Molten Salt Synthesis of Nitrate-Exchanged Magnesium and Aluminum Sodalites

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Nitrate-exchanged sodalite $Na_8Al_6Si_6O_{24}(NO_3)_2$ and mixed sodium magnesium silicate with sodalite-like structure $Na_8Mg_3Si_9O_{24}(NO_3)_2$ were obtained by reaction of Mg or Al salts with silica or glass in molten $NaNO_3$ fluxes in the range of temperatures 673−823 K, in the presence of Na_3VO_4 as mineralizer.

Molten salts are completely ionized nonaqueous solvents having original and rich chemistry. Reactions in molten salts provide a source of new, often unexpected techniques for preparation of solids.[1] Among the ionic fluxes molten nitrates possess high reactivity toward different inorganic species[2] and relatively low melting points which makes them convenient for preparation of inorganic materials.[3] Recently, molten nitrates showed their potential as a medium for syntheses of simple and mixed oxides for catalysis[4] and mixed phosphates, including lamellar zirconium phosphates and NASICONS.[5] Low-temperature synthesis of commercially important $LiNbO_3$[6] is another example of molten nitrates applications. Recently, zeolitization of natural minerals (fly ash, kaolinite, zeolite waste) was reported by Park et al.,[7] upon action of NaOH and NH_4F dissolved in molten $NaNO_3$, which led to formation of sodalite, mixed with the initial minerals.

Generally, useful inorganic materials might be elaborated in molten salts by means of reactions of precursors of metals in the oxidation states II−IV (like Mg, Zn, Al, Ni, Zr, and others), combined with polyvalent oxoanions (such as phosphate, niobate, molybdate, etc.). However during the last several years our attempts to prepare any interesting silicate materials starting from alkali metal silicates or silica precursors were not very fruitful. Until recently, the products were highly dispersed amorphous silicas or poorly crystalline alumosilicates, sometimes including sodalites, but never pure silicate compounds.

Here we report on the nitrate flux synthesis of single-phase well-crystallized sodalite compounds. Formation of mixed silicates was observed by accident, when studying syntheses of vanadates in molten nitrate fluxes. To carry out molten salt reaction, the mixtures were applied, containing ca. 1 g of a metal precursor salt (chlorides or nitrates of Ca, Mg, Al, La, Y, Ni, Co, Cu, Fe, etc.), with 5 g of Na_3VO_4 and 15 g of $NaNO_3$. The mixtures were placed in a thick wall glass or silica reactor and treated under a nitrogen flow. Dehydration at 423 K and reaction at 523−823 K were subsequently carried out for a time varying from 2 to 24 h. After reaction, the products were washed at room temperature by distilled water and then dried in air at 373 K for 24 h. In some cases, the experimental procedure was modified. Sometimes a quartz reactor was used instead of the glass one, or amorphous silica gel was placed into the reaction mixture; in other cases Na_3VO_4 was replaced by equivalent amounts of NaOH, NaF, or Na_2CO_3.

Solid products were characterized using several physicochemical techniques. X-ray diffraction (XRD) patterns were recorded on a Bruker diffractometer using Cu Kα radiation. Indexing of phases was made using TREOR[8] and DIVCOL[9] programs. Chemical analyses were carried out using atomic emission with a spectroflame ICPD device. Scanning electron microscopy (SEM) images were obtained on a Hitachi S800 device, at the Center of Electronic Microscopy of Claude Bernard University (Lyon, France). FT-IR spectra were obtained on a Bruker device.

The experiments described above were carried out with the initial goal of obtaining mixed vanadates. Indeed, using $NaVO_3$ or NH_4VO_3 as vanadium sources, mixed vanadates have been prepared (to be published elsewhere). It was observed, though, that when Na_3VO_4 was applied, several metal salts yield products containing no vanadium (less than 0.5 wt %) but much silicon. Since no silicon compounds were put into the reaction mixture, we inferred that the glass or silica reactor walls served as a silica source. Indeed, advanced corrosion of glass reactor walls was noted after the reaction. All the silicon containing products showed similar XRD patterns, which were indexed in the cubic space group with

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(1) Kanatzidis, M. G.; Sutourik, A. G. *Prog. Inorg. Chem.* **1995**, *43*, 151.

(2) Kerridge, D. H. In *Chemistry of Nonaqueous Solvents*; Lagovski, J. J., Ed.; Academic Press: New York, 1978; Vol. VB, p 270.

(3) Afanasiev, P.; Geantet, C. *Coord. Chem. Rev.* **1998**, *178/180*, 1725.

(4) Hamon, D.; Vrinat, M.; Breysse, M.; Durand, B.; Jebrouni, M.; Robin, M.; Magnoux, P.; des Courieres, T. *Catal. Today* **1991**, *10*, 613.

(5) Afanasiev, P. *Chem. Mater.* **1999**, *11*, 1999.

(6) Afanasiev, P. *Mater. Lett.* **1998**, *34*, 253.

(7) Park, M.; Choi, C. L.; Lim, W. T.; Kim, M. C.; Choi, J.; Heo, N. H. *Microporous Mesoporous Mater.* **2000**, *37*, 81.

(8) Werner, P. E. *Z. Kristallogr.* **1964**, *120*, 75.

(9) Louer, D.; Louer, M. *J. Appl. Crystallogr.* **1972**, *5*, 271.

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Table 1. Solid Products of Reactions in Molten $NaNO_3$ Fluxes (Silica or Glass Reactor; Reaction Duration 4 h)

T, K	precursor	additive	products: XRD phases
673	$MgCl_2 \cdot 6H_2O$	Na_3VO_4	$NaMg_4(VO_4)_3$ (JCPDS 36-0009); MgO
773	$MgCl_2 \cdot 6H_2O$	Na_3VO_4	$Na_{8.15}Mg_3Si_{8.9}O_{23.87}(NO_3)_2$ (cubic, $a = 9.08$ Å)
773	$MgCl_2 \cdot 6H_2O$	NaOH, NaF Na_2CO_3	MgO and poorly crystallized SiO_2
823	$MgCl_2 \cdot 6H_2O$	Na_3VO_4	$Na_{8.1}Mg_3Si_{8.8}O_{23.62}(NO_3)_{2.07}$ ($a = 9.06$ Å)
823	$MgCl_2 \cdot 6H_2O$	Na_3VO_4	$Na_8Mg_3Si_9O_{24}(NO_3)_2$ and Mg_2SiO_4 (impurity)
673	$AlCl_3 \cdot 6H_2O$	Na_3VO_4	Al_2O_3
773	$AlCl_3 \cdot 6H_2O$	Na_3VO_4	$Na_{7.9}Al_6Si_{6.2}O_{24.28}(NO_3)_{2.02}$ ($a = 8.98$ Å)
773	$AlCl_3 \cdot 6H_2O$	NaOH, NaF Na_2CO_3	poorly crystallized $Na_8Al_6Si_6O_{24}(NO_3)_2$ and Al_2O_3
823	$AlCl_3 \cdot 6H_2O$	Na_3VO_4	$Na_{7.92}Al_6Si_{6.1}O_{24.17}(NO_3)_{1.98}$ ($a = 8.96$ Å)

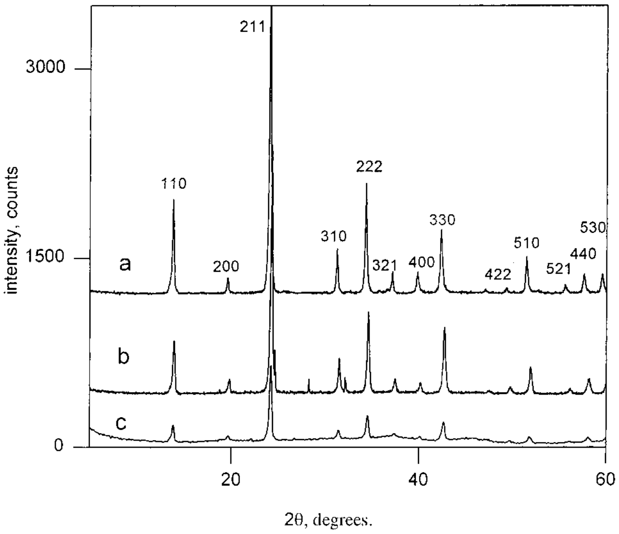

Figure 1. XRD patterns of solid products obtained from $NaNO_3$–Na_3VO_4 flux from $AlCl_3 \cdot 6H_2O$ at 773 K (a), $AlCl_3 \cdot 6H_2O$ at 823 K (b), and $MgCl_2$ at 823 K (c).

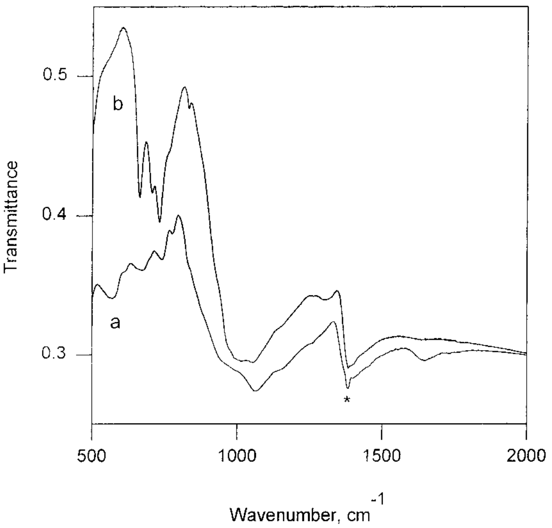

Figure 2. Infrared spectra of the solids $Na_8Mg_3Si_9O_{24}(NO_3)_2$ (a) and $Na_{7.9}Al_6Si_{6.2}O_{24.28}(NO_3)_{2.02}$ (b). The peak marked with an asterisk is the nitrate band at 1395 cm^{-1}.

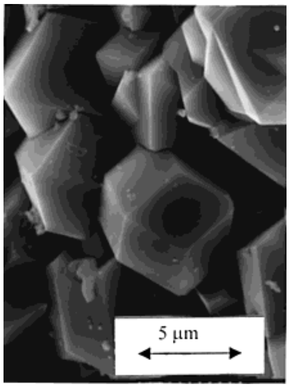

Figure 3. SEM picture of $Na_8Mg_3Si_9O_{24}(NO_3)_2$ obtained in molten $NaNO_3$–Na_3VO_4 flux at 773 K.

the lattice parameter varying as a function of composition (Table 1). They were assigned to a Na−Al nitrate-exchanged sodalite, and the lattice parameters observed (a = 8.96 and 8.98 Å) were close to that observed previously (a = 8.97 Å).[10] Chemical analysis of the solid showed good correspondence to the nitrate-exchanged sodalite (Table 1).

Mg-containing solids showed all the same lines as Al sodalite but a somewhat bigger lattice parameters. It follows from the chemical analyses that the Mg silicate composition close to $Na_8Mg_3Si_9O_{24}(NO_3)_2$ can be derived from the sodalite formula $Na_8Al_6Si_6O_{24}(NO_3)_2$ replacing every 2 Al with Mg + Si. Magnesium sodalites have been obtained previously using solid-state reaction at 973 K in air.[11] Nitrate-exchanged Mg sodalite was not described previously. The lattice parameter we report (a = 9.06−9.08 Å) is bigger than that observed by Thompson et al.[11] for $Na_8Mg_3Si_9O_{24}Cl_2$ (a = 8.989 Å) in agreement with the increased lattice parameter for nitrate-exchanged Al sodalite compared to its chloride counterpart.

FT-IR spectra confirm that the products contain nitrate ions enclathrated in the sodalite cages since the intense and broadened line at ca. 1395 cm^{-1} was observed in both Al and Mg solids (Figure 2).

SEM studies with EDX analysis showed good homogeneity of the crystals obtained at 773 and 823 K for the reaction times 4−8 h. The samples prepared at 823 K consist of large (tens of micrometers) and well-shaped crystals (Figure 3). At 823 K and for long durations of reaction (24 h), the Mg sodalite tends to decompose, reacting further with the flux to produce highly dispersed Mg_2SiO_4, with particular dendrite morphology (Figure 4).

Similar results were obtained using as a reactors quartz containers. Silica gel and quartz wool were also tried as a precursors. When added to the reaction mixture, dispersed SiO_2 reacts easily, but after the reaction some unreacted silica, if eventually present, is impossible to remove from the product. To rationalize the preparation technique, we also carried out the sytheses in the steel and nickel containers, using the

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(10) Buhl, J. C.; Loens, J. *J. Alloys Compd.* **1996**, *235*, 41.

(11) Thompson, J. G.; Gougherty, J.; Melnitchenko, A.; Lobo, C.; Withers, R. L. *J. Mater. Chem.* **1996**, *6* (12), 1933.

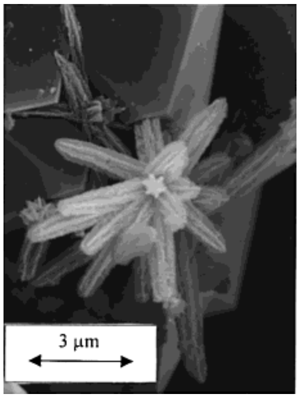

Figure 4. SEM picture of Mg_2SiO_4, grown on the $Na_8Mg_3Si_9O_{24}(NO_3)_2$ crystal at 823 K.

same contitions and the same mixtures of Mg or Al precursor salts, Na_3VO_4 and $NaNO_3$, but adding stoichiometric amounts of SiO_2 in the form of commercial quartz wool or silica powder. In this case well-crystallized solalites were also obtained, but they contained NiO and Fe_3O_4 impurities due to corrosion of metallic reactors. For the product obtained in a steel reactor, sodalite product could be easily purified, because Fe_3O_4 could be easily removed with a magnet.

It is known that molecular sieve materials are metastable phases with respect to simpler dense oxides. Hydrothermal preparations obey Ostvald's law of successive formation of more and more stable compounds. We suggest that the same sequence of transformations occurs in molten salts. Sodalite is just a kinetic product and transforms into a more stable ternary silicate after long reaction times. The question arises whether the sodalite is the most complex structure available in such syntheses or whether there are other metastable products similar to open framework zeolites.

Sodalites were formed only in the case of reactions of relatively electropositive metals, namely Mg and Al (Ca showed also some sodalite diffraction lines in the XRD, but pure compounds were not obtained). Transition metals such as Ni and Cu gave just dispersed oxides such as CuO. Our attempts to use nitrate flux to prepare any silicates of Ti or Zr were unsuccessful.

Obviously, Na_3VO_4 has the peculiar property to promote silicate formation. Indeed, applying $NaVO_3$ instead of Na_3VO_4, we obtained either oxides or mixed vanadates but no sodalites. At first, the higher oxobasicity of Na_3VO_4 was suspected to be the reason of this difference. Then, we studied the effect of replacing Na_3VO_4 with other strong oxobases, namely NaOH and Na_2CO_3 (we used also NaF, known as a strong mineralizer for molten nitrate preparations[12]). However, using these additives we obtained only amorphous or poorly crystallized oxides−dispersed Al_2O_3 and MgO with important amounts of alkali metal and vanadate impurity. Sometimes the products involved much silicon impurity because of advanced corrosion of the reactor walls. However in the most favorable case, using NaOH at 773 K poorly crystallized sodalite was identified, but the product was not pure, containing amorphous alumina, as established by SEM study with simultaneous EDAX analysis. Therefore we suggest that some complexes between metal ions and orthovanadate anions dissolved in the melt are highly reactive toward glass or silica. Indeed, a flux without vanadate (e.g. hydrated $MgCl_2$ in $NaNO_3$) was not reactive toward the walls of glass reactor, and the product contained only the corresponding metal oxide (MgO). Moreover, a Na_3VO_4–$NaNO_3$ flux without Mg or Al salt does not react rapidly with glass or silica at 773−823 K. Therefore, not any couple of the reactants but only their ternary combination provides some species able to attack glass or silica. The nature of these complexes need to be further studied. Understanding of mechanisms of sodalite formation in molten salt will hopefully provide an alternative way for elaboration of new framework solids.

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(12) Afanasiev, P. *J. Mater. Sci. Lett.* **1997**, *16*, 1691.