Low temperature heat capacity and thermodynamic functions of anion bearing sodalites Na$_8$Al$_6$Si$_6$O$_{24}$X$_2$ (X = SO$_4$, ReO$_4$, Cl, I) ☆

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ABSTRACT

Heat capacities of sulfate, perrhenate, chloride, and iodide sodalites with the ideal formula Na$_8$Al$_6$Si$_6$O$_{24}$X$_2$ (X = SO$_4$, ReO$_4$, Cl, I) were measured from 2 K to 300 K using a Quantum Design Physical Property Measurement System (PPMS). From the heat capacity data, the standard thermodynamic functions were determined. All four sodalites undergo a phase transition below room temperature for which thermodynamic parameters were determined. Additionally, the heat capacity of one of the constituent compounds (NaReO$_4$) was measured.

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1. Introduction

The safe disposal of radioactive waste generated by the nuclear fuel cycle and nuclear weapons production remains one of the most challenging and potentially costly environmental endeavors facing the United States and the international community [1–3]. The ability of feldspathoid bearing multiphase ceramic waste forms, such as glass bonded sodalite [4–6] and sodium aluminosilicate fluidized bed steam reformers [7–10], to resist aqueous corrosion and retain highly radioactive anionic radionuclides (e.g., ^{99}TcO$_4^-$, ^{129}I$^-$, ^{79}SeO$_4^{2-}$) provides a significant safety component to geologic repository performance assessment [7,11,12].

Feldspathoid phases, including nosean (X = SO$_4$) and sodalite (X = Cl), having ideal formula Na$_8$Al$_6$Si$_6$O$_{24}$X$_2$ (X = monovalent or divalent anion), consist of a three dimensional (3D) framework composed of alternating TO$_4$ (T = Al or Si) tetrahedral units that share corner oxygens. The framework contains micropores (2.5–20 Å in diameter) with the ability to encase various guest anions (including Br$^-$, Cl$^-$, F$^-$, I$^-$, OH$^-$, MnO$_4^-$, SO$_4^{2-}$, SeO$_4^{2-}$, ReO$_4^-$, TcO$_4^-$, and WO$_4^{2-}$) by cooperative changes in the T- O - T bond angles [13–19]. Improving the scientific and technical basis for using the versatile feldspathoid porous framework for sequestering relatively long lived ions of radionuclides (e.g. ^{99}TcO$_4^-$, ^{129}I$^-$, ^{79}SeO$_4^{2-}$) requires an understanding of which type of anion bearing feldspathoid phase forms under specific conditions and its stability. The primary objective of the present study is to measure the heat capacities of four such materials; nosean (SO$_4^{2-}$), perrhenate (ReO$_4^-$ as a chemical analogue for pertechnatate, TcO$_4^-$), chloride (Cl$^-$) and iodide (I$^-$) sodalites. This study complements published [19] and ongoing measurements of heats of formation [20] and helps provide a complete picture of the thermodynamic stability of this family of compounds.

2. Experimental methods

2.1. Sample synthesis

The I- and Cl-sodalites were synthesized using hydrothermal methods by treating zeolite 4A with 8 M NaOH in the presence of

Table 1
Details of the calorimetric experiments for the PPMS measurements including pressure, p, sample mass, M_s, molar mass, M, and copper mass, M_{Cu}.

	SO_4-sodalite	Cl-sodalite	I-sodalite	ReO_4-sodalite
p/mPa	1.2	1.2	1.2	1.2
M_s/mg	12.19	10.96	10.12	25.03
M/g·mol^{-1}	1046.50	1099.28	1219.25	1398.72
M_{Cu}/mg	23.09	23.54	19.62	20.22

[a] The estimated standard uncertainties in the masses $M_{s,Cu}$ and pressure p are $u(M_{s,Cu})$ = 0.06 mg and $u(p)$ = 0.1 mPa.

Table 2
Lattice parameters and density of SO_4-, I-, Cl-, and ReO_4-sodalites. The errors are one standard deviation of the mean.

Compound	Experimental lattice parameter, Å	Z	Density, g/cm^3
SO_4–sodalite	9.0898 ± 0.0005	1	2.21 ± 0.02
I-sodalite	9.0058 ± 0.0003	1	2.25 ± 0.02
Cl-sodalite	8.8816 ± 0.0003	1	2.29 ± 0.03
ReO_4–sodalite	9.1515 ± 0.0001	1	2.980 ± 0.04

excess sodium salt. Zeolite 4A has a chemical composition of $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 9/2H_2O$ and a SiO_2/Al_2O_3 ratio of approximately two. The hydrothermal synthesis was carried out in a Teflon-lined Parr pressure vessel. The synthesis of the ReO_4-sodalite was described in detail previously [20].

Sulfate sodalite was also synthesized using a modified solid state reaction by reacting sodium sulfate decahydrate ($Na_2SO_4 \cdot 10H_2O$) with Ludox HS-40 colloidal silica (SiO_2) and sodium aluminum oxide ($NaAlO_2$). The solid state reaction was initiated dissolving dehydrated Na_2SO_4 and dehydrated $NaAlO_2$ in 150 mL of deionized water for 10 min in a Teflon beaker. Ludox was then added to the mixture and then placed in a constant temperature oven at 105 °C for 8 h. The resulting solid was removed, ground, added in a 95% Pt – 5% Au crucible, and heated in a furnace at 900 °C for 90 h.

The purity of the samples and the starting materials as well as the characterization methods as shown in Table 3.

2.2. Characterization

The particle size of the anion sodalites was determined using SEM and laser diffraction particle size analyses. Details of both measurements are provided in [20].

The powder X-ray diffraction (XRD) patterns of the samples was measured with a Panalytical X'Pert PRO diffractometer using CuKα radiation (λ = 1.54060 Å). Data were collected in 0.017° steps over the 2θ range of 5–110°.

The homogeneity and stoichiometry of the samples were verified by wavelength dispersive analysis using a Cameca SX-100 electron microprobe with voltage of 15 kV, beam current of 2 nA and beam size of 5 μm (ReO_4- and Cl-sodalite) [20] and 10 μm (SO_4 and I-sodalite). Elemental analysis was also performed by Galbraith Laboratories, Inc. using GLI Procedure E35-2 for iodine, GLI Procedure E17-1 for chlorine, and GLI Procedure ME-70 for the other elements.

Fourier transform infrared (FTIR) spectroscopy was carried out on a Bruker Equinox 55 FTIR spectrometer for all compounds to determine the presence of both structural and adsorbed surface water.

Thermogravimetry has been described in detail previously [20].

2.3. Heat capacity measurements

The low temperature heat capacities of all four samples were measured at P = 1.2 mPa using a Quantum Design Physical Properties Measurement System (PPMS) with 0.15 K spacing at T = (1.8–10) K, logarithmic spacing at T = (10–100) K, and 10 K increments at T = (100–300) K. Samples were prepared for heat capacity measurement by mixing about (10–25) mg of each powder with about 5 mg of copper strips (Alfa Aesar, 0. 99999 mass fraction purity) and putting this into copper cups (about 15 mg). The cups were then pressed into pellets approximately 3 mm in diameter and 1 mm in height. After running an addenda measurement, which contains the heat capacities of the calorimeter and the Apeizon N grease used to mount the sample, the samples were successively mounted onto the PPMS puck, and the heat capacities were measured. The PPMS automatically corrects for the addenda heat capacity, and the copper contribution was subtracted using data from [21] yielding the constant pressure heat capacities of SO_4-sodalite (nosean, sulfate sodalite), Cl-sodalite, I-sodalite, and ReO_4-sodalite. The uncertainties for the PPMS measurements of the standard molar heat capacities $C°_{p,m}$ following this method are estimated to be ±0.02 $C°_{p,m}$ for 2 < T/K < 10 and ±0.01 $C°_{p,m}$ for 10 < T/K < 302 [22]. Details of the PPMS measurements and sample masses are given in Table 1.

Table 3
The composition of the anion sodalites are the best estimate, determined from electron microprobe, elemental analysis, and thermogravimetric measurements. The one standard deviation of the mean Al and Si content in all four sodalites is 1% or less. The one standard deviation of the sodium and the respective anion amount for the SO_4 sodalite is approximately 1–2% and around 3–4% for the Cl, I, and ReO_4 sodalites.

Name	Formula	Water content (mol H_2O/mol)	Manufacturer	Lot#	Stock #	Phase purity	Characterization method
Sodium perrhenate	$NaReO_4$		Alfa Aesar	B08L39	11412	0.99+	XRD
Sodium sulfate decahydrate	Na_2SO_4	$10H_2O$	Fisher Scientific	075817	S419	0.995	COA
Ludox HS-400 colloidal silica, 40 wt% suspension in water	SiO_2		Sigma Aldrich	06914BH	420816	40% SiO_2	COA
Sodium aluminum oxide	$NaAlO2$		Alfa Aesar	C17N38	35453	Technical grade	COA
Zeolite 4A	$Na_2O \cdot Al2O3 \cdot 2SiO2$	$9/2H_2O$	Sigma Aldrich	07328DB	688363		COA
SO_4–sodalite	$Na_{7.98}Al_{6.00}Si_{6.06}S_{1.02}O_{28} \cdot$	$2.79H_2O$	synthesis			>0.99	XRD, SEM, EMP, FTIR, GLI procedure
Cl-sodalite	$Na_{8.04}Al_{6.06}Si_{5.94}O_{24}Cl_{1.92} \cdot$	$7.33H_2O$	synthesis			>0.99	XRD, SEM, EMP, FTIR, GLI procedure
I-sodalite	$Na_{7.64}Al_{6.02}Si_{5.95}O_{24}I_{1.64} \cdot$	$6.77H_2O$	synthesis			>0.99	XRD, SEM, EMP, FTIR, GLI procedure
ReO_4-sodalite	$Na_8Al_6Si_6O_{24}(ReO_4)_2$		synthesis			>0.99	XRD, SEM, EMP, FTIR, GLI procedure