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A new high-pressure gas hydrate phase in the sulfur hexafluoride–water system

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A gas hydrate of the cubic structure I (CS-I) was detected in the title system at pressures higher than 50 MPa with the use of *in situ* X-ray diffraction analysis.

In recent years, the formation of a number of new high-pressure gas hydrate phases was detected in studies of the phase diagrams of systems that form gas hydrates.[1–3] The techniques used in these studies (differential thermal analysis, visual observations and Raman spectroscopy) cannot provide exhaustive information on the structure of new gas hydrates. In this context, the use of diffraction techniques for examining these compounds is of considerable scientific and practical interest.

Sulfur hexafluoride forms a gas hydrate of the cubic structure II (CS-II) at atmospheric pressure.[4] All hydrates of this structure are destabilised by pressure and transformed into denser hydrates.[5] Therefore, a similar behaviour would be expected in the sulfur hexafluoride–water system. In this work, we examined hydrate formation in this system at high pressures by X-ray powder diffractometry.

Experiments were performed in a specially designed high-pressure plunger–cylinder apparatus with the use of synchrotron radiation from a VEPP-3 accelerator (Institute of Nuclear Physics, Siberian Branch of the Russian Academy of Sciences). A gas hydrate sample was placed in a thick-walled beryllium capsule; a hydrostatic pressure in the capsule was produced by compressing an excess of the hydrate-forming agent (SF_6). The gas hydrate was formed directly in the chamber on reaction between finely crushed ice and sulfur hexafluoride at a pressure of 20 MPa and a temperature of –10 °C. The diffraction patterns were recorded at room temperature (about 22 °C) with the use of a one-coordinate detector and an image plate (the latter technique was used only at 650 MPa). The angular resolution of the one-coordinate detector was 0.05°. The image plate was positioned at a distance of 334.1 mm from the sample perpendicularly to the primary beam; the angular resolution was 0.02° in the recording of diffraction patterns by this technique. To obtain high-quality diffraction patterns, the exposure time was chosen by a trial method. Radiation with $\lambda = 0.3635$ Å was used. The experimental procedure was described in detail elsewhere.[6]

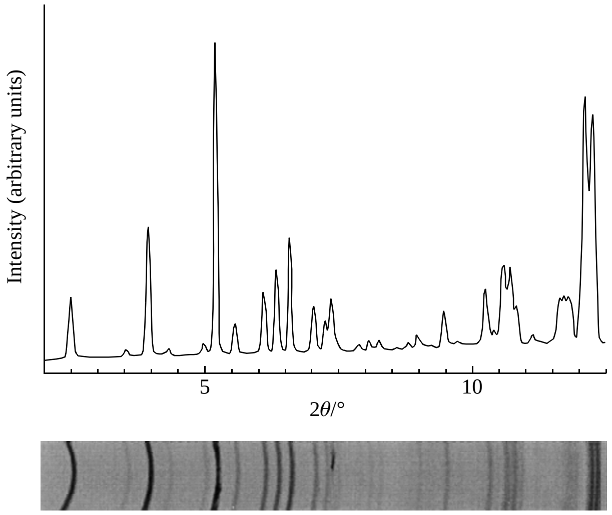

Figure 1 Powder diffraction pattern of an SF_6 gas hydrate at 650 MPa.

Table 1 Interplanar spacing, indexing and interpretation of reflections on a powder diffraction pattern of a sulfur hexafluoride gas hydrate at a pressure of 650 ± 50 MPa at room temperature.[a]

$2\theta/°$	d_{expt}/Å	D^{b}_{calc}/Å	Phase	*hkl*
2.49	8.336	8.386	CS-I	110
3.52	5.910	5.930	CS-I	200
3.95	5.284	5.303	CS-I	210
4.31	4.829	4.841	CS-I	211
4.99	4.179	4.193	CS-I	220
5.16	4.038		SF_6 (s)	
5.57	3.742	3.750	CS-I	310
6.09	3.417	3.423	CS-I	222
6.35	3.282	3.289	CS-I	320
6.59	3.164	3.170	CS-I	321
7.02	2.961	2.965	CS-I	400
7.25	2.874	2.876	CS-I	410
7.36	2.828		SF_6 (s)	
7.48	2.787	2.795	CS-I	330, 411
7.87	2.647	2.652	CS-I	420
8.05	2.585	2.588	CS-I	421
8.24	2.528	2.528	CS-I	332
8.61	2.420	2.421	CS-I	422
8.78	2.374	2.372	CS-I	430
8.98	2.323		SF_6 (s)	
9.31	2.327		CS-I + SF_6 (s)	510, 431
9.47	2.202	2.202	CS-I	520, 432
9.72	2.147	2.165	CS-I	521
10.25	2.034		app. + CS-I	433, 530
10.40	2.005		CS-I + SF_6 (s)	531
10.56	1.972		Be[c] + CS-I	600, 442
10.71	1.947		Be[c] + CS-I	610
10.82	1.927	1.924	CS-I	532, 611
11.12	1.876	1.875	CS-I	620
11.23	1.856	1.852	CS-I	540, 621
11.43	1.824	1.830	CS-I	621
11.62	1.795		Be[c] + SF_6 (s)	
11.71	1.782		Be[c] + CS-I	622
11.81	1.766	1.760	CS-I	630, 542
12.12	1.722		Be[c] + CS-I	444
12.25	1.704		Be[c] + CS-I	632, 710

[a]CS-I is the sulfur hexafluoride gas hydrate of the cubic structure I; SF_6 (s) is the solid sulfur hexafluoride; Be, app. are the parts of the high-pressure apparatus (Be = beryllium capsule). [b]The interplanar spacing was calculated for the CS-I gas hydrate with the unit-cell parameter 11.859 Å (space group *Pm*3*n*). Only reflections that did not interfere with the reflections of other substances were taken into account in the calculation of the unit-cell parameter. [c]The reflections of beryllium were split because of diffraction by different walls of the beryllium capsule.

We obtained the powder diffraction patterns of an SF_6 gas hydrate sample in the range of pressures from 50 (partially decomposed gas hydrate) to 650 MPa. Figure 1 shows a typical diffraction pattern obtained using an image plate. All of the reflections can be subdivided into three groups. The first group corresponds to reflections from parts of the experimental apparatus (the beryllium capsule and construction units of the high-pressure chamber). The positions of reflections of this group were determined in experiments with an uncharged chamber. The second group of reflections appeared only in the region of existence of solid sulfur hexafluoride[7] and is consistent with a theoretically calculated powder diffraction pattern[8,9] of a cubic body-centred phase of solid SF_6 (in contrast to the diffraction rings corresponding to the gas hydrate, spots due to individual crystallites are appreciable in the rings that correspond to this group in the image-plate diffraction pattern). All the other reflections (the third group) can be interpreted on the basis of published data on the structure of gas hydrates with the cubic structure I (CS-I).[10] Table 1 summarises the interplanar spacing, the assignment and indexing corresponding to all observed reflections.

Over the entire pressure range examined, the sulfur hexafluoride gas hydrate retained its structure (CS-I); the unit-cell parameter a varied from 12.06(1) Å at 50±2 MPa to 11.859(7) Å at 650±50 MPa. No less than 10 most intense reflections (five at 50 MPa) were used for calculating the unit-cell parameter. This result agrees with the general rule that denser phases form at increased pressures. The unit-cell parameter a of the CS-II hydrate of SF_6 was found[4] to be 17.21 Å at 0.1 MPa and 0 °C. Under the assumption that small D cavities are vacant in both structures, the densities of the hydrates were calculated to be 1.179 (at 0.1 MPa and 0 °C) and 1.615 g cm^{-3} (at 50 MPa and 22 °C) for the CS-II and CS-I hydrates of SF_6, respectively. The values of the a parameter calculated from the diffraction patterns were equal to within the experimental error [11.84(2) and 11.859(7) Å at 650 MPa, as found using the one-coordinate detector and the image plate, respectively]. After melting the hydrate (at pressures lower than 50 MPa), a repeated increase in the pressure above the pressure of hydrate formation resulted in a hydrate that exhibited the same diffraction pattern.

Thus, based on the data of *in situ* X-ray diffraction analysis, we found that a gas hydrate formed in the sulfur hexafluoride–water system at pressures above 50 MPa and room temperature exhibits the gas hydrate structure I (CS-I). This is the first reliable evidence for the formation of a CS-I gas hydrate in the system for which the appearance of CS-II gas hydrates is typical at atmospheric pressure.

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