THE STRUCTURE OF THE SOLID ELECTROLYTE Li$_{1.6}$Ag$_{0.4}$SO$_4$ AT 565°C

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The structure of the high-temperature solid solution Li$_{1.6}$Ag$_{0.4}$SO$_4$ has been determined from neutron and X-ray powder diffraction data. The sulphate groups form a fcc lattice where the lithium ions are found to occupy the $\pm$(1/4, 1/4, 1/4) tetrahedral sites. The silver ions partly occupy the same sites and partly the larger (1/2, 1/2, 1/2) octahedral site. The results strongly support earlier conclusions for the fcc phase of Li$_2$SO$_4$. Exceptionally high temperature factors are found. The consistency of the structural model with other characteristic properties of the high-temperature fcc phase is briefly discussed.

1. Introduction

In a recent paper [1] the structure of the high-temperature fcc phase of Li$_2$SO$_4$ was discussed. It has attained interest for its high ionic conductivity, varying from 1–3 Ω^{-1} cm^{-1} in its region of existance, 575°C to 860°C [2]. Several other interesting properties have been reported; it has been shown to be a plastic phase (thixotropic) [3], it possesses a very high latent heat of transformation, 23.53 kJ mole^{-1} [4], which is approximately three times the heat of fusion. Not only Li$^+$ ions but several other mono- and divalent cations are very mobile in the fcc lattice, including large ions like K$^+$ and Rb$^+$ [5]. In the previous work [1] it was suggested that these properties and the results of structure refinements based on neutron and X-ray diffraction data were consistent with a model where the sulphate groups experience strong rotational disorder processes and thereby give rise to enhanced cation diffusion via vacancy sites in the lattice.

In order to study more closely the influence of the reorientation processes on the cation diffusion it is important to investigate other fcc-sulphate systems which have high ionic mobilities. In this group of sulphates the interesting question arises whether the same disordered structure exists for the sulphate groups and the cation sites as in Li$_2$SO$_4$. The Li$_2$SO$_4$–Ag$_2$SO$_4$ system has been chosen for this purpose primarily for the following reasons:

(1) The solubility limit for Ag$_2$SO$_4$ in the fcc-phase of Li$_2$SO$_4$ is high, 21 mole %.

(2) The ionic radius and the mass of Ag$^+$ are significantly larger than for Li$^+$. The structural properties as well as the cation processes are therefore expected to be significantly dependent on doping.

(3) High ionic mobilities are reported for both Li$^+$ and Ag$^+$ in the fcc-phase.

(4) The neutron scattering length and the X-ray scattering factor are large for Ag, thereby increasing the detectability of cation sites in the lattice.
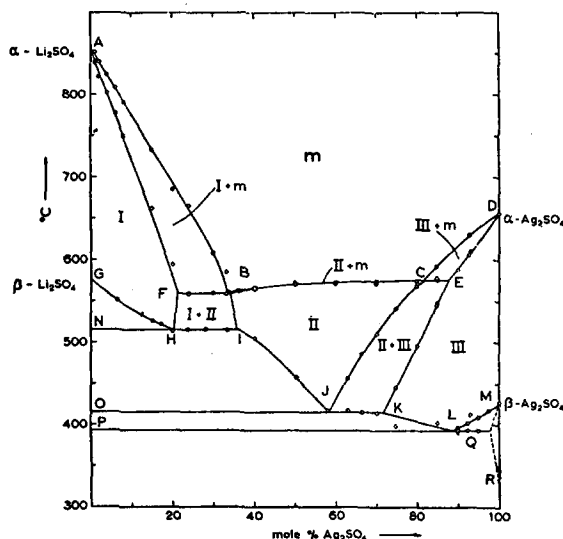
The system Li$_2$SO$_4$–Ag$_2$SO$_4$ has been studied by

Fig. 1. The phase diagram of the binary system Li₂SO₄–
Ag₂SO₄ according to Øye [6]. The solid solution phase I is
the subject of the present study.

Øye [6], who used concentration cell technique and
thermoanalysis methods to establish the phase dia-
gram and to measure transport numbers for Ag^+ and
Li^+. Referring to the phase diagram, fig. 1, the sub-
ject of the present study is the phase marked I, but
the phase II is also of great interest. The latter has
been found to be of bcc symmetry and is a solid elec-
trolyte with a conductivity of 1.01 Ω^{-1} cm^{-1} at
530°C [7]. Øye reported the lattice constant $a =$
5.77 Å for the bcc phase and $a = 7.14$ Å for the fcc
phase at the temperature and Ag-concentration appli-
cable to the present investigation. The lattice con-
stant for the fcc phase was numerically confirmed in
this study.

2. Experimental

The high-temperature solid electrolyte sulphate
phases are known to give very few diffraction peaks
due to high symmetry and very high thermal parame-
ters for all atoms. Consequently experiments were
carried out both by neutron and X-ray diffractometry
since the demand of a good fit to both sets of observed
data has been shown to constitute a very discriminat-
ing criterion for testing the various possible structural
models [1].

The preparation of the powder samples, using iso-
tropically enriched $^7Li_2SO_4$ (Oak Ridge National
Laboratory) and p.a. quality Ag_2SO_4 (Merck), closely
followed the technique described in [1].

The TAS IV triple-axis spectrometer at Risø Na-
tional Laboratory was used for the neutron experi-
ment. The incident neutron wavelength was 1.3955 Å
and the diffracted neutrons were energy analyzed for
zero energy transfer to better than $\Delta E = 4.2$ meV.
The instrument was aligned and calibrated with a
standard Al_2O_3 powder sample. Heating of the sam-
ple was obtained with a cylindrical Al-mantled vacu-
um furnace. It had water-cooled ends and employed
a Kanthal wire-wound resistance heating element em-
bedded in a cement of magnesia and water glass. The
diffractograms were taken at the temperature 565°C
and showed 8 non-zero Bragg reflections. These had a
very rapid drop-off of intensity with increasing dif-
fraction angle, demonstrating the extremely high
temperature factors of this phase. The background
contains a considerable amount of diffuse scattering
which may be of partly quasi-elastic origin. All high-
order reflections were very weak and a technique of
least-square fitting of Gaussian profiles to the observed
data was used to evaluate the intensities with optimum
statistic credibility. The curve-fitting was performed
on each reflection individually, i.e. the profile param-
eters were not constrained to any specific angle-depen-
dence as in, for instance, the Rietveld profile-refine-
ment technique. Finally, the observed integrated
intensities were corrected for the Lorenz and multi-
plicity factors.

X-ray diffraction analysis was performed at the
Physics Department, Chalmers University of Technol-
ogy. A technique of applying the powder in the form
of a suspension in ethyl alcohol to the sample holder
was used in order to minimize preferred orientation
effects [1]. The X-ray data proved to be very insensi-
tive to Li^+ but sensitive to the localization and occu-
pancy of Ag^+ in the lattice as well as to the orienta-
tion of the sulphate groups. The X-ray scans were
made with $\theta-2\theta$ step-scan technique ($\Delta 2\theta = 0.01°$)
and the intensities were evaluated as the sum of the
counts in the Bragg peaks over a linear background.
The statistical standard deviations for both neutron
and X-ray data were assumed as $\sigma = (\Sigma Int.)^{1/2}$, where
the $\Sigma Int.$ includes the background. Figs. 2 and 3
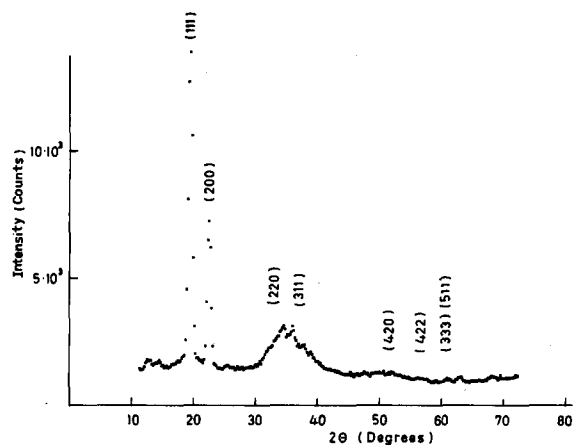exhibit the observed neutron and X-ray diffractograms
respectively.

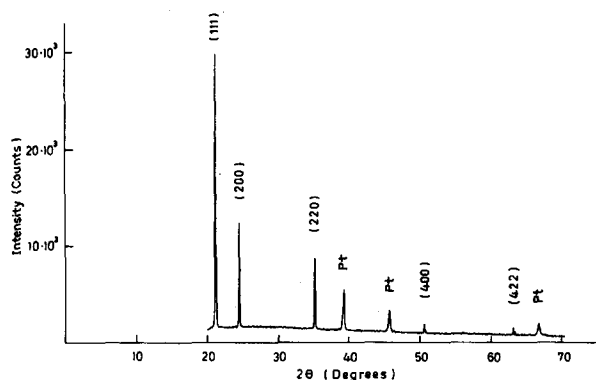Fig. 2. Powder neutron diffractogram of fcc $Li_{1.6}Ag_{0.4}SO_4$. Data from TAS IV, Risø National Laboratory.

Fig. 3. X-ray diffractogram of fcc $Li_{1.6}Ag_{0.4}SO_4$. Cu–Kα radiation.

3. Structure refinements

Several structural models have been proposed for the sulphate lattice in the fcc phase. A series of structure refinements was attempted for each of the considered models, varying the tested cation distribution in a systematic way within each model. A full-matrix least-squares refinement program minimizing $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2$ and F_o and F_c are the observed and calculated structure factors, was used for the refinement of the neutron data. Two different R-factors were considered when the output of the refinements were studied. They were defined in the usual manner: $R = \Sigma ||F_o| - |F_c||/\Sigma F_o$. One, which will be referred to as $R(8)$ in the text, contained only the 8 observed Bragg reflections. The $R(11)$ factor includes also the 3 non-observed but symmetry-allowed reflections that would fall into the studied angular interval. It is an important additional condition that a structural model is capable of accounting also for the $F_o = 0$ reflections, especially in a case like the present, where the number of observed reflections is low. Examples of the best fits for the various models are given in table 1 and the corresponding observed and calculated X-ray intensities in table 2. The results for the structural parameters for the tested models are summarized in table 3.

Table 1
Observed and calculated neutron structure factors for the various structural models 1–4. Arbitrary units

h	k	l	F_o	$F_c(1)$	$F_c(2)$	$F_c(3)$	$F_c(4)$
1	1	1	18.13	17.79	15.70	16.53	18.13
2	0	0	16.33	12.15	14.27	15.71	16.31
2	2	0	2.50	2.22	0.23	1.29	2.48
3	1	1	2.75	3.91	2.08	2.58	2.83
2	2	2	–	6.44	7.35	5.55	0.70
4	0	0	–	0.96	1.51	0.28	2.00
3	3	1	–	3.49	3.09	1.28	0.52
4	2	0	2.42	3.71	4.48	1.74	1.97
4	2	2	2.71	1.05	0.71	2.47	1.81
3	3	3	2.70	2.30	1.79	4.61	2.82
5	1	1	2.70	2.30	1.75	2.09	2.82
	$R(8)\%$			19.3	26.5	14.0	3.1
	$R(11)\%$			40.9	50.2	28.1	9.5

Table 2

Observed and calculated X-ray intensities for the structural models 1–4. Data have been normalized for clarity

h	k	l	I_0	$I_C(1)$	$I_C(2)$	$I_C(3)$	$I_C(4)$
1	1	1	100.0	8.3	100.0	8.2	100.0
2	0	0	31.6	100.0	40.2	100.0	21.5
2	2	0	30.9	47.6	24.4	33.6	28.6
3	1	1	<1.5	1.1	10.0	1.6	1.9
2	2	2	–	6.6	2.3	6.9	0.1
4	0	0	2.9	2.2	1.1	2.2	1.3
3	3	1	–	0.7	2.5	0.0	1.0
4	2	0	–	2.6	1.4	2.7	0.5
4	2	2	2.7	1.5	1.3	2.1	1.5
3	3	3	–	0.1	0.2	0.0	0.2
5	1	1	–	0.3	0.6	0.0	0.6

Table 3

A summary of the structural characteristics of the tested models for $Li_{1.6}Ag_{0.4}SO_4$. The analysis was carried out in series of refinements where several combinations of cation distributions and temperature factors were used as program input. Only a few parameters were refined in each computer run – they are presented with standard deviations included in parenthesis

Model	Cation occupancy factors	Temperature factors (A^2)	R-factors (%)
1	Li : (3/4, 3/4, 3/4) : 1.0 (1/4, 1/4, 1/4) : 0.6 Ag : (1/2, 1/2, 1/2) : 0.4	$B(Li) = 15$ $B(Ag) = 25(14)$ $B(S) = 10$ $B(O) = 61(18)$	$R(8) = 19.3$ $R(11) = 40.9$
2	Li : ±(1/4, 1/4, 1/4) : 1.6 Ag : (1/2, 1/2, 1/2) : 0.4	$B(Li) = 15$ $B(Ag) = 96(73)$ $B(S) = 10$ $B(O) = 41(14)$	$R(8) = 26.5$ $R(11) = 50.2$
3	Li : ±(1/4, 1/4, 1/4) : 1.0 (1/2, 1/2, 1/2) : 0.6 Ag : (1/2, 1/2, 1/2) : 0.4	$B(Li) = 15$ $B(Ag) = 15$ $B(S) = 10.$ $B(O) = 17(4)$	$R(8) = 14.0$ $R(11) = 28.1$
4	Li : ±(1/4, 1/4, 1/4) : 1.6 Ag : ±(1/4, 1/4, 1/4) : 0.28 (1/2, 1/2, 1/2) : 0.12	$B(Li) = 18$ $B(Ag) = 27(3)$ $B(SO_4) = 9(1)$	$R(8) = 3.1$ $R(11) = 9.5$

3.1. Model 1

The space group $F\bar{4}3m$ was suggested by Førland and Krogh-Moe [8]. They assumed the following atomic coordinates from space-group considerations:

S: $(0, 0, 0)$
O: $(x, x, x); (x, \bar{x}, \bar{x}); (\bar{x}, x, \bar{x}); (\bar{x}, \bar{x}, x)$
Li: two of the three sets of coordinates:
    $(1/4, 1/4, 1/4); (3/4, 3/4, 3/4)$ and $(1/2, 1/2, 1/2)$

and suggested $x = 0.12$, which would give a realistic

S–O distance of 1.50 Å within the sulphate group. The first two of the Li positions are 4-coordinated to the sulphate groups and are usually referred to as the tetrahedral sites. The $(1/2, 1/2, 1/2)$ site is 6-coordinated to the sulphate groups and will be referred to as the octahedral site. The $F\bar{4}3m$ model is non-centro-symmetric and leads to some unlikely interatomic distances: Li–O 4-coordinated at 1.61 Å with Li in the $(1/4, 1/4, 1/4)$ site, and Li–O 12-coordinated at 2.95 Å with Li in the other tetrahedral site. The octahedral site is the most spacious; it gives a 12-coordi-

nated Li–O distance of 2.97 Å. The expected value for Li–O is 1.98 Å for 4-coordination and 2.16 Å for 6-coordination [9]. A value of 2.42 Å is expected for the Ag–O contact. Consequently Førland and Krogh-Moe also discussed disordered models (model 3 below).

The best-fitted model of cation distribution gave R-factors $R(8) = 19.3\%$ and $R(11) = 40.9\%$, with all Ag^+ ions in the octahedral site and Li^+ distributed over the tetrahedral sites with 60% of the Li^+ ions in the larger (3/4, 3/4, 3/4) position. Unrealistic temperature factors were found, $B = 61$ Å^2 for the oxygens. B is here the isotropic temperature factor, $B = 8\pi^2\bar{u}^2$, where $\bar{u}$ is the root-mean square displacement of the atom due to thermal vibrations. The corresponding X-ray results further demonstrates that the model fails to give a satisfactory fit to the observed data.

3.2. Model 2

If the condition for centrosymmetry is added to the coordinates of model 1, the space group Fm3m results. It represents a simple disordered model for the sulphate lattice where the number of sites for oxygens exceed the number of atoms with a factor two. The best fit was obtained if all Li^+ ions were placed in the now equivalent tetrahedral sites $\pm(1/4, 1/4, 1/4)$ and all Ag^+ ions in the (1/2, 1/2, 1/2) octahedral site. It resulted in R-factors $R(8) = 26.5\%$ and $R(11) = 50.2\%$. Again unrealistic temperature factors were found, $B = 41$ Å^2 for oxygens and $B = 96$ Å^2 for Ag. The great differences in the quality of the fitting to the neutron and X-ray data clearly demonstrates how strictly discriminating the demand of good agreement for both sets of data is.

3.3. Model 3

Førland and Krogh-Moe [8] suggested a disordered model where the sulphate groups are rotated through 45° around the cube axes relative to the orientation in space group F43m. The result can be described as space group Fm3m with the oxygens in positions 96(j). There are 6 distinguishable orientations of the sulphate groups and consequently 24 O-positions are generated for each sulphate group, with coordinates of the type:

O: $(0, x, \sqrt{2}x)$; $(\sqrt{2}x, 0, x)$; $(x, \sqrt{2}x, 0)$, etc.

The oxygens were assigned occupancy factors 1/6 and the structure thus represents a high degree of orientational disorder. It is centrosymmetric, with a Me^+–O distance of 2.07 Å with Me^+ in the tetrahedral $\pm(1/4, 1/4, 1/4)$ sites, 24-coordinated to the disordered O-sites. The corresponding distance for the octahedral site is 2.48 Å, again 24-coordinated. The best results were found for a model where all Ag^+ and 40% of the Li^+ ions occupied the octahedral site and the remaining Li^+ ions were situated in the tetrahedral sites. The temperature factors were reasonable, $B = 15$ Å^2 for the cations and $B = 17$ Å^2 for the oxygens. Final R-factors were $R(8) = 14.0\%$ and $R(11) = 28.1\%$. The F_c for the (222) reflection was too large, however, and the calculated X-ray intensities did not show sufficiently good agreement with the observed data. It seemed clear that the increasing degree of oxygen disorder in models 2 and 3 produced a better fit with the observed neutron data and thus a model with a spherical distribution of oxygens was finally tested.

3.4. Model 4

The entire sulphate group was represented by the molecular pseudo-formfactor:

$$f(SO_4) = f(S) + 4f(O) \sin(kr)/kr , \qquad (10)$$

where $k = 4\pi \sin(\theta)/\lambda$ and r is the S–O distance. The resulting structure represents an isotropic distribution of the oxygens over a sphere and is therefore centrosymmetric. Thus only two sets of distinguishable sites for the cations exist. A series of refinements in analogy with the former models were performed to test cationic distribution, temperature factors and the S–O distance. The best result was found with all Li^+ ions occupying the $\pm(1/4, 1/4, 1/4)$ tetrahedral sites. 30% of the Ag^+ ions were situated in the octahedral site, and the remaining Ag^+ ions were statistically distributed over the lithium positions. The S–O distance $r = 1.49$ Å, which is close to that found in all anhydrous metal sulphates, gave the best convergency in the refinements. The resulting R-factors were $R(8) = 3.1\%$ and $R(11) = 9.5\%$. The found temperature factors are extremely high and they demonstrate that the concept of fixed lattice positions for cations in fast-ion conductors of this kind is only approximately valid. For the extreme case, Ag^+, the temperature factor corresponds to a mean thermal displacement of

0.6 Å in the harmonic model ($B = 8\pi^2\overline{u}^2$). Unfortunately the nature of the observed data does not permit an analysis of the anisotropy of the thermal motions, though it must be assumed to be substantial, as for instance in α–AgI [11]: The calculated X-ray intensities show good agreement with the observed data, well within the estimated experimental errors. The fit to the X-ray data showed an additional improvement if a somewhat higher occupancy of Ag in the octahedral site was assumed. The explanation may be that in the neutron case the scattering length for ^{7}Li is negative, so that a small degree of occupancy of lithium in the octahedral site cancels out a part of the Ag scattering. The effect is, however, small.

4. Discussion

It is clear from the present study that the structural model found for FCC Li_2SO_4 [1] is indeed valid also for the solid solution in the present investigation. The concept of oxygens disordered over a large number of sites spherically arranged around the sulphurs and the evident possibility of rapid coupled reorientations of the sulphate groups qualitatively agrees with several other observed characteristics of the fcc phase, such as the plasticity, the high enthalpy of transformation, the large density change at the phase transition and the remarkably high mobility of large ionic dopant species. This kind of mechanisms have been discussed earlier [12,13] though the arguments at that time were based solely on macroscopic data.

The diffusion in the fcc lattice takes place via translations from alternating tetrahedral and octahedral sites. It has been demonstrated [7] that the specific electrical conductivity of the fcc phase increases with the addition of Ag_2SO_4. The activation energy in an Arrhenius model is, however, unchanged by the doping. According to Øye [6] the mobility, measured by concentration cell technique, is slightly larger for Ag^+ than for Li^+. These facts support the suggestion that the dynamical properties of the sulphate lattice are the decisive factors for the rate of diffusion rather than conventional material parameters such as large excess of cation positions and cationic radius and mass.

A direct measurement of the suggested correlation

between the cation diffusion and the reorientation processes of the sulphate groups might be possible from quasielastic neutron scattering experiments. A necessary condition for the interpretation of such data requires, however, that single crystals are available. Experience has showed that these cannot survive a passage through the phase transition at 575°C. Investigations of methods for growing single crystals of fcc-phase Li_2SO_4 from the melt in measuring position on the triple-axis instrument have therefore been initiated.

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