SYNTHESIS AND STUDY Mo- and W- BEARING SODALITES

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Introduction

Creation of matrix materials for radionuclides immobilization on the basis of mineral solid solutions - actual task of experimental mineralogy. For the first time the opportunity of application of sodalites as matrixes for fixing of elements of radioactive waste has shown by Pentinghaus et al. [1]. Then the synthesis iodine- bearing sodalite ceramic was carried out in work [2]. The study of leaching resistance have shown high stability of sodalite solid solutions and opportunity of their use as matrix materials. The purpose of the present work was study of molybdenum and tungsten incorporation in sodalites and opportunity of creation of matrixes on a basis Mo- and W- bearing sodalites.

Synthesis Mo- and W- bearing sodalites

Starting materials. For synthesis Mo- and W-containing sodalites and their solid solutions gels of nepheline ($NaAlSiO_4$) used. Natural chlorine containing sodalite (2-4 mg on 100-150 mg gel mixture) added in starting material. For solution preparation in experiments the distilled water and following salts of high purity ($Na_2MoO_4*2H_2O$ and $Na_2WO_4*2H_2O$) used.

Run procedure and analitycal techniques. The experiences carried out in the welded platinum tubes (5mm in diameter and 600mm^3 volume). Starting materials (gel mixtures, salts and distilled water) loaded into the tubes. The concentration of starting solution was 40-60wt.%. Tubes put into cold seal hydrothermal vessels with external heating. The impermeability of the tubes before and after runs was controlled by weighing.

The experiences carried out at 450-800°C and P_{H2O}=1-2 kbar. The accuracy of temperature controle was not worse 5°C and pressure - 50 bars. The duration of experiences was 10-35 day.

The unit cell parameters refined for all synthesized sodalites. Samples recorded in the continuous scan mode of the full X-ray diffraction profile on a PC/HZG-4 automated diffractometer. Angular positions of reflections estimated by the Spectr-8 program (A.V.Okhulkov, IEM RAS) with correction by the internal standard (spectrally pure Si, a=5.4305 A). Unit cell parameters refined by 12-17 reflections in the angular range of 7-39 degrees (θ) by the LCC, PUDI [3, 4], REFLAT [5] programs.

The chemical compositions of solid products analysed by the "Camebax" microprobe with energy-dispersive detector Link AN-10000. The ZAF- correction procedure used for calculation of the solid solutions compositions. The accuracy of microprobe analysis was not worse then 2.5 mol.%. The DTA study carried out for a number of synthesized samples.

Results of experiments. The molybdenum and tungsten- containing sodalites and their solid solutions synthesized in the hydrothermal conditions at 450-800°C and P_{H2O}=1-2 kbar. The run conditions and results of X-ray study are given in Table 1.

The DTA study shows that there is a weight loss (in sodalites synthesized at 450°C) during heating which terminates at 185°C. This effect connects with loss of water (1.6 wt.%) evidently. The structural transformation connected to allocation of heat exists above 720°C. As it is visible from data of Table 1 the unit cell parameters of Mo- containing sodalites synthesized at low temperature are a little bit larger than for ones synthesized at high temperatures. This effect is connected with incorporation of water in sodalite structure apparently. There is no weight loss during heating the sodalites synthesized at 800°C as it is shown by DTA study. It confirms absence of water in these sodalites.

The solid solutions of (Mo,W)- bearing sodalites are synthesized under hydrothermal conditions at 800°C and P_{H2O}=2 kbar. The synthesized samples are characterized of high crystallinity and their compositions are closely to stoichiometric formula. The crystallochemical formula of the synthesized solid solutions of the (Mo,W)- bearing sodalites and the refined unit cell parameters are presented in table 2.

Table 1

Conditions of synthesis and unit cells parameters of Mo and W- containing sodalites

Run no.	Phase	T, °C	P, kbar	Run duration, days	a, [A]	V, $[A]^3$
4899	Mo- Sod	450	1	35	9.142(1)[1)]	764.0(1)
5001	Mo- Sod	450	1	16	9.142(1)	764.1(1)
4921	Mo- Sod	700	2	11	9.140(1)	763.4(1)
5022	Mo- Sod	800	2	10	9.137(1)	762.8(1)
5121	Mo- Sod	800	2	10	9.137(1)	762.9(1)
5125	W- Sod	800	2	10	9.148(1)	765.7(1)
-	Mo- Sod[2)]	-	-	-	9.125	759.5
-	W- Sod[2)]	-	-	-	9.132	761.6

1) standard errors are given in parentheses and refer to the last decimal place;
2) the PDF-2 data.

Table 2

The crystallochemical formula and unit cell parameters of the of the (Mo,W)- bearing sodalite solid solutions synthesized from gel mixtures at 800°C and P_{H2O}=2 kbar

Run no.	Crystallochemical formula (calculation to 28 oxygen atoms)	X_W^{Sod} [1)]	a, [A]	V, $[A]^3$
5121	$Na_{7.71}[Al_{5.98}Si_{6.14}]_{12.12}(MoO_4)_{0.97}O_{24.12}$	0	9.137(1) [2)]	762.9(1)
5122	$Na_{8.02}[Al_{5.96}Si_{6.16}]_{12.12}(Mo_{0.73}W_{0.18}O_{3.64})O_{24.36}$	0.21	9.140(1)	763.7(1)
5123	$Na_{8.03}[Al_{5.89}Si_{6.14}]_{12.03}(Mo_{0.53}W_{0.39}O_{3.84})O_{24.16}$	0.40	9.142(1)	764.1(1)
5124	$Na_{7.95}[Al_{6.00}Si_{6.11}]_{12.11}(Mo_{0.24}W_{0.62}O_{3.72})O_{24.28}$	0.72	9.143(1)	764.3(1)
5125	$Na_{8.24}[Al_{5.96}Si_{6.10}]_{12.06}(WO_4)_{0.97}O_{24.36}$	1.00	9.148(1)	765.7(1)

1) mole fraction of W in sodalite solid solution;
2) standard errors are given in parentheses and refer to the last decimal place.

Concentration dependences of unit cell parameters of the (Mo,W)- bearing sodalite solid solutions are approximated by the following equations:

$$a = 9.1369 + 0.024136*X - 0.0428783*X^2 + 0.0297945*X^3 \text{ [A] } (\pm 0.001) \quad (1)$$

$$V = 762.9 + 6.5134*X - 12.7779*X^2 + 9.074614*X^3 \text{ } [A]^3 \ (\pm 0.1) \quad (2)$$

Where X - mole fraction of W in (Mo,W)- sodalite solid solution.

The parameters of Margules model (W1 and W2) for the description of excess volume of (Mo,W)- bearing sodalite solid solutions are -4.38(17) cm^3/mol and 2.19(9) cm^3/mol accordingly. Excess volume is described by the equation:

$$V^e = X*(1-X)*[-4.38*X + 2.19*(1-X)] \ (cm^3/mol) \quad (3)$$

Where X - mole fraction of W in (Mo,W)- sodalite solid solution.

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