- and two-phase ISC have structures with similar average size of grains, but two-phase ceramics is more porous. At the same time, the increase of the grains of the two-phase ceramics is more steep than that of the single-phase ISC. Comparing BSC with ISC, at same conditions bigger average size of grains is obtained in BSC.

To investigate the dependence of the average size of the grains on pressure, a series ($p = 25$–200 MPa) of two-phase ISC ($x = 0.6$, $T_{pr} = 1200$ °C, $t = 40$ min) was prepared. At lower pressures, 25–50 MPa, the big grains with a number of defects appeared. Obtained ceramics is porous and particularly nonrecrystallized. Rising the pressure caused a decrease of the average size of the grains of the ceramics (Fig. 7, points A). More perfect grains are formed and thickness of the ceramics is higher.

For investigating the dependence of the average size of grains on the pressing time, the two-phase ISC ($x = 0.6$, $T_{pr} = 1200$ °C, $p = 200$ MPa) was used. The structure of the ceramics was studied in the interval 1–100 min. No significant changes in the average size of the grains were found. It means that the recrystallization processes in the ceramics last for a short time (less than 1 min). Continuous hotpressing of ceramics causes only a small thickening of the structure and some improvement in transparency.

To investigate the dependence of the structure and average size of grains of the ceramics ($T_{pr} = 1200$ °C, $p = 200$ MPa, $t = 40$ min) on the filling stage of Al–Si carcass with halogen ions, the described ISP powders were used as a starting material. All ceramics with filling stage less than 0.8 contained the second-phase
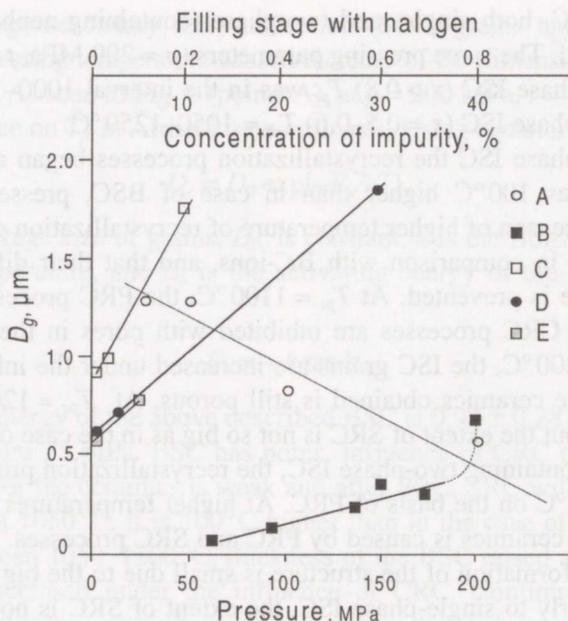
Fig. 7. Dependence of D_g: A – on pressure, two-phase ($x = 0.6$) ISC; B – ISC, on filling stage with halogen; C – NaCl, on impurity in BSC; D – NaI, on impurity in BSC; E – NaCl, on impurity in ISC.

nephelin. At low filling stages, the obtained grains of the ceramics are very small. Structure is thick and formed by PRC. At higher filling stages, the quota of CRC and SRC is increased. At $x = 0.6$, more perfect structure without pores is obtained. As seen in Fig. 7 (points B), raising of the filling stage caused increase in average size of the grains of the ceramics. In the range $x = 0.7$–0.8, the ceramics transform into the single-phase substance and average size of grains increases sharply. The smaller grains in two-phase ceramics can be explained by preventive influence of the second phase to recrystallization.

Addition of other halogen salts to BSC and ISC causes large changes in the structure of the ceramics.

In the case of addition of NaCl to single-phase BSC ($T_{pr} = 1200\,°C$, $p = 200$ MPa, $t = 40$ min), the SRC grain sizes and quota increases. At the same time the porosity of ceramics raises too. Addition of 1% NaCl causes anomalous increase of SRC grains. Some of them are a thousand times bigger than average grains. In the case of addition of 10% NaCl, the structure of the obtained ceramics is built from big and very defective grains. After short etching in 50% NaOH solution, the ceramics was smashed to pieces.

Addition of a small amount of NaI (3%) to the same BSC caused thickening of ceramics, and grains of the ceramics increased. The PRC processes took place and CRC started. It means that, contrary to NaCl impurity, the addition of a small amount of NaI to BSC has the unification effect on the sodalite structure.

Addition of a big amount of NaI (30%) destroys the structure of the ceramics. Similarly to the addition of 10% NaCl, big defective grains are formed and the obtained ceramics are opaque.

Impurity due to 5% NaCl had to the single phase ISC ($T_{pr} = 1200\,°C$, $p = 200$ MPa, $t = 40$ min) structure a unification effect. The ceramics thickened and CRC processes took place.

In all cases the addition of other halogen salts to the structure of the ceramics caused increase in the average size of grains (Fig. 7, points C, D, and E). In the case of BSC, the increasing was faster when NaCl was used as the impurity material.

The size of microcrystals of the initial powder, used in hotpressing of the ceramics, had a considerable influence on the formation of the ceramics structure. Dimensions of microcrystals were measured with XRPD method at Tartu University [3].

Depending upon the size of the microcrystals, different recrystallization processes took place in formation of the ceramics. As seen in Fig. 8 (curve A), the rise of the average size of BSP microcrystals caused increase in the grains of the ceramics D_g; D_g obtained maximum value at 500–900 Å. Continuous rising caused the decrease in the average size of grains of the ceramics. In the case of ISC, similar dependence was found (Fig. 8, curve B). At $D_g \sim 600$ Å, the average size of grains obtained maximum value. Following increasing of D_g to 800 Å did not cause any changes in average size of the ceramics.

As seen in TEM photos, depending on the powder crystallite size, different recrystallization processes take place in sodalite ceramics. In the case of small and biggest D_{cr} values, obtained ceramics are formed only as a result of PRC processes and, as seen in Fig. 8, the obtained D_g values are the smallest. Ascending and falling parts of the curve A in Fig. 8 correspond to the development of CRC processes in BSC. Near the maximum of the curve, the SRC processes take place and obtained ceramics are more porous.
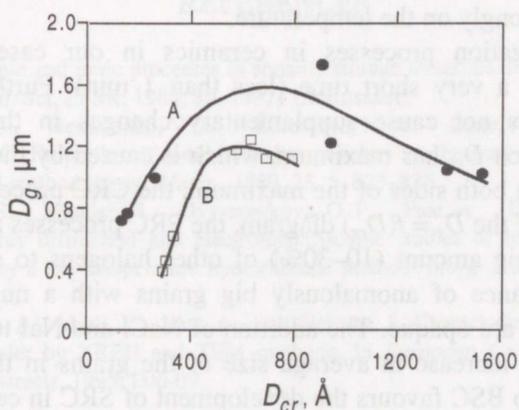

Fig. 8. Dependence of D_g on D_{cr}: A – bromide sodalite; B – iodide sodalite.

It follows that for the investigation of sodalite powders and ceramics it is necessary to use the TEM method. To obtain thick and transparent sodalite ceramics the recrystallization of initial powder is needed. For activation of recrystallization processes in sodalite both high temperature ($> 0.7\ T_{ml}$) and pressure (200 MPa) are needed (hotpressing). Quality of obtained ceramics depends on properties of the initial powder and on several hotpressing parameters.

Experiments show that in hotpressing similar principles are valid as in the case of thermal treatment. In the case of $p = 25$–100 MPa, used temperature values (1000–1250 °C) are not sufficient for obtaining transparent and thick ceramics and PRC processes are not conclusively developed. Raising of the pressure can cause increasing or decreasing of D_g, depending on the pressure value. For obtaining transparent ceramics, PRC processes must be finished. Following CRC processes cause thickening of the ceramics. Structure of the obtained ceramics is less defective, transparent, and grains of the ceramics are bigger. In some cases the SRC processes are developed as well. Then the grains grow bigger and obtained ceramics are porous and their transparency is lower.

The behaviour of BSC and ISC in hotpressing is rather similar, only the quantitative values are different. In BSC, the recrystallization processes are clearly observable. At $T_{pr} \sim 1000$ °C, the PRC processes take place in BSC. Temperature rise by 50–100 °C causes development of CRC, and continuous increasing of T_{pr} to 1200–1250 °C starts SRC processes. Temperature rise causes increase in D_g. This dependence can be approximated by a straight line in Arrhenius co-ordinates $\{\ln (D_g/D_0) = f(1/T)\}$. The angle of the slope of that line gives the activation energy E_a. In the case of $p = 200$ MPa, pressed BSC has activation energy 0.92 ± 0.28 eV.

In ISC, the PRC processes take place at temperatures higher than ~ 100 °C, and obtained ceramics are porous. Porosity retards CRC and SRC processes. Thereby the D_g value in the case of ISC is smaller than in corresponding BSC. In the case of two-phase ISC ($x < 0.8$), the D_g is smaller than in single-phase ISC, and D_g depends strongly on the temperature.

The recrystallization processes in ceramics in our case ($p = 200$ MPa, $T_{pr} = 1200$ °C) last a very short time (less than 1 min). Further increasing of pressing time does not cause supplementary changes in the structure. The dependence of D_g on D_{cr} has maximum, which is caused by the development of SRC processes. On both sides of the maximum, the CRC processes predominate and on the edges of the $D_g = f(D_{cr})$ diagram, the PRC processes are developed.

Addition of a big amount (10–30%) of other halogens to sodalite ceramics causes the appearance of anomalously big grains with a number of defects. Obtained ceramics are opaque. The addition of NaCl and NaI to BSC, and NaCl to ISC, causes the increase in average size of the grains in the ceramics. The addition of NaCl to BSC favours the development of SRC in ceramics. Addition of a small amount (3%) of NaI to BSC and (5%) NaCl to ISC causes the

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unification effect to ceramics structure and spread of collecting recrystallization. Obviously, by addition of small amounts of other halogens to sodalite structure the obtained structure depends upon ionic radiuses of the halogens.

4. CONCLUSIONS

By investigation of the structure of bromide and iodide sodalite powders the scanning and transmission electron microscopy are indispensable. Using these methods the three-step hierarchical structure of sodalite powders has been determined. In the study of the sizes of the first-step particles, in addition X-ray powder diffraction is to be used. Electron microscopy investigations permit the determination of optimal conditions for obtaining sodalite powders with wanted parameters.

For the study of the structure of sodalite ceramics the transmission electron microscopy investigations are necessary. The structure of the obtained ceramics depends on initial sodalite powder as well as on hotpressing parameters. Properties of the ceramics depend on the powder recrystallization and on the recrystallization rate (primary, collecting or secondary). This problem needs further investigations.

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HALOGEENSODALIITIDE UURIMINE ELEKTRONMIKROSKOOPIA MEETODITEGA

Valdek MIKLI ja Aadu PAAT

On selgitatud elektronmikroskoopia meetodite kasutatavust sodaliitpulbri sünteesi ja optiliselt läbipaistva sodaliitkeraamika kuumpressimise optimaalsete parameetrite määramiseks. Töötati välja sodaliitpulbri ja -keraamika prepareerimise metoodika nii skaneeriv- kui ka transmissioonelektronmikroskoopilisteks uuringuteks. Tulemuste analüüsil kasutati kujutiste töötlust. Selgitati tehnoloogiliste parameetrite mõju sodaliitpulbri ja -keraamika struktuurile, samuti vaadeldi sodaliitpulbri struktuuri ja granulomeetria sõltuvust jahvatusest. Pulbri kristalliitide suurus määrati röntgendifraktsiooni ja elektronmikroskoopia meetoditega. Näidati, et sodaliitpulbril on kolmeastmeline hierarhiline struktuur ja sodaliitkeraamika struktuur oleneb rekristallisatsiooniprotsessi iseloomust.

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