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Properties of Ferroelectric Ice

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Various forms of ice exist within our galaxy, from interstellar clouds to comets, moons and planets. Particularly intriguing type of ice - “ferroelectric ice”, which can sustain a giant electric field was discovered experimentally and is stable in the temperature range 57-74 K. This form of ice, named ice XI, can generate enormous electric fields and can play an important role in planetary formation. We measured neutron diffraction profiles of D_2O ice with impurities to investigate the formation of ice XI under atmospheric pressure. We made powder samples of ice doped with KOD, NaOD, LiOD, DCl, ND_3 and $Ca(OD)_2$. We carried out Rietveld analysis for diffraction profiles and obtained the mass fraction f (the ratio of the mass of ice XI to that of the doped ice). A significant amount of ferroelectric ice is observed in ice samples with dopants, which produce L-defect. The values of f of ice doped with 0.01 – 0.001-M KOD or NaOD is generally higher than those with 0.1-M KOD or NaOD. On the other hand, ice samples with D-defect, did not become ferroelectric ice. On the basis of the neutron diffraction data we have discussed the properties of ferroelectric ice.

KEYWORDS: neutron, water, hydrogen bond, phase transition, ferroelectric

1. Introduction

In the outer solar system, most water ice exists in a crystalline phase [1, 2]. Infrared observation provides evidence that crystalline ice exists on Pluto [3]. Below 200 MPa, crystalline ice has two kinds of structure, which are named ice Ih and ice XI. Whether or not ice in the outer solar system exists as ice XI is a question that has attracted scientific interest, because ice XI is ferroelectric. Long-range electrostatic forces, caused by the ferroelectricity, might be an important factor for planet formation [4]. Studies concerning ice films suggest that a millimeter-sized ferroelectric ice particle has a 10,000 V charge and unusual properties for planetary formation [4-6]. Ice sheets with a thickness of several kilometers on outer planets and the satellites should become a huge source for an electric field because each crystal grain will be similarly aligned due glacial flows like in the polar ice sheets on Earth.

Hydrogen atoms of ice under high-pressure (> 2.1 GPa) become readily ordered upon cooling. For an ice doped with 0.1 M KOH, Kawada [7] proposed the existence of a transition from ice Ih to a structure with ordered hydrogen, ice XI. The KOH are ionized, and the OH^- ions, which replace H_2O sites in the ice are considered to increase the mobility of the hydrogen and shorten the transition time. Using this method Fukazawa *et al*. [4, 8-10] created samples of ice XI, which exists in the narrow temperature range of 57-66 K. This is the temperature range at the surfaces of the outer planets of the solar system – Uranus, Neptune and Pluto, their satellites and rings, and rings and moons of Saturn.

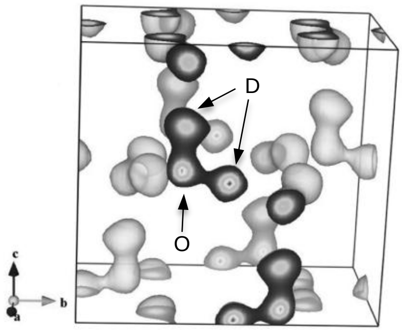

Fig. 1. Structure of ferroelectric ice XI. Scattering length density map of ice XI; obtained from the maximum entropy analysis of neutron powder diffraction data.

Neutron is useful to investigate of structural changes in water because of the large neutron scattering cross sections of deuterium and oxygen. In this paper we report various neutron experiments, which related with the ferroelectric ice and hydrogen ordering. On the basis of the experimental and some theoretical aspects, we have renewed an insight into the properties of the ferroelectric ice in universe.

2. Experiment

All neutron diffraction measurements were performed on deuterium-substituted water ice. We made powder ices by rapid solidification of misted solution at 77 K. The powder ices (0.1 – 5 g) was sealed in a vanadium can with helium gas or high-pressure cells. The sample was kept at T_1 and annealed for t_1, where T_1 and t_1 respectively signify the first annealed temperature (K) and time (h). The temperature of many samples was then raised to T_2 and annealed for t_2 to increase the ferroelectricity, where T_2 and t_2 respectively represent the second annealed temperature and time. Some of them were warmed up to T_3 and T_4 and annealed for t_3 and t_4.

Neutron diffraction measurements were performed using the WAND [11] (at the HFIR at Oak Ridge), HRPD (at JRR-3 research reactor at the Japan Atomic Energy Agency). HERMES (JRR-3), iMATERIA and TAKUMI spectrometers (at J-PARC). Most of data were newly obtained while a part of Table 1 is extracted from references. Rietveld analysis and calculations about maximum entropy method were performed by RIETAN-FP and RIETAN-2000 [12].

3. Results and Discussion

3.1 Doped ice

Table I. Mass fraction *f* (the ratio of the mass of ferroelectric ice XI to sample) in ice

Dopant	Concentration (mol/l)	T_1 (K)	t_1 (h)	T_2 (K)	t_2 (h)	T_3 (K)	t_3 (h)	T_4 (K)	t_4 (h)	f	Ref.
-	Pure D_2O ice	60	168							0	
		65	720							0	
KOD	0.13	57	20	62	94					0.046	
		57	69	65	17					0.079	
		57	18	68	73					0.13	
		57	10	68	62					0.062	8
		57	69	70	52					0.15	
		74	96							0	
	0.013	57	20	68	71					0.23	19
		57	20	68	78					0.25	
		57	20	68	98					0.14	19
	0.01	60	18	68	23					0.17	
		62	435							0.33	
	0.001	57	22	68	456					0.32	
		60	29	70	47	72	20	74	43	0.39	20
		65	29	70	106					0.59	4
	0.0001	65	90							0	
NaOD	0.1	57	20	68	78					0.10	
		60	45	65	24	70	23			0.15	21
		70	100							0	21
	0.01	60	15	68	165					0.24	
	0.001	60	75							0.14	
		60	75	65	14					0.17	
		60	18	65	48	68	5			0.10	
		60	75	65	18	70	11			0.25	
		65	186							0.48	
LiOD	0.1	60	15	68	91					0.11	
DCl	0.1	57	24	68	11					0	
ND_3	0.14	57	22	60	9	65	17	70	24	0	
	0.01	65	53	68	20					0	
$Ca(OD)_2$	0.0005	60	2	65	28	70	20	61	21	0	

We created powder samples of ice doped with KOD, NaOD, LiOD, DCl, ND_3 and $Ca(OD)_2$. Those dopants are considered to increase defects of hydrogen atoms in the ice, such as L- and D-defects [13]. We carried out Rietveld analysis for diffraction profiles under the assumption of the existence of two phases ($P6_3/mmc$ for ice Ih and $Cmc2_1$ for ice XI). Figure 1 shows the obtained structure of ice XI using the maximum entropy method analysis of the diffraction data. The scattering length density distribution of H_2O was calculated using MEM after the Rietveld analysis. The analysis provides firm evidence that hydrogen with a positive charge is aligned along the *c*-axis and ice XI becomes ferroelectric. Figure 2 shows a typical profile of doped ice with f = 0.59 (0.001M-KOD doped D_2O ice), which has the peak of 131 plane at 40º.

Table I shows the mass fraction *f* (the ratio of the mass of ice XI to that of the doped ice). The values of *f* of ice doped with 0.01 – 0.001-M KOD or NaOD is generally higher than those with 0.1- and 0.13-M KOD or NaOD. The lower concentration of the dopant is suitable for the formation of ferroelectric ice. A significant difference is not observed in samples doped with KOD, NaOD and LiOD. Those dopants act as a catalyst, which increases L-defect. The doped ice with DCl or ND_3, which makes D-defect, did not become ferroelectric ice.

3.2 Pure ice

We measured neutron powder diffraction of pure D_2O ice, which annealed at 60 K and 65 K for 1 week and 1 month at HRPD and iMATERIA, respectively. The diffraction profiles do not have any sharp peak, which caused by a hydrogen ordering. As described in 3.1 the neutron diffraction profile of ice XI had a diffraction peak of 131 plane that is forbidden in ice Ih. However the 131 peak is not observed in our profiles of pure D_2O ices. Thus a pure ice crystal does not become ice XI with ordered hydrogen in a laboratory time scale.

3.3 Property of ferroelectric ice

A significant amount of ferroelectric ice is observed in ice samples with dopants, which produce L-defect. The L-defect is a crystallographic defect that is no hydrogen along hydrogen bond. The area with ferroelectricity is formed by the passing of the L-defect. As described in the introduction, defects in ice are considered to increase the mobility of the hydrogen and shorten the transition time. In the case of L-defect, OH^- ions diffuse in ice and it makes a reorientation of water molecules. Thus hydrogen-ordered domains are formed in ice by passing of the L-defect. The neutron diffraction data shows the existence of large domains of ferroelectric structure. Therefore, we conclude that the L-defect acts as an effective catalyst to accelerate the formation of ferroelectric ice.

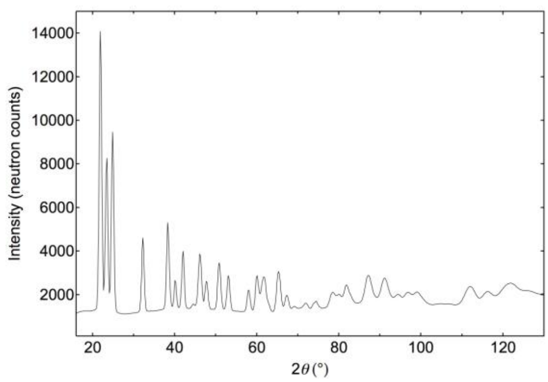

Fig. 2. Neutron powder diffraction of 0.001-M KOD-doped D_2O ice at 70 K.

Since a pure ice also has the L-defect, it is reasonable to assume that pure ice at low temperature also has a small domain with ordered hydrogen. The domain may be established from the future neutron experiments by using more intense neutron beam and detailed analysis of distribution functions of hydrogen. The growth of ice XI in doped samples is a matter of hours compared with astronomical timescale for the hydrogen ordering in pure ice, estimated for thousands of years. Therefore, ice in space is considered to include the ferroelectric ice XI.

It is plausible that icy bodies, such as Pluto, Charon and Edgeworth-Kuiper Belt Object, include thick ferroelectric ices. Since the ice XI exists until about 1GPa, thickness of ferroelectric ice XI is 1,000 km. Especially large icy planets, such as OGLE-2005-BLG-169 [14], may have ferroelectric ice, because the surface temperature is estimated for 50 – 70 K and the internal is also low temperature. In order to confirm it we plan to do the further experiments by using a state-of-art instrument that is specialized for high-pressure study.

Features of the infrared and vibrational spectrum of ice XI became better known due to recent studies [15,16]. Especially important is the region of the librational motions of water molecules, presented because there is a uniquely large difference in the spectra in this region between ice XI and ice Ih. Librational band of ice Ih has more simple structure with only two bands – one very broad at about 800-1020 cm^{-1} and the second with small intensity at about 610 cm^{-1}. In the case of ice XI the librational spectrum is different and is composed of four narrow bands. The origin of librational motions will be analyzed from detailed dispersion curves obtained by inelastic neutron scattering measurements.

The ordered ice in molecular cloud, protosolar nebula, and the outer solar system is detactable using the infrared telescope. Figure 3 shows a scenario for evolution of icy particles in space and the existence of ferroelectric ice. The ferroelectric ordered ice is important for material evolution, such as, formation of materials of origin of life, because the electrostatic force caused by the ferroelectricity affects agglomeration of materials in space [17, 18]. The ordered ice particles play a role in molecular evolution because the ferroelectric ice particles attract polar organic materials. Discovery of ferroelectric ice in space will significantly affect the study of planetary formation and possibly the origin of life.

Ferroelectric materials have interesting electrical properties, such as the ability to form capacitors and energy sources. For example decreasing temperature makes huge voltage inside icy bodies and increasing temperature releases the energy. The dense ferroelectric ice under pressure becomes highly efficient energy converters. The ferroelectric has very highly value of dielectric constants and reflectivity near transition temperature. For instance this would reduce the electromagnetic and heat flux through the core.

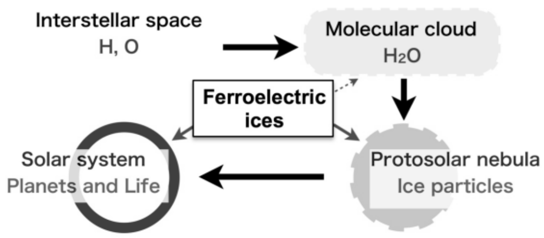

Fig. 3. Scenario for evolution of icy particles in space and the existence of ferroelectric ice

4. Conclusion

We measured neutron diffraction profiles of powder ice doped with KOD, NaOD, LiOD, DCl, ND_3 and $Ca(OD)_2$. We observed the peak of 131 plane, which caused by the ferroelectric hydrogen ordering, in the profiles of ice doped with KOD, NaOD and LiOD. The values of *f* of ice doped with 0.01 – 0.001-M KOD or NaOD is higher than those with 0.1- and 0.13-M KOD or NaOD. The lower concentration of the dopant is suitable for the formation of ferroelectric ice. A significant difference is not observed in samples doped with KOD, NaOD and LiOD. Those dopants act as a catalyst, which increases L-defect. We discussed that L-defect diffuses in ice and it makes a reorientation of water molecules. Hydrogen-ordered domains are formed in ice by passing of the L-defect. In this paper we report neutron diffraction of ice and provide clear evidences of the existence of ferroelectric ice under atmorphsric pressure.

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