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Physica B 403 (2008) 2643–2648

www.elsevier.com/locate/physb

Infrared study of proton–deuteron mutual diffusion in a $CsHSO_4/CsDSO_4$ solid under high pressure

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Received 3 September 2007; received in revised form 15 January 2008; accepted 22 January 2008

Abstract

Proton–deuteron mutual diffusion in a $CsHSO_4/CsDSO_4$ solid at 373 K was examined up to 3 GPa by an infrared mapping measurement. Phases HPHT1 and HPHT2 appeared at 1.5 and 2.3 GPa, respectively, after heating. These phases were found to be stable at room temperature, while phase IV, which appeared on compression at room temperature, was metastable. The pressure dependence of the proton–deuteron mutual diffusion coefficient was determined from the temporal change in the deuteron distribution of the solid. The coefficient decreased from 7×10^{-16} to $1\times10^{-16}\,m^2/s$ during the transition from phase II to HPHT1 at 1.5 GPa, and showed no significant change during the transition to phase HPHT2. These results suggested that in addition to the hydrogen bond length, other structural factors might also have had an influence on the rate of diffusion.

PACS: 62.50.+p; 66.30.hd; 66.30.jp; 78.30.Hv

Keywords: Infrared spectra; Mutual diffusion coefficient; High pressure; Proton diffusion; Solid acid; Phase transition

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1. Introduction

Proton diffusion in solid acid is related to the nature of hydrogen bonds. The solid acid like hydrogen sulfates contain protons which become charge carriers in the crystal structure. These substances show proton conductivity without hydration. The solid acids are investigated as a solid electrolyte in a fuel cell. They have been shown to contain many polymorphs in the temperature–pressure phase diagram [1]. All polymorphs have the same chemical composition but show different proton conductivities for each crystal structure. The superprotonic phases of $RbHSO_4$ [1] and $(NH_4)HSO_4$ [1,2] only appear when the melting is suppressed under high pressure. The proton conductivities of a phase in $Rb_3H(SeO_4)_2$ and $(NH_4)_3H(SO_4)_2$ increase as the pressure increases [3]. The clarification of relationship between the structure and proton conductivity for many polymorphs is important for understanding the ionic conducting mechanism.

The diffusion process in the proton conductor is the key to understanding the properties of substances. The rate of ionic diffusion is generally measured by electrical methods; however, an isotope diffusion method, which is a complementary approach, makes it possible to observe the migration of the chemical species directly. For example, a diffusion coefficient for $NH_4H_2PO_4$ was obtained by tritium diffusion [4]; however, the radioisotope analysis was difficult to apply to in-situ measurement at high pressures. In our previous work, we measured the proton–deuteron mutual diffusion in a H_2O/D_2O solid under high pressure on the infrared reflection spectra [5,6], and were able to use the spectroscopic method effectively to measure the diffusion coefficient under high pressure with a diamond-anvil cell. The diffusion processes of the ionic species were investigated on an H_2O/D_2O ice bilayer. The infrared reflection spectra of the interface between diamond and ice were measured. The protons that eventually arrived on the D_2O surface formed O–H bonds instead of O–D bonds. The diffusion coefficient was obtained from the temporal change in O–H concentration on the surface. However, it was difficult to apply this

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doi:10.1016/j.physb.2008.01.031

method to other samples such as $CsHSO_4$, since their infrared reflection peaks of the O–H (O–D) stretching mode were much weaker than those of H_2O/D_2O.

$CsHSO_4$ is a typical solid acid-type proton conductor where phase II transforms to superprotonic phase I at 414 K under ambient pressure [7]. $CsHSO_4$ has recently received much attention as a solid electrolyte of a fuel cell, which operates in the middle temperature range of around 400 K. A two-step mechanism (Grotthuss mechanism) consisting of a reorientation motion of the HSO_4^- ion and a proton transfer between the ions along the hydrogen bond axis, has been suggested for its proton conduction [8]. Phase III, which is stable at room temperature, transforms to phase II at around 333 K. On cooling, phase II continues as it is without returning to phase III even at room temperature. Compression is necessary to cause a transition from phase III to III′ and subsequently to phase IV, which appears above 1.0 GPa at room temperature [9,10]. On the other hand, phase II is a stable phase at room temperature for $CsDSO_4$. Pressure dependencies in proton conductivity along the crystal axes have been reported up to 1 GPa for phases III and III′ of $CsHSO_4$ and for phase II of $CsDSO_4$ [9]. The proton conductivity for phase II did not change significantly as the pressure increased. Pressure dependencies for proton conductivity for phase IV above 1 GPa has not yet been discussed. Recently we reported a new phase transition diagram for $CsHSO_4$ up to 5 GPa and 570 K by a Raman measurement [11], and obtained different transition pressures, i.e., phase IV appeared at 1.8 GPa at room temperature. In addition, we found high-pressure and high-temperature phases (HPHT1 and HPHT2), which appeared above 1.8 GPa and 390 K [11].

The purpose of this study is to clarify the pressure dependence of a proton–deuteron mutual diffusion coefficient in a $CsHSO_4/CsDSO_4$ solid. We measured the infrared absorption spectra for the sample that formed an in-plane joint between the $CsHSO_4$ and $CsDSO_4$ solids. The mapping of the infrared absorption peak that originated from the deuteron provides a deuteron distribution in the plane. We succeeded in tracking the temporal change in the O–D distribution in the sample at high pressures using the infrared mapping measurement.

2. Experimental

A high pressure was generated using a small DAC with 48 mm diameter and 30 mm height. The body of DAC was made of martensitic heat-resisting steel (SUH3). The sample was sandwiched between opposing type II diamond anvils with 0.6 or 0.7 mm culet diameter and 1.2 mm thickness. The anvils were fixed on tungsten-carbide backing plates, which had aperture angles of 70° to match the aperture angle of the reflection objectives used for the IR measurement of about 70° (N.A. 0.57). A sample chamber, 0.35 or 0.40 mm in diameter and 20 μm in thickness, was made by drilling a hole into an Inconel 600 metal plate. A thickness of about 20 μm was appropriate for the observation of an infrared O–D bending peak, which is described later. Eight disc-spring washers were inserted into each clamp screw to suppress the changes of the load in the heating process.

$CsHSO_4$ with 99% purity was commercially obtained from Mitsuwa Chemicals Co., Ltd. The $CsHSO_4$ sample was heated at 373 K in an electric oven to create a phase II, which is similar to that of $CsDSO_4$, since phase II is a stable form for $CsDSO_4$ at room temperature, and phase III is stable for $CsHSO_4$. $CsDSO_4$ crystals were grown from the D_2O solution of Cs_2SO_4 and D_2SO_4 (1:1) by slow cooling [12]. Half of the sample chamber was packed with $CsHSO_4$ and the other half with $CsDSO_4$ without any pressure medium, as shown in Fig. 1. This sample assembly was prepared as follows. First, $CsDSO_4$ was put into a gasket hole and compressed lightly. Next, the sample was cut lengthwise by a razor. One-half of the sample was removed and replaced by a $CsHSO_4$ pellet, which was made by pressing between tungsten-carbide blocks. Small ruby balls were put into the sample to monitor the pressure [13]. The pressure difference in the sample chamber was within 0.3 GPa around room temperature without a pressure medium. The phase behaviors would not be affected whether or not the experiment was conducted with a pressure medium. In our previous study [11], the Raman measurement was taken without a pressure medium. The results agreed with the infrared data, which were obtained using a pressure medium of CsI. The sampling procedure in DAC was carried out in a stream of nitrogen gas. The clamped cell was heated in an electric oven up to 373 K. To monitor the progress of diffusion, the cell was taken out of the oven at time intervals varying from 1 h to few nights. After the sample cooled down to room temperature, its infrared absorption spectra were taken. An accumulated annealing time of several hundred hours was required for one experimental run. The transient times in the warming and cooling processes were negligibly short compared to the thermal annealing time of several hours minimum at 373 K, hence no correction for the transient time was made in the accumulation of the annealing time.

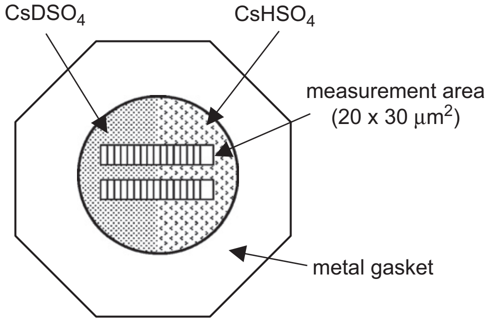

Fig. 1. Sketch of the sample assembly in the diamond-anvil cell. Half of the sample chamber was packed with $CsHSO_4$ and the other half with $CsDSO_4$. We formed a linear junction between $CsHSO_4$ and $CsDSO_4$. The measurement area of $20 \times 30\,\mu m^2$ moved in 10 μm steps. The infrared measurement was taken multiple rows at a time, and the diffusion coefficients were estimated for each row.