Photoinduced Cooperative Phenomena in Ferroelectric Layered Perovskites Pb$_2$Bi$_4$Ti$_5$O$_{18}$ Studied by High Resolution Raman Scattering

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Abstract. The UV photo induced effect in bismuth layered perovskite Pb$_2$Bi$_4$Ti$_5$O$_{18}$ has been investigated by a low frequency Raman scattering. The temperature dependences of Raman spectra both under and without a UV irradiation were observed around the ferroelectric to relaxor phase transition temperature. The central peak in the Raman spectrum shows narrowing under a UV irradiation below Tc. The correlation length of the ferroelectric fluctuation should be enhanced as a UV photo induced effect in the ferroelectric state.

1. Introduction
A Control of a phase transition with a photo irradiation has attracted much attention because of applications for future-device technologies.[1,2] This phenomenon is called a photo-induced phase transition. A study of the photo irradiation effect on ferroelectrics started from the investigations on SbSI.[3] Nonequilibrium electrons excited by the photo irradiation should affect the microscopic and macroscopic properties of the ferroelectric materials. The effect of the nonequilibrium electrons in ferroelectrics is known as the photorefractive effect, screening effect (the photo-induced shift of the Curie point Tc etc.), and anomalous photovoltaic effect.[4] Recently, the phenomena of the photo-induced phase transition have been reported on low-dimensional materials.[5-9] In the quantum paraelectric perovskite oxides, SrTiO$_3$ and KTaO$_3$, an anomalous increase of dielectric constant has been observed as a photo-induced cooperative phenomenon.[10-12]

Bismuth layered perovskite oxides have been studied extensively as attractive materials for non-volatile memory devices. There is no polarization fatigue with electric field cycling, that gives a big advantage for practical applications.[13] Most of these oxides have a ferroelectric or ferroelectric-like phase transition. Pseudo-perovskite units in their layered structures are interleaved with semiconductive layers of bismuth oxides. An effect of their two-dimensional layered structure has been reported on a property of electrical anisotropy.[14,15] A strategy for photo-induced phase transition is the exploration of low-dimensional materials. The low dimensional materials focused in this paper are the bismuth layered perovskite oxides of Pb$_2$Bi$_4$Ti$_5$O$_{18}$ which shows a behavior of the relaxor[16].

Many of ferroelectric perovskite oxides show a soft mode behavior at Tc, which is characterized with the displacive-type ferroelectric phase transition. Recently, the ideal displacive-type transition with the perfect softening of the ferroelectric mode has been reported in the isotope exchanged
strontium titanate,[17,18] Pb$_2$Bi$_4$Ti$_5$O$_{18}$ shows a relaxational-type soft mode behaviors in the low frequency region.[19,20] From the view point of instability near $T_c$, electrons excited by photo irradiation should affect the soft mode dynamics. Furthermore, relaxational phenomena related to the photo-induced excited state should be observed.

In the present study we investigate the low frequency modes under UV photo irradiation on the bismuth-layered perovskite oxide of Pb$_2$Bi$_4$Ti$_5$O$_{18}$ to clarify the dynamical property on the photo-induced state.

2. Experimental Procedure

A specimen of ferroelectric bismuth layered ceramics Pb$_2$Bi$_4$Ti$_5$O$_{18}$ was synthesized by a solid reaction method at 1400 K during 48 hours.[21,22] An X-ray diffraction pattern with MoK$_{α1}$ was collected with Huber IP Guinier Camera system at room temperature in order to check crystallinity. Any extra line was not presented in the X-ray diffraction pattern in the obtained Pb$_2$Bi$_4$Ti$_5$O$_{18}$ ceramics. The lattice constants were observed at room temperature to be $a=5.46591(1)$, $b=5.4425(3)$, and $c=49.602(2)$ Å, which is very close to $a=5.46(1)$, $c=49.7(0)$ reported by E. C. Subbarao.[23]

The spectra of the low energy mode were observed by low frequency Raman scattering using a Sandercock-type tandem Fabry-Perot interferometer on six-pass stage with the finesse more than 100. A He-Cd laser with a wavelength of 325 nm was used as a light source for UV photo irradiation. The ceramics sample of Pb$_2$Bi$_4$Ti$_5$O$_{18}$ was mounted in a microscope hot stage (THMS600, Linkam) controlled from room temperature to 900 K. The temperature was stabilized within an error of 0.1 K.

3. Results and Discussion

The UV photo-induced spectra were observed in Pb$_2$Bi$_4$Ti$_5$O$_{18}$ from room temperature to 650 K. The spectrum at 313 K was observed without a UV irradiation as shown in Figure 1. The spectrum has a central peak component with a half width at half maximum (HWHM) of about 140 GHz around zero frequency. The temperature dependence of an HWHM of central peak spectrum ($Γ$) without a UV irradiation was shown in Figure 2. The value of $Γ$ decreases critically with approaching to $T_c$, which is consistent with the previous reported results under no UV irradiation [19]. The central peak should relate to the dipole fluctuation in the ferroelectric phase transition at $T_c$. On the other hand any anomaly of $Γ$ has not been observed at the temperature $T_m$, where the dielectric anomalous peak was reported previously [16,23]. The result support that a macroscopic ferroelectric phase transition does

![Figure 1](image1.png)

Figure 1. The low frequency Raman scattering spectra without a UV irradiation (gray line) and under UV (black line) at 313K and 393 K in Pb$_2$Bi$_4$Ti$_5$O$_{18}$.  

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not take place at $T_m$ [16,20]. The anomaly of dielectric constant at $T_m$ should indicate a relaxor phenomenon related to a heterogeneous structure with polar nanoregions.

The spectra were also observed under a UV irradiation. The comparisons of spectra between under and without a UV irradiation at 313K and 393 K are shown in Figure 1, respectively. The photoinduced effect was not observed at 313K as shown in Figure 1. On the other hand the narrowing of the central peak has been obtained at 393 K as a photo induced effect. The temperature dependence of a width $\Gamma$ in the central peak under a UV irradiation is shown in Figure 2. A photoinduced effect has been observed as represented in comparison between the values of $\Gamma$ observed under and without a UV irradiation. The photoinduced effect can not be explained by simple Curie point shift under a UV irradiation. Below $T_c$ the width $\Gamma$ decreases under a UV irradiation. The result indicates that relaxation time becomes long under a UV irradiation. That is, the correlation length of ferroelectric fluctuation is enhanced in the ferroelectric state as a UV photo induced effect. The most remarkable difference is observed around 400 K where is not $T_c$. It seems that the observed difference becomes rather small at $T_c$. However, the results of the spectral analyses around 100 GHz near $T_c$ include an ambiguity by an influence of the broad component [20] of the acoustic phonon modes exist below about 60 GHz in the ceramic sample. An observation of spectrum is needed in a single crystal for an accurate clarification of the photoinduced effect near $T_c$. The central peak might become narrowing down to less than 100GHz in the ambiguous region with approaching to $T_c$.

![Figure 2](image-url)

Figure 2. The temperature dependence of the spectral width in the central peak in Pb$_2$Bi$_4$Ti$_5$O$_{18}$. The open and solid circles are observed without and under a UV photo irradiation, respectively.
Above $T_c$ the width of $\Gamma$ shows an increase under a UV irradiation. Namely the decrease of correlation length of the ferroelectric fluctuation was observed in the relaxor state of paraelectric phase as a UV photoinduced effect. The observed photoinduced effect is opposite between the paraelectric and ferroelectric state. On the other hand the UV photoinduced effect in the paraelectric state could be explained by a simple Curie point shift originated in a screening effect in the dipole interaction.

In summary a photoinduced effect in low dimensional material of bismuth layered perovskite has been observed in $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ using a low frequency Raman scattering. An anomalous increase of correlation length of ferroelectric fluctuation has been observed as a UV photo induced cooperative phenomenon in the ferroelectric phase. The low dimensional materials of the bismuth-layered perovskites are very sensitive by a photo excitation. A new photoinduced phase transition might be discovered by a further research in the bismuth-layered perovskites.

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