

Ion Desorption from Cesium Chloride and Cesium-adsorbed Soil by Surface Ionization

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1 Introduction

When a solid is heated in vacuum, a part of the surface layer desorbs as ions. This phenomenon, known as “surface ionization” (or thermal ionization), was already found in 19th century, and then its basic mechanism was formulated [1]. After that, surface ionization has been investigated in various fields such as production of ions in accelerator and sample preparation technique in mass spectrometry.

The mechanism of surface ionization has been investigated for simple systems such as adsorbed atoms and molecules on metal substrates. It has been clarified that the ionic species are considerably hard to be desorbed compared with neutrals [2]. On the other hand, surface ionization from bulk compounds has scarcely been investigated due to the complex process of the surface ionization.

In this report, we present the results for surface ionization of bulk cesium chloride (CsCl). This material was chosen, because it is expected that Cs easily desorbs as Cs⁺ ions due to the lowest ionization potential ($I_p=3.9$ eV) among all the elements. As an application of surface ionization of Cs, we also investigated the desorption of Cs from Cs-adsorbed soil. This experiment was conducted aiming to develop a method to desorb radioactive Cs from soil, which was contaminated by the accident of the Fukushima Daiichi Nuclear Power Station occurred in March 2011.

2 Experiment

The cesium chloride (CsCl) was powder of special grade. It was used without any pre-treatments. For Cs-adsorbed soil, we used vermiculite (clay) collected from Ono-machi, Fukushima Prefecture. It was stirred in a 5 mM water solution of nonradioactive CsCl for 24 h several times. The excess CsCl was washed with ethanol. The content of Cs was 4.7 wt%.

For the measurement of thermal desorption, an electron bombardment (EB) heating system was used. The schematic of the EB system is shown in Fig. 1. The sample of 5 mg was put in the crucible made of tantalum. The crucible was heated by the bombardment of electrons from the tungsten hot filament. The crucible was electrically isolated from the ground, and positive voltage

can be applied to the crucible. The desorbed species were measured by a quadrupole mass spectrometer. For ion measurements, the filament in the mass spectrometer was shut off. The base pressure of the chamber was 10^{-6} Pa.

To compare the desorption yield of ions with that of neutrals, a movable aluminum plate was put above the crucible. Desorbed ions or neutrals were deposited on the aluminum plate for a certain time, and then the surface of the aluminum plate was measured by X-ray photoelectron spectroscopy (XPS). For Cs-adsorbed clay, the chemical states and contents of Cs before and after heating were measured by XPS. The XPS measurements were performed at the BL-27A of the Photon Factory. The typical photon energy was 3000 eV, which enables bulk-sensitive XPS measurements.

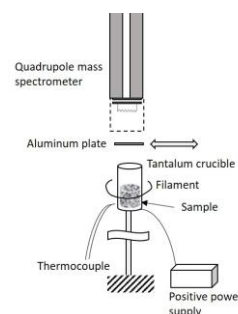


Fig. 1: Schematic view of the electron bombardment (EB) heating system.

3 Results and Discussion

3.1 Surface ionization of CsCl

Figure 2 shows the mass spectrum of neutral species desorbed from CsCl at 460°C. The H₂O peak originating from adsorbed water on the powder is the most intense among all masses. Among the fragments of CsCl, the intensity of the Cs peak is the highest reflecting the low ionization potential of Cs. The other fragments are Cl and double charged Cs. This mass spectral pattern is different from that of ion desorption (Fig. 3).

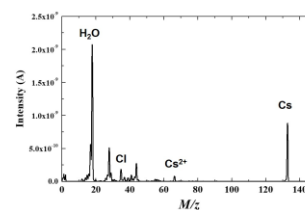


Fig. 2: Mass spectrum for desorbed neutrals from CsCl at 460°C.

Fig. 3 shows the mass spectra of positive ions desorbed from CsCl at 460°C. In this measurement, various positive potentials were applied to the crucible, which are shown in Y axis. When the crucible was grounded, no desorbed ions were observed. On the other hand, when the positive potential was applied to the crucible, Cs⁺ ions began to appear from around +50 V. The intensity of the Cs⁺ ions almost saturates at +300 V (The crucible potential of 100 V corresponds to the electric field of 670 V/m at the surface.).

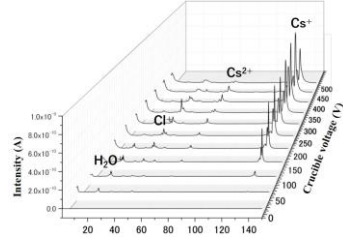


Fig. 3: Mass spectra for desorbed ions from CsCl at 460°C. Various positive potentials were applied to the crucible, which are shown in the Y axis.

The effect of such low electric field on the ion desorption was reported by Butman et al. [3] for thin films of alkali metal compounds. They discussed the enhancement of the ion desorption from KCl single crystal by positive electric field in terms of the excess charge depending on the surface topography such as steps and kinks [3]. However, the ion emission they treated plays a minor part in the total desorption, so the present results cannot be explained only by the surface topography. At present, we consider that the enhancement of ion emission by electric field is explained by the space charge effect as follows.

The electric field applied at the surface form a space-charge zone. This space-charge first hinders the ion emission. With increasing the potential of the extraction field, ions are extracted from the surface more efficiently resulting in the increase in the ion desorption. This phenomenon is known as Langmuir–Child behavior [4,5]. Actually, in the study of ion source, it was reported that the emission of potassium and cesium ions from leucite-type materials is enhanced by the space charge following the Langmuir–Child law under small electric fields (<1000 V/cm) [6]. Although further study is needed to clarify the effect of surface electric field on ion emission, we consider that the observed enhancement of Cs⁺ ion emission by the electric field is due the space charge effect produced at the surface.

Next, we compare the desorption yield of ions and neutrals. Figure 4 shows the intensity ratios of ions to neutrals (I_{Cs^+}/I_{Cs}) desorbed from CsCl as a function of the temperature. The I_{Cs^+}/I_{Cs} value shows a maximum at around 415°C. This temperature is about 230°C lower than the melting point of CsCl. To the best of our knowledge, such high yield of ion desorption from alkali-metal halides at low temperature has not been reported. Let me consider the mechanism of high ion desorption yield at such low temperature.

When the CsCl molecules are firstly dissociated in the surface and then atomic neutrals and ions desorb, the ratio

of ions to neutrals (Y_{Cs^+}/Y_{Cs}) desorbed from a surface is expressed by the Saha-Langmuir equation [7],

$$Y_{Cs^+}/Y_{Cs} = (g_{Cs^+}/g_{Cs}) \cdot \exp(-(E_i - \phi)/kT) \quad (1)$$

where g is the statistical weight (degeneracy), E_i is the ionization potential of cesium, ϕ is the surface work function, k is the Boltzmann constant, and T is the Kelvin temperature. The subscripts Cs⁺ and Cs indicate the ions and neutrals, respectively. (In case the molecules firstly desorb and then they are decomposed and ionized, the value of E_i is substituted by a dissociative ionization energy [8].)

The experimentally obtained I_{Cs^+} and I_{Cs} values are expressed as

$$I_{Cs^+} = \varepsilon_{Cs^+} \cdot Y_{Cs^+} \quad (2)$$

$$I_{Cs} = \varepsilon_{Cs} \cdot Y_{Cs} \quad (3)$$

where ε is the detection efficiency of the mass spectrometer. Thus, the I_{Cs^+}/I_{Cs} value is shown as

$$I_{Cs^+}/I_{Cs} = A \cdot \exp(-(E_i - \phi)/kT) \quad (4)$$

where A is the constant corresponding to $(\varepsilon_{Cs^+}/\varepsilon_{Cs}) \cdot (g_{Cs^+}/g_{Cs})$. The equation (4) shows that when E_i is larger than ϕ , the value of I_{Cs^+}/I_{Cs} increases with the temperature, and when E_i is smaller than ϕ , the value of I_{Cs^+}/I_{Cs} decreases with the temperature. Since the values of E_i are constant ($E_i=3.9$ eV), the observed maximum of the I_{Cs^+}/I_{Cs} value in Fig. 4 seems to be due to the changes in the work function ϕ depending on the temperature. In the case of simple metals,

the surface work function changes depending on temperature because of the thermal vibrations of the atoms. Compared with simple metals, work functions of compounds are difficult to determine both theoretically and experimentally. For alkali-metal halides, the reported values of the work function are widespread [9]. Considering the gradient of the I_{Cs^+}/I_{Cs} values, it is deduced that the work function at the temperature lower than 415°C is smaller than E_i , and that at the temperature higher than 415°C is larger than E_i . In Fig. 4, the slopes of the experimental data are simulated using equation (1) by setting arbitral A value and two different ϕ values. At the

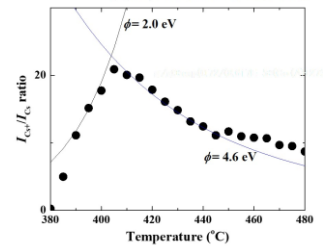


Fig. 4: Temperature dependence of the desorbed intensity ratio of ions to neutrals (I_{Cs^+}/I_{Cs}). The crucible voltage for ion measurements was +150 V. Two simulation lines calculated by the Saha-Langmuir equation are shown for two work function values ($\phi=2.0$ and $\phi=4.6$ eV).

temperature lower than 415°C, the slope is fitted by setting $\phi=2.0$ eV. This value is close to the work function of metallic Cs. At the temperature higher than 415°C, $\phi=4.6$ eV well reproduces the slope. Although the reason of such changes in the work function is not clear, it can be qualitatively explained as follows.

As to the structure of CsCl, it has two polymorphic form; the CsCl-type and NaCl-type. The crystal structure of CsCl changes from CsCl-type structure to NaCl-type one around 445 °C [10]. Also, the molar volume of CsCl increases about 16% at this temperature [11]. With this phase transformation, the standard enthalpy of CsCl formation i.e., lattice energy increases at the transition temperature [9]. The increase in the lattice energy induces the increase in the work function. Although the temperature of the I_{Cs^+}/I_{Cs} maximum is tens of degree lower than the phase transition temperature, we consider that the changes in the structure from CsCl-type to NaCl-type is the origin of the work function change at this moderate temperature region, which induces the maximum of I_{Cs^+}/I_{Cs} value.

It should be noted that the values of I_{Cs^+}/I_{Cs} shown in Fig. 4 are only relative values. A question may be raised as to which of ions or neutrals desorb with higher desorption yield in these temperature range. So, we compared the absolute desorption yield of ions with that of neutrals using the aluminum plate located above the crucible shown in Fig.1. Desorbed ions or neutrals were deposited on the aluminum plate for 30 s at 460°C. Then, the surface of the aluminum plate was measured by XPS. By comparing the $I_{Cs3d_{5/2}}/I_{Al1s}$ ratio, it was revealed that the desorption yield of Cs^+ ions with a crucible potential of +200 V is about ten times higher than that of neutrals. This is surprising result, because the desorption yield of ions by surface ionization is generally few orders less than that of neutrals [12]. Also, desorption of ions by surface ionization happens at the temperature higher than the desorption temperature of neutrals [12]. At present, we consider that this phenomenon is specific to cesium, because it has unique property that the ionization potential is the lowest in all the elements.

3.2 Desorption of Cs^+ ions from Cs-adsorbed soil

Fig. 5 shows the mass spectra for neutrals and ions desorbed from Cs-adsorbed clay at 460°C. Desorption of Cs was not observed in neutral mass spectrum. While Cs^+ was clearly observed in ion mass spectrum. In order to verify the applicability of surface ionization to the decontamination of

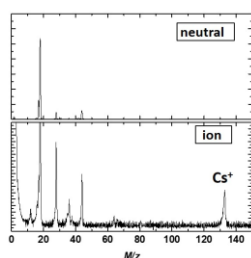


Fig. 5: Mass spectra for neutrals and ions desorbed from Cs-adsorbed clay at 460°C. For ion desorption, a potential of +200 V was applied to the crucible.

cesium, XPS spectra for clay was measured before and after heating.

Fig. 6 shows the XPS spectra in Cs 3d region for clay before and after heating at 460 °C for two hours. Although the chemical states did not change after heating, the intensity of the Cs 3d_{5/2} peak decreased. The quantitative analysis revealed that the contents of cesium was decreased by 13% after heating. The present results show that the a part of cesium can be desorbed as Cs^+ ions at low temperature by applying electric field.

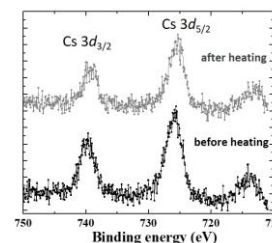


Fig. 6: XPS spectra for Cs-adsorbed clay before and after heating at 460 °C for 2 hours. A potential of +200 V was applied to the crucible during heating.

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