Alkali-ion concentration dependence of the structure of proton-conducting alkali thio-hydroxogermanates investigated with neutron diffraction

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ABSTRACT

The proton-conducting hydrated alkali thio-hydroxogermanate's $M_xGeS_x(OH)_{4-x} \cdot yH_2O$ ($M = $ Na and K; $x = 1 - 4$, $y \approx 0.5 - 2$) were investigated by means of neutron diffraction with the aim to elucidate how the structure changes as a function of alkali-ion concentration, x, type of alkali ion, M, and water content, y. For $x = 1 - 3$ we find that the materials are amorphous and composed of thio-hydroxogermanate anions, water molecules, and charge balancing alkali ions, whereas for $x = 4$ we find that the materials contain also a crystalline phase, suggesting that it is difficult to prepare purely amorphous materials for the highest alkali-ion concentration, for both the Na and K based materials. For $x = 1 - 3$, the structure is reflected by an intermediate-range ordering, with a characteristic length-scale ranging from approximately 6 to 9 Å, which is dependent on both x and M and which may be related to the separation distance between dimers of thio-hydroxogermanate anions. As x increases, the intermediate-range ordering shortens, possibly as the result of an increasing level of hydration water that may act as a dielectric medium that reduces the repulsive interaction between the negatively charged thio-hydroxogermanate anions and/or between the positively charged alkali ions. A comparison of the structural results to the reported conductivities of the same materials indicates a non-trivial relationship, which depends on both the type and concentration of alkali ions, as well as on the level of hydration water.

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1. Introduction

Research on materials applicable in *clean* energy technologies is one of the fastest growing areas in materials science. A particularly up-and-coming, yet challenging, future clean energy technology is the hydrogen based intermediate temperature (≈ 100–300 °C) fuel cell. At the heart of this device is the transport of protons through a solid-state or semi-solid proton-conducting electrolyte material. A promising, yet relatively unexplored, class of proton-conducting materials is hydrated alkali thio-hydroxogermanates, of the form $M_xGeS_x(OH)_{4-x} \cdot yH_2O$, where $M = $ Na, K, Rb or Cs, $1 \leqslant x \leqslant 4$, and y varies between 1 and 8 [1,2]. Their conductivities typically reach a maximum value of around 10^{-3} Scm^{-1} in the temperature range of interest (≈ 100–300 °C) and the conductivity is related mainly to the proton bearing species and depends on both the water content and temperature [1,2]. Recent nuclear magnetic resonance studies of the Na$_x$GeS$_2$(OH)$_{4-x} \cdot yH_2O$ ($x = 2, 3$ and $y \approx 1$–4) series suggest a proton conduction mechanism described by a combination of proton and H$_2$O diffusion, with H$_2$O motion limiting proton dynamics at elevated temperatures [3]. The water molecules can be

removed reversibly from the materials by heating them to about 180 °C [4]. Studies have shown that the larger the value of y, the lower the temperature at which the loss of water begins [4,5]. The conductivity of the dehydrated equivalents is up to five orders of magnitude lower than for the corresponding hydrated materials, because in the dehydrated materials the alkali ions are the predominating charge carriers [1,2].

Structural studies of hydrated and dehydrated alkali thio-hydroxogermanates have so far focused on the M_2Ge S$_2$(OH)$_2 \cdot yH_2O$ ($M = $ K, Rb and Cs) series, using a combination of neutron diffraction, infrared spectroscopy and first-principles calculations. The results from these studies suggest that the materials are amorphous and built up of dimers of thio-hydroxogermanate anions, with water molecules acting as bridges between such dimers and with the alkali ions located in "voids" formed by the network of thio-hydroxogermanate anion dimers [6,7]. The structure of the dehydrated equivalents is built up of a percolating network of dimers of thio-hydroxogermanate anions, which are linked to each other via hydrogen bonds and where the alkali ions, as for the hydrated materials, are located in "voids" formed by the thio-hydroxogermanate anion dimers [7]. However, little is known about how the structure changes as a function of alkali-ion concentration. Such information is important for the understanding and further development of these materials, for example in relation to higher proton conductivity.

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In this study, we therefore investigate the structure of the proton-conducting alkali thio-hydroxogermanates $M_xGeS_x(OH)_{4-x} \cdot yH_2O$ with $M = $ Na and K and $x = 1 - 4$, whereby the role of the type and concentration of alkali ion can be investigated systematically. The investigations were performed by the use of thermal analysis together with neutron diffraction. To decrease the featureless background in the neutron diffractograms, related to incoherent scattering on protons, the neutron diffraction measurements were performed on deuterated equivalents.

2. Experimental

2.1. Sample preparation and thermal analysis

The sample preparation followed the scheme of Poling et al. [1]. The two $Na_xGeS_x(OD)_{4-x} \cdot yD_2O$ ($x = 1 - 4$) and $K_xGeS_x(OD)_{4-x} \cdot yD_2O$ ($x = 1 - 4$) series were prepared by mixing aqueous solutions (of 99.9% D_2O) containing stoichiometric amounts of the alkali deuterosulfide MSD and quartz-type GeO_2 (99.998%), where after the excess heavy water was allowed to evaporate at ≈ 70 °C for a period over five days. Most starting materials were purchased from Sigma-Aldrich, however, $KSD \cdot H_2O$ was prepared in our own laboratory. The preparation of $KSD \cdot H_2O$ was done by first dissolving KOH ($\geq 90\%$, Sigma-Aldrich) in methanol, followed by bubbling of H_2S gas through the solution for a period over 3 h. The methanol was then allowed to evaporate from this solution overnight by a gentle stream of N_2 gas above the solution. Subsequently, KSD was prepared by dissolving the non-deuterated equivalent in D_2O, followed by gentle rotary evaporation of the molecular water. The latter procedure was repeated three times in order to allow all H to be exchanged with D. The corresponding reaction for the synthesis of the deuterated alkali thio-hydroxogermanates may be written as

$$xMSD + GeO_2 + yD_2O \rightarrow M_xGeS_x(OD)_{4-x} \cdot yD_2O$$
$$x = 1, 2, 3, 4; M = Na, K, \tag{1}$$
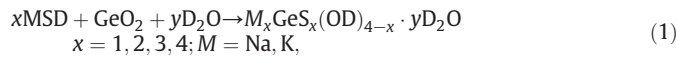
where the number of D_2O molecules (y) was determined by means of thermal gravimetric analysis (TGA), using the TG 209 F1 Iris instrument from Netzsch. For each TGA measurement, about 20 mg of sample was placed in an open aluminum pan, which was heated under a flow of He gas (25 ml/min) from room temperature up to 70 °C. At this temperature, the samples were kept for 60 min, followed by further heating up to 500 °C, with a heating rate of 3 °C/min. The heating curves for all the samples that were investigated are shown in Fig. 1. The y values were estimated from the mass loss during the temperature increase from 70 to 500 °C. Table 1 displays the y values obtained for all the samples and also displays the data for the bulk and atomic densities. The densities were determined using a gas-pycnometer "AccuPyc II 1340 Pycnometer" from Micrometrics.

2.2. Neutron diffraction

The neutron diffraction experiment was performed at the SANDALS diffractometer of the ISIS neutron facility of Rutherford Appleton Laboratory, UK. The SANDALS diffractometer, described in detail in Ref. [8], receives neutrons with wavelengths from 0.05 to 5 Å. The 660 detectors are summed into 18 groups, which cover an angular range of 3.8–39°, yielding scattering vectors (Q) in the range of 0.1–50 Å^{-1}. The samples were ground into fine powders using an agate mortar and a pestle, and loaded in flat sample cells of a 68% titanium and 32% zirconium alloy, which does not contribute to any coherent scattering. The sample thickness was between 2 and 4 mm, with a typical measuring time between 6 and 12 h, and all measurements were performed at room temperature. The measurements of the empty sample cans, the empty sample chamber, and on a vanadium standard, were used for correcting for the background and detector efficiency, and hence for the normalization of the data onto an absolute scale of barns per steradian per atom. Using
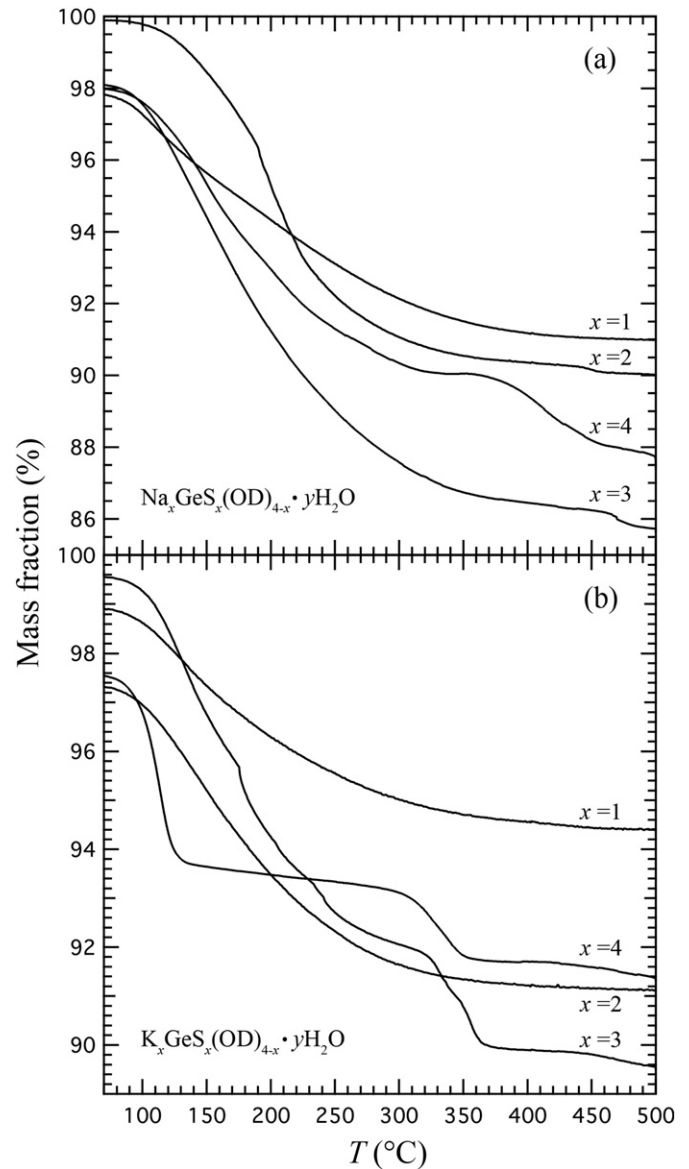

Fig. 1. Heating curves for (a) $Na_xGeS_x(OH)_{4-x} \cdot yH_2O$ ($x = 1 - 4$) and (b) $K_xGeS_x(OH)_{4-x} \cdot yH_2O$ ($x = 1 - 4$), as measured with a heating rate of 3 °C/min.

the GudrunN software [9] as developed for the SANDALS diffractometer, the raw data was corrected for multiple scattering, absorption, inelasticity effects, that generate a fully corrected structure factor, $S(Q)$, suitable for analysis in terms of the atomic pair-correlations. The level of the measured differential neutron scattering cross-section, related to the $S(Q)$, was well within the range of expected values, which shows that the data reduction and hence the sample composition and density

Table 1
Densities and deuterium content of deuterated alkali thio-hydroxogermanates.

Material	Bulk density (g/cm³)	Atomic no. Density (atoms/Å³)	y
$NaGeS(OD)_3 \cdot yD_2O$	2.801	0.0988	0.6
$Na_2GeS_2(OD)_2 \cdot yD_2O$	2.486	0.0778	1.3
$Na_3GeS_3(OD) \cdot yD_2O$	2.311	0.0686	1.9
$Na_4GeS_4 \cdot yD_2O$	2.285	0.0585	1.8
$KGeS(OD)_3 \cdot yD_2O$	2.649	0.0820	0.5
$K_2GeS_2(OD)_2 \cdot yD_2O$	2.657	0.0736	0.8
$K_3GeS_3(OD) \cdot yD_2O$	2.265	0.0551	1.7
$K_4GeS_4 \cdot yD_2O$	2.235	0.0427	1.2