

Time-Resolved Investigation of Photocurrent Relaxation in Ionic Conductor Beta-AgI for Different Temperatures

Farzana Sabeth*, Toshifumi Iimori, and Nobuhiro Ohta

Abstract— Time-resolved measurements of photoirradiation effects provide an intimate understanding of the processes involved in photoexcited systems. In this work, we measured time-resolved photocurrents of KI-treated β -AgI polycrystals, which provide information about the primary process underlying the photoinduced change in the ionic conductivity of β -AgI. Two excitation wavelengths, 450 nm and 532 nm, corresponding to excitation at the band-gap edge and in the sub-band-gap region, respectively, were used to photoirradiate the samples. The transient photocurrents measured by shining β -AgI pellets with a nanosecond pulsed laser show fast and slow decay components in the nanosecond and microsecond time regions at both room temperature (298 K) and liquid nitrogen temperature (77 K). The remarkable photocurrent observed at room temperature was significantly suppressed at 77 K. The photocurrent relaxation also showed a clear temperature dependence: the photocurrent relaxation time (the averaged decay time) observed at room temperature was in the range of 2-3 μ s, while a faster photocurrent relaxation in the range of 0.3-0.4 μ s was observed at 77 K. Although the decrease in average relaxation time at 77 K does not represent a uniform decrease across all relaxation processes, the component 3 (τ_3) process shows a significant increase at 77 K compared to 298 K.

Index Terms— Beta-AgI, bandgap, Decay dynamics, Photocurrent, Time-resolved measurement

I. INTRODUCTION

The physical properties of solid-state ionic conductors have attracted significant interest for many decades due to their technological relevance, particularly in the fabrication of solid-state electrochemical devices. Several models, based on various structural and non-structural factors, have been proposed to elucidate the mechanism of fast ionic

conductivity, and numerous investigations have been carried out to explain the macroscopic and microscopic behavior of the conducting ion and the mechanism of phase transitions [1], [2], [3], [4]. Despite significant advancements, many aspects of ionic conductivity remain enigmatic. For instance, the precise mechanisms underlying the high ionic mobility in certain materials are not fully understood. The interplay among structural defects, ionic interactions, and overall lattice dynamics remains an active area of research.

Silver iodide (AgI) is a fascinating material for studying ionic conductivity and related phenomena due to its unique structural and transport properties. The structural and ion-transport properties of AgI have been studied using a wide variety of techniques, including neutron scattering, EXAFS, Raman scattering, molecular dynamics, frequency-dependent conductivity and dielectric function, and thermoelectric power [5], [6], [7], [8].

AgI indeed exhibits complex and interesting phase behavior. Its phase transitions and structural properties are particularly fascinating due to its ionic nature and interactions. It exhibits at least six crystalline polymorphs and undergoes phase transitions induced by temperature and pressure. At room temperature (around 298 K) and ambient pressure (1 atmospheric pressure) (see the Pressure Temperature phase diagram of ref 10), the two phases β -AgI (the hexagonal wurtzite structure) and γ -AgI (the zincblende type structure) can co-exist, and above 420 K, AgI undergoes a first-order phase transition to the superionic state, α -AgI, with an extremely high ionic conductivity [9]. At elevated pressure (ref 10), a rock salt phase becomes stable, and below room temperature, the β + γ and rock salt phases become separated by an intermediate phase [10]. Hanson et al. reported that a phase transition from the hexagonal wurtzite structure, i.e., β -AgI, to the rock salt structure occurs at 76 K, when a pressure of 0.3 GPa was applied [11]. However, due to limited investigations of the pressure induced phase transitions at low temperatures, the phase diagram of AgI below 200K is still not fully understood. Many attempts have been made in the past and are still being tried to stabilize the highly conducting α -phase at room temperature by adopting various methods [12]. For example, the pseudo-binary system of AgI (90.1 mol %)- Ag_3BO_3 (9.9 mol %), which was synthesized by a melt-quenching technique, has superionic α -AgI stabilized at room temperature and exhibits high ionic conductivity of about $10^{-1} \Omega^{-1} \text{cm}^{-1}$ [13]. The conductivity of AgI depends on the particle size; that is, the smaller particles of silver halides exhibit higher ionic conductivities, and therefore, much attention has recently been paid to the preparation and characterization of

Farzana Sabeth was with the Research Institute for Electronic Science, Hokkaido University, Sapporo 001-0020, Japan. Currently she is an Associate Professor at Department of Natural Science (Physics), American International University – Bangladesh, Dhaka 1230, Bangladesh (email: fsabeth@aiub.edu) <https://orcid.org/0009-0002-9535-2705>

Toshifumi Iimori was with the Research Institute for Electronic Science, Hokkaido University, Sapporo 001-0020, Japan. Now he is a Professor, at Department of Sciences and Informatics, Muroran Institute of Technology, Mizumoto-cho 27-1, Muroran 050-8585, Japan, (email: iimori@muroran-it.ac.jp) <https://orcid.org/0000-0003-2158-4378>

Nobuhiro Ohta (Professor) was with the Research Institute for Electronic Science, Hokkaido University, Sapporo 001-0020, Japan. He is now a Lifetime Chair Professor at the Department of Applied Chemistry and Institute of Molecular Science, and Center for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, 1001 Ta-Hsueh Road, Hsinchu 300093, Taiwan (e-mail: nohta@nycu.edu.tw) <https://orcid.org/0000-0003-4255-6448>

AgI nanoparticles [14], [15], [16], [17], [18]. Wang et al. observed the crystal transition from β -AgI to α -AgI for AgI nanoparticles, precipitated in situ in nanopores of alumina, which interestingly occurred at a higher temperature (433 K) compared with that of bulk AgI at 420 K, because the nanopores of the alumina matrix strongly restricted the thermal motion of AgI[19].

Reversible photoswitching behavior in the bulk resistance of ionic and superionic phases, and a photomemory effect, have been reported in AgI films [20], [21], [22], [23]. The photoexcitation dynamics and their temperature dependence have also been investigated for single crystals of β -AgI[24]. However, photoconductivity below 150 K and the possibility of photoinduced phase transitions have been scarcely investigated in AgI. We have reported that the ionic conductivity of AgI crystals can be controlled by photoirradiation [20], [21], [22]. In our previous impedance spectroscopy study, we observed a giant decrease in bulk resistance accompanied by a reduction in the equivalent circuit relaxation time with continuous photoirradiation of KI-treated β -AgI at 77 K. These observations suggested the possibility of photoinduced lattice distortion or a structural phase transition. However, the primary photoinduced processes responsible for these changes remained unsolved. Unlike our previous steady-state measurement, the present study employs nanosecond pulsed laser light excitation to investigate the transient photocurrent of KI treated polycrystalline β -AgI to enable the direct observation of the primary processes of the photoinduced change in the ionic conductivity of the β -AgI crystal at room temperature (298 K) and at the low temperature of liquid nitrogen (77 K). By comparing the TRPM responses at 298 K and 77 K under both 450 nm and 532 nm excitations, the present work reveals a significant temperature dependence of photocurrent relaxation, including the disappearance of the longest decay component at 77 K, and provides a new insight into early-stage photoinduced carrier dynamics and relaxation process in KI treated β -AgI.

II. METHODOLOGY

β -AgI pellets of diameter 13 mm and thickness 0.7-0.8 mm were prepared [20], [21]. The AgI pellets were immersed in the saturated KI solution for 2 days to increase the percentage of the β -component. The pellets were rinsed with Milli-Q water and dried in a vacuum desiccator for further use. β - and γ - phases usually coexist immediately after preparing the AgI pellets and the percentage of the γ -component is very high under ambient conditions without KI treatment. The distance between two parallel carbon electrodes coated on the AgI sample used for time-resolved photocurrent measurements (TRPMs) was 3-4 mm. The samples were characterized by XRD and complex impedance spectra (Cole-Cole plots). The complex impedance spectra were measured with an ac voltage of 0.1 V in the frequency range from 5 MHz to 42 Hz or 5 MHz to 50 mHz using impedance analyzers (Hioki 3532-50, and Solartron, 1260 + 1296) to characterize the samples by the four-probe method. A variable dc voltage supply and an oscilloscope were connected in series with the sample to

perform TRPM (the schematic diagram for TRPM is shown in Fig. 1). A nanosecond pulsed laser with a pulse width of ~ 10 ns, using an optical parametric oscillator unit mounting a BBO crystal pumped by a third harmonic of the output of a pulsed Nd:YAG laser (QuantaRay, LAB-150), was employed as a light source to illuminate the central portion between the electrodes coated on the AgI round crystal sample (see Fig. 1). The repetition rate of the laser pulse was 2 Hz and the intensity of the irradiated light was adjusted with a variable neutral-density filter. Since the peak of the photocurrent excitation spectrum of β -AgI is located around 450 nm at room temperature [20], [21], the TRPM measurements were carried out with excitation at 450 nm, ensuring that the light was strongly absorbed at the surface. The applied DC voltage was varied from 5 V to 50V for both temperatures. However, at 77 K, reliable photocurrent data could not be obtained at the lowest applied voltage of 5 V because the photocurrent signal became comparable to the experimental noise level, resulting in an insufficient signal-to-noise ratio for reliable decay analysis. Therefore, the 5 V data at 77 K were excluded from the quantitative analysis (Table 1). Similar measurements were carried out at a longer excitation wavelength of 532 nm, following the measurements at 450 nm. Liquid nitrogen was used as a cryogen in a homemade cryostat to lower the temperature to 77 K, at which TRPMs were performed using the two excitation wavelengths mentioned above. The sample was immersed directly in liquid nitrogen. Laser power was measured to be 1.25 – 1.3 mW (0.625 – 0.65 mJ/pulse) at both excitation wavelengths.

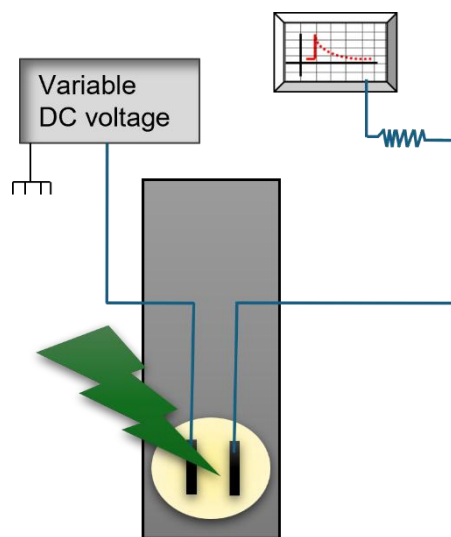


Fig. 1: The schematic diagram of TRPM

III. RESULTS AND DISCUSSION

At first, the samples were characterized as β - and γ -polymorphs from their XRD patterns. Fig. 2a revealed the peaks at 2θ values of 22.4° , 23.68° , 39.2° , and 46.32° for the corresponding planes [100], [111], [220], and [311], [JCPDS No.78-6041], respectively, confirming the γ -phase of AgI [25].

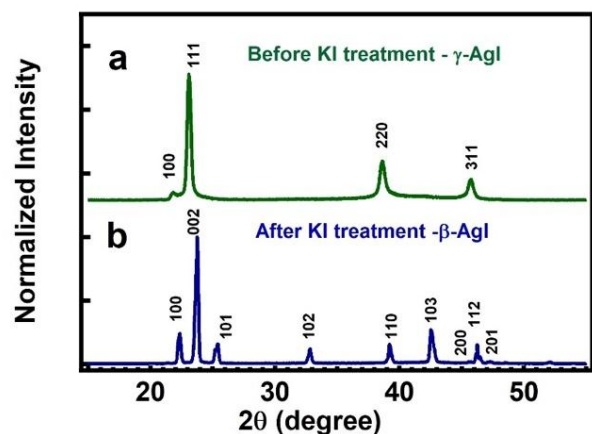


Fig. 2: XRD patterns of AgI (a) Before KI treatment (γ -AgI) (b) After KI treatment (β -AgI). Reproduced from Ref. [21] with permission from THE AMERICAN CHEMICAL SOCIETY. COPYRIGHT © 2012 AMERICAN CHEMICAL SOCIETY.

Similarly, Fig. 2b depicts the peaks at 22.4°, 23.76°, 25.38°, 32.8°, 39.2°, 42.54°, 45.66°, 46.25° and 47.26°, corresponding to the planes [100], [002], [101], [102], [110], [103], [200], [112], [201], respectively. The peaks are matched with the (wurtzite phase) JCPDS card no. 78-1614 [26]. The sharpness of the peaks confirms the high crystallinity of the phases.

The bulk resistances estimated from the complex impedance spectra (Cole-Cole plots) of β -AgI are presented in Fig. 3. The red dotted line shows the Cole-Cole plots measured at 298 K, and the blue squared line represents the same at 77 K. The bulk resistances of β -AgI are 9.7 M Ω and 4.5 G Ω at 298 K and 77 K, respectively.

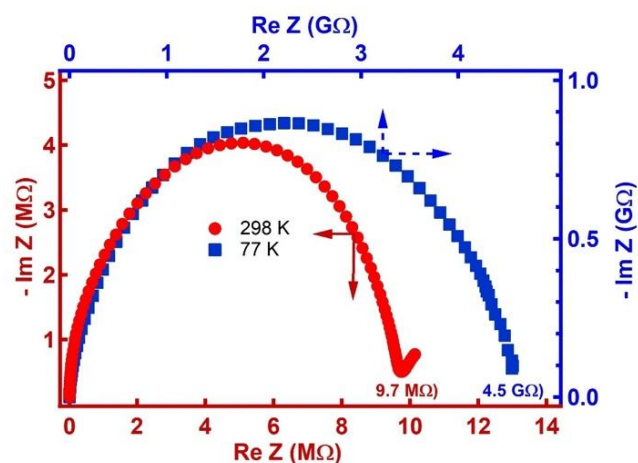


Fig. 3: Cole-Cole plots of β -AgI at 298 K (red dots) and 77 K (blue squares). The 298 K data were measured in the present study, whereas the 77 K data were reproduced from Ref. [21] using a different sample, with permission from the American Chemical Society. Copyright © 2012 American Chemical Society.

The transient change in the photocurrent in the ns to μ s time region was examined at different temperatures and applied electric field strengths. Fig. 4 represents decay profiles of the transient photocurrent measured for KI treated β -AgI with excitation at 450 nm for different DC voltages ranging from

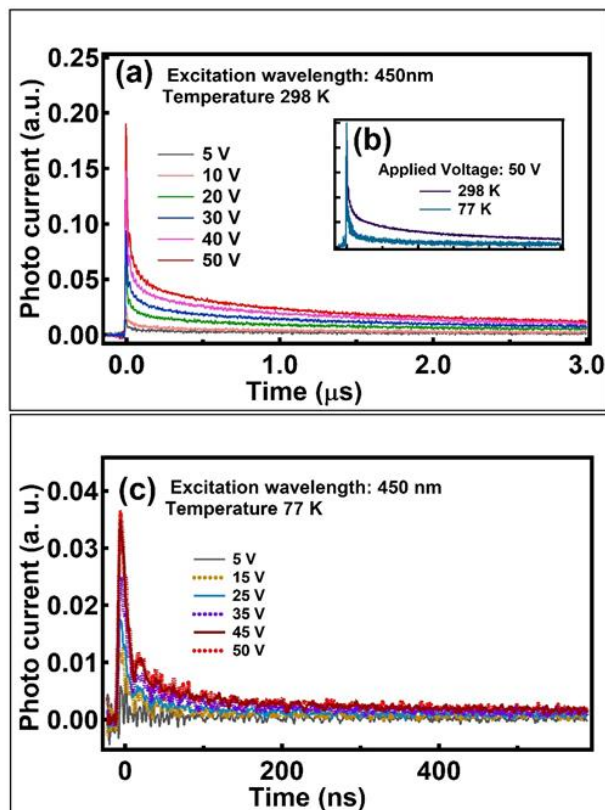


Fig. 4: The time profiles of the transient changes in the photocurrent of KI treated β -AgI obtained by photoirradiation at 450 nm with different voltages at 298 K (a) and 77 K (c). The normalized time profiles obtained with 50 V at 298 K and 77 K are shown in (b).

5V to 50V at room temperature (a) and at 77 K (c). The decay profiles of the transient photocurrent show a sharp peak right after the photoirradiation and a gradual decrease with time.

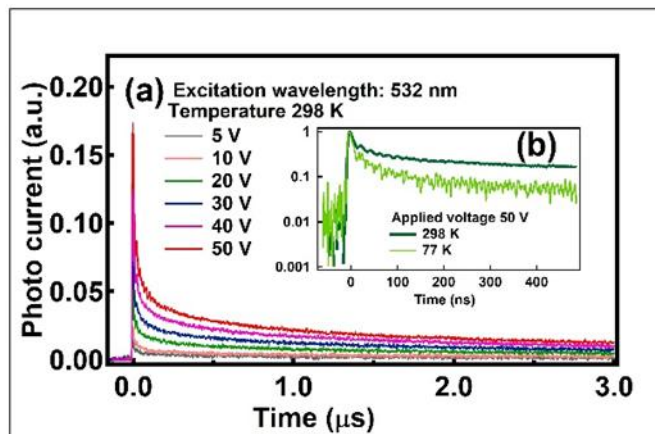


Fig. 5: (a) Decay profiles of the photocurrent measured with 532 nm excitation at different voltages, where the current is given on a linear scale, and (b) the decay profiles observed with 50 V at 298 K and 77 K given on a log scale.

The peak heights exhibit significant dependence on electric fields and temperature. At room temperature, the photocurrent peak values are almost twice those at 77K. A clear temperature dependence of the relaxation of the photocurrents is also perceptible in Fig. 4(b). In addition, no significant change in photocurrent was observed with 450 nm and 532 nm excitations at 77 K. This may be related to the low-temperature shift of the band edge [32], which could place 450 nm below the band edge at 77 K.

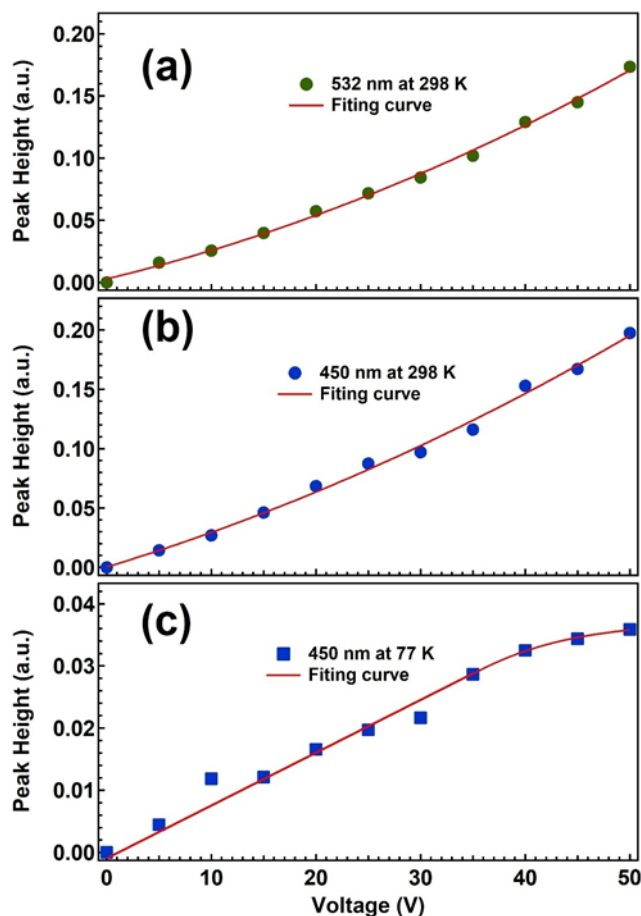


Fig. 6: Applied electric field strength dependence of the peak heights of KI treated β -AgI for 450 nm (a) and 532 nm (b) excitation at room temperature and 450 nm at 77 K (c)

The photocurrent decay profiles of the samples excited with energy in the sub-band gap region, i.e., 532 nm excitation, were also studied at room temperature and at 77K. Fig. 5 represents a comparative picture of the decay profiles of the transient changes in the photocurrent of KI treated β -AgI obtained by photoirradiation at 532 nm with different voltages, and a comparison of decay profiles is made at 298 K and 77 K for the applied voltage of 50 V, as shown in Fig. 5b. A comparatively smaller photocurrent and a slight change in the relaxation time were observed for the excitation in the sub-band gap region (532 nm). This difference in photocurrent may arise from differences in optical penetration depth with different excitation energies.

Fig. 6 shows the peak height of the transient photocurrent as a function of applied electric field strength using two

excitation wavelengths, 450 nm and 532 nm at 298 K and 450 nm at 77 K. In all cases, the peak height increases with voltage, but the nature of the increase differs at higher voltages. The voltage-dependent rise in peak height indicates that a stronger electric field enhances the separation and transport of photogenerated charge carriers. As the voltage increases, recombination decreases, and more carriers contribute to the measured photocurrent. At low applied electric fields, a linear field dependence was observed at both temperatures. At higher field strengths, nonlinear behavior and photocurrent saturation were observed at 298 K and 77 K, respectively (see Fig. 6c).

The voltage dependence of the photocurrent can be expressed by a power-law relation

$$I_{ph} \propto V^n \dots \dots \dots (1)$$

where I_{ph} is the photocurrent, V is the applied voltage, and n represents the degree of nonlinearity. The room-temperature measurements exhibit mildly superlinear behavior ($n > 1$), the increase in electric field facilitates the extraction of photogenerated carriers and suppresses carrier recombination, resulting in enhanced photocurrent response. In contrast, the low-temperature response tends toward sublinear ($n < 1$) saturation. The sublinear behavior at higher voltages may therefore be attributed to carrier trapping and space-charge-limited transport mechanisms [27], [28], [29], [30].

The relaxations of the photocurrent observed in the time profiles are characterized by an initial fast decay followed by comparatively slower decays. A single exponential cannot describe the decay profiles; each case exhibits multi-exponential decay. The pre-exponential factors and the lifetimes of each decaying component are shown in Table I.

TABLE I

The fitting parameters of the time-resolved decay profiles of the transient photocurrent measured for KI treated β -AgI at room temperature and at 77 K for different applied D.C. voltages for two excitation wavelengths. The pre-exponential factors are given in parentheses.

Wavelength nm	Temperature/ K	Voltage/ Volt	$\tau_1/\mu\text{s}$	$\tau_2/\mu\text{s}$	$\tau_3/\mu\text{s}$	$\tau_4/\mu\text{s}$	$\tau_{avg}/\mu\text{s}$
450	298	5	0.020 (0.55)	0.180 (0.20)	2.72 (0.20)	41.3 (0.05)	2.82
		30	0.011 (0.56)	0.053 (0.18)	1.32 (0.21)	46.6 (0.05)	2.65
		50	0.033 (0.68)	0.420 (0.14)	2.70 (0.14)	41.0 (0.04)	2.02
	77	15	0.013 (0.65)	0.111 (0.27)	4.75 (0.08)		0.40
		30	0.011 (0.72)	0.080 (0.22)	5.00 (0.06)		0.33
		50	0.007 (0.69)	0.080 (0.25)	4.75 (0.06)		0.30
532	298	5	0.015 (0.64)	0.220 (0.18)	3.20 (0.14)	35.0 (0.04)	2.00
		30	0.015 (0.66)	0.322 (0.17)	2.84 (0.12)	32.7 (0.05)	1.93
		50	0.022 (0.79)	0.360 (0.10)	2.83 (0.08)	33.8 (0.03)	1.15
	77	15	0.001 (0.56)	0.050 (0.40)	5.91 (0.04)		0.34
		30	0.002 (0.61)	0.060 (0.34)	5.30 (0.05)		0.31
		50	0.002 (0.63)	0.070 (0.32)	4.56 (0.05)		0.26

The summation of pre-exponential factors is assumed to be one. The complex decay profiles were modeled using a linear

interpreted as uniquely resolved kinetic processes. The simulation followed the expression

$$y(t) = \sum_{i=1}^N a_i \exp \frac{-t}{\tau_i} \dots \dots \dots (2)$$

where τ_i represents the characteristic lifetime of each decay phase, and the pre-exponential factors a_i represent their relative contributions to the overall profile. The average lifetime was calculated using the following equation (3),

$$\tau_{avg} = \frac{\sum_{i=1}^N A_i \tau_i}{\sum_{i=1}^N A_i} \dots \dots \dots (3)$$

The observed decrease in average carrier lifetime with increasing applied voltage at both 298 K and 77 K suggests that the recombination dynamics become faster under stronger electric fields. At 298 K, the average lifetime decreases from 2.82 μ s (5 V) to 2.65 μ s (30 V) and further to 2.02 μ s (50 V), while at 77 K it decreases from 0.40 μ s to 0.33 μ s and finally to 0.30 μ s. This behavior indicates that higher bias voltages enhance carrier transport and extraction, reducing the lifetime of photogenerated charge carriers within the material. The stronger electric field can also increase the probability of field-assisted recombination through defect or trap states, leading to shorter decay times. Either direct recombination of free electrons or recombination through the recombination centers is responsible for the faster decay component, and the trapped carriers that slowly detrapp later give rise to the slowly decaying components. It is reported that in the case of β -AgI, Frenkel defects may act as traps for charge carriers, that is, silver-ion interstitials as electron traps and silver-ion vacancies as shallow-hole traps [27], [28]. In this work, all the decay profiles exhibit decay components with lifetimes in the ns to μ s time range, in agreement with results observed by other researchers [28], [31]. Accordingly, the shortest fitted component at 77 K under 532 nm excitation ($\tau_1 = 1-2$ ns) is considered an upper bound associated with the instrumental response rather than a quantitatively resolved relaxation lifetime. The longer-time components are used to discuss the photocurrent relaxation dynamics.

In highly strained AgBr crystals, it has been found that the presence of dislocations provides sites for deep electron traps and reduces electron lifetimes, with consequent enhancement of the hole lifetimes to as much as 50 μ s [31]. On the other hand, the hole lifetime of single crystals of β -AgI was reported to be 6 μ s by Govindacharyulu and Bose in transient photoconductivity measurements [28]. They also investigated the temperature dependence of the hole lifetime. They suggested a trend of longer lifetimes at low temperatures. However, they measured from room temperature to around 207 K. We have observed an average lifetime of the order of 2~3 μ s at room temperature, but the lifetime became 0.3~0.4 μ s at 77 K. The longest component observed at room temperature, i.e., component 4 having a lifetime of 35~41 μ s, was absent at 77 K. The small changes in the relaxation time and suppression in the photoconductivity were observed when the sample was photoexcited in the sub-band gap region (532 nm). The changes can be described by adopting the idea that carrier generation is low due to reduced absorption of light by β -AgI, that is, with excitation in the sub-band gap region. G. Cochrane studied the temperature dependence of the optical

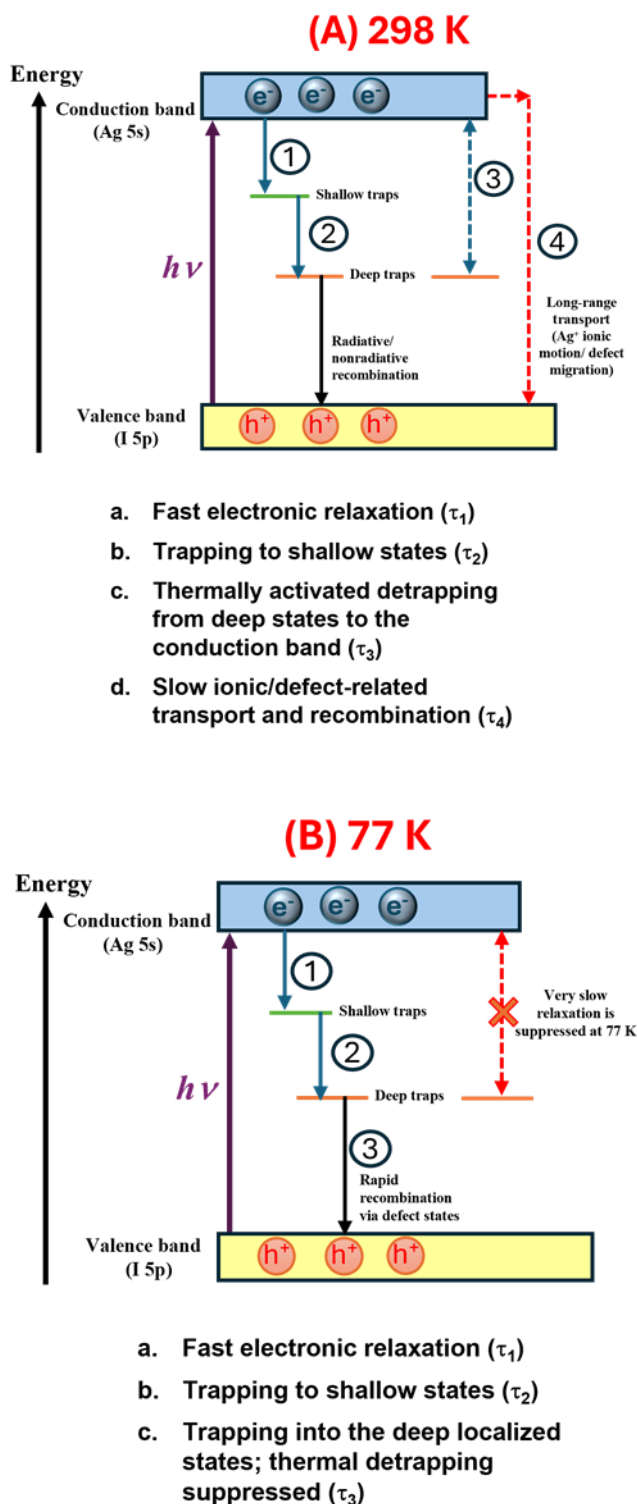


Fig. 7: Schematic diagram of proposed mechanism of photocurrent relaxation of KI treated β -AgI (A) at room temperature (298 K) (B) at Low temperature (77 K)

combination of independent exponential decays. The multi-exponential components used here are empirical descriptors of the complex photocurrent relaxation and should not be

band gap and observed a blue shift in the band gap at 77 K for the single crystals of β -AgI [32]. In the present work, the observed suppression in the photocurrent and the faster relaxation at 77 K may be attributed to the change in the absorption band gap. But the energy shift in the absorption band suggested by Cochrane (approximately 0.1 eV) is too small to explain an order-of-magnitude change that occurred in the relaxation time [32]. A much shorter average lifetime is observed at 77 K than at 298 K. The longest decay component ($\tau_4 \approx 35 - 41 \mu\text{s}$) has disappeared completely at 77 K. This suggests that the slow relaxation process responsible for τ_4 is thermally activated. Since thermal activation is suppressed, carrier detrapping and transport through shallow energy states are also suppressed. Consequently, carriers become more strongly localized and recombine rapidly through available defect centers or localized states. Most importantly, the temperature dependence of τ_3 provides further evidence that uniform acceleration at low temperature does not characterize the relaxation dynamics. While τ_3 becomes longer at 77 K, thermally activated detrapping is expected to be strongly suppressed, favoring carrier trapping or localization in deeper states. Thus, the τ_3 component is associated predominantly with thermally activated detrapping at room temperature (Fig. 7A), whereas at 77 K it is more appropriately interpreted as trapping/localization in deeper states (Fig. 7B). This temperature-dependent change should be interpreted as the dominant relaxation contribution rather than as evidence for two uniquely resolved microscopic processes.

The reduced lifetime at 77 K, therefore, indicates dominant trap-assisted or localized-state recombination mechanisms (Fig. 7B), consistent with previous reports on defect-mediated relaxation in silver halides and ionic conductors [33], [34], [35]. In KI treated β -AgI, Frenkel defects, including Ag^+ interstitials and Ag^+ vacancies, act as trapping centers for photogenerated carriers. The carriers trapped at these defect states can be released and give rise to the delayed photocurrent relaxation component at room temperature. Whereas at 77 K, the detrapping process is completely suppressed within the experimental time frame, as thermal activation is significantly reduced. Consequently, the delayed component is no longer observed, and the photocurrent decay is dominated by the faster recombination pathways associated with localized carriers. Because β -AgI is an ionic conductor, the disappearance of τ_4 may also indicate suppression of the slow ionic relaxation associated with Ag^+ hopping, which becomes increasingly restricted at low temperature. Although the present measurements do not permit identification of the dominant mechanism, the observed behavior is consistent with the suppression of thermally activated defect-mediated relaxation.

In addition, the smaller variation of lifetime with voltage at 77 K suggests that recombination is already strongly governed by frozen carrier dynamics and defect-related trapping states. Future investigations will focus on extending transient photocurrent measurements over a wider temperature range and under different excitation wavelengths and electric fields to obtain a more comprehensive understanding of charge-carrying mechanisms in β -AgI. Advanced spectroscopic techniques with higher temporal resolution, together with

complementary electrical characterization methods, will be employed to identify defect states, carrier trapping processes, and ionic transport mechanisms. Furthermore, theoretical modelling and studies on doped or nanostructured β -AgI are expected to provide deeper insights into the coupling between electronic and ionic conduction, thereby facilitating the development of β -AgI-based optoelectronic and solid-state ionic devices.

IV. CONCLUSION

In this study, time-resolved photocurrents following excitation with nanosecond-pulsed laser light were measured to elucidate the primary process underlying the photoinduced change in the ionic conductivity of the KI-treated β -AgI crystal. Using two different excitation wavelengths (450 nm and 532 nm), transient photocurrents were measured at room temperature (298 K) and at liquid-nitrogen temperature (77 K). A significant temperature dependence in both the magnitude and relaxation time of the photocurrent was observed. A large photocurrent observed at room temperature was significantly suppressed at 77 K. Furthermore, the relaxation time of the photocurrent was significantly faster at the low temperature, with an average lifetime of 0.3–0.4 μs , compared to 2–3 μs at room temperature, indicating a fundamental difference in the underlying photoexcitation dynamics of AgI crystal at different temperatures. Also, at 77 K, the decrease in τ_{avg} arises from the disappearance of the longer τ_4 component and redistribution of amplitude, while τ_3 increases. Again, the pressure-induced phase transition reported for β -AgI at 76 K requires a pressure of approximately 0.3 GPa and is therefore not expected under the ambient-pressure conditions of the present study. Since the origin of the significant temperature dependence of photocurrent relaxation is not clear at this moment, future investigations are necessary to elucidate the microscopic mechanisms responsible for the temperature-dependent photocurrent behavior. In addition, studying other solid ionic conductors would also clarify whether the observed ultrafast relaxation behavior is a general characteristic of superionic conductors, and such investigations may contribute to the development of photo-responsive ionic conductors to use in optoelectronic devices, optical switching, and light-controlled ionic transport applications.

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AUTHOR CONTRIBUTIONS

The authors confirm their contributions to the paper as follows:

Farzana Sabeth Conceptualization and design, data curation, analysis and interpretation, manuscript writing, result review and approved the final version of the manuscript.

Toshifumi Iimori Experiment design, analysis and interpretation of results, manuscript review.

Nobuhiro Ohta Conceptualization and interpretation of results, manuscript review and approved the final version of the manuscript.

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The author declares that no AI technology tools were utilized during the preparation and writing of this article. Artificial Intelligence (AI)-based language assistance tools were utilized for grammatical refinement and language improvement.

CONFLICT OF INTEREST

The author declares that there is no conflict of interest regarding the publication of this article.

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Dr. Farzana Sabeth began her academic journey by earning a Bachelor of Science and a Master of Science in Physics from the University of Dhaka, laying the foundation for her subsequent specialization. In November 2002, she began her professional career as a Lecturer at the American International University-

Bangladesh. In 2008, she pursued advanced doctoral studies at Hokkaido University in Japan, culminating in a PhD in 2012. Following her doctoral success, she continued her scholarly pursuits through a postdoctoral fellowship at the same institution, further refining her experimental methodologies. Her current research focuses on advancing the understanding of physical phenomena, reflecting a sustained engagement with both theoretical inquiry and practical applications within the academic sphere. Her scholarly output is characterized by a multidisciplinary approach, emphasizing the synthesis and analysis of advanced materials to address contemporary scientific challenges. Furthermore, her recent work explores the optimization of nanostructured systems, contributing to a broader understanding of energy efficiency and material performance.

photoelectric and photobioelectric phenomena, with a particular focus on electric field effects on the structure, dynamics, and functions of photoexcited molecules and molecular systems, including optoelectronic materials, molecular conductors, ionic conductors, and living cells. Prof. Ohta has extensively investigated electroabsorption and electrophotoluminescence spectroscopy, time-resolved photoluminescence, and photocurrent measurements to elucidate the properties of functional materials. In the field of biological systems, his work centers on autofluorescence lifetime microscopy and the effects of ultrashort pulsed electric fields on intracellular functions, particularly in distinguishing normal cells from cancerous cells. He has authored numerous influential publications and made significant contributions to the advancement of photophysics, spectroscopy, and functional materials research. He has received numerous awards such as The Japan Photochemistry Association Award (1997), The Chemical Society of Japan Award for Creative Work (2001), The Japan Photochemistry Association Lectureship Award (2012), The Spectroscopical Society of Japan Award (2014), The Japan Society of Molecular Science Award (2014), The Fellow of The Chemical Society of Japan (2016), Yushan Fellow in Taiwan (2022), Honorable Member of The Japan Society of Molecular Science (2025).



Dr. Toshifumi Iimori is a Professor in the Graduate School of Engineering at Muroran Institute of Technology. He earned a Doctor of Science degree and has developed an interdisciplinary research career encompassing photochemistry, molecular spectroscopy, nanomaterials, coordination chemistry, magneto-optical effects, nonlinear spectroscopy, and

electroabsorption spectroscopy. His research has been published extensively in international peer-reviewed journals, and he has contributed to the development of advanced spectroscopic techniques for the non-destructive optical analysis of functional components in plant leaves. In addition to his research activities, Prof. Iimori has co-authored several book chapters, led numerous funded research projects, and received several awards, including the Japanese Photochemistry Association Award for 2022 in recognition of his contributions to photochemistry.



Prof. Nobuhiro Ohta received his Ph.D. from Tohoku University, Sendai, Japan, and subsequently conducted postdoctoral research at Marquette University, Milwaukee, USA. He served as a Professor at Hokkaido University, Japan, until March 2015 and is currently a

Lifetime Chair Professor at National Yang Ming Chiao Tung University, Hsinchu, Taiwan, as well as Professor Emeritus at Hokkaido University. His research interests encompass