Photo-transport properties of Pb_2CrO_5 single crystals

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We report nontrivial photo-thermoelectric transport phenomena in Pb_2CrO_5 single crystals. Without illumination, this material exhibits an insulating behavior characterized by an activation-type temperature variation of the electrical conductivity. The Seebeck coefficient contrastingly shows a crossover from high-temperature insulating to low-temperature metallic behavior, which is attributed to degenerate carriers in a donor level. We have found that, under illumination, both the conductivity and the Seebeck coefficient increase in magnitude with increasing photon flux density in the degenerate-conduction regime. This result is difficult to be understood within a simple photo-doping effect, which usually leads to a decrease of the Seebeck coefficient under illumination. The observed phenomenon is discussed in terms of a two-carrier contribution to the transport properties.

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I. INTRODUCTION

Thermoelectric material can convert heat into electricity directly used for solid-state devices. Presently, the thermoelectric energy-conversion technology is highly desirable for harvesting electricity from waste heat due to large demand for energy. It is simple and environmentally-friendly, but the efficiency is still low. To improve the efficiency of thermoelectric materials, various efforts have been made[1–4] and new concepts have also been proposed.[5,6]

The optimization of electrical transport properties is one of the primary issues in developing good thermoelectric materials. Conventional chemical substitution has been used for the optimization through the carrier concentration tuning. It has been shown that the carrier concentration can also be tuned by photon irradiation, which creates electron-hole pairs.[7] Such photo-excited carriers contribute to the transport through the variations of carrier concentration and mobility, and along with photoconduction, the thermoelectric transport of photo-excited carriers (i.e. photo-Seebeck effect) is also expected.[8] Usually, the Seebeck coefficient S decreases with increasing electrical conductivity σ under light illumination, which can be understood as a photo-induced charge carrier doping effect in an intrinsic semiconductor.[7–12] On the other hand, a nontrivial Seebeck effect of photo-induced carriers has been observed in p-type Si near room temperature, where both the Seebeck coefficient and the conductivity increase with illumination,[13] complicating the underlying thermoelectric transport mechanism of photo-induced carriers. The increase of power factor $S^2\sigma$ under illumination offers a new way to optically control the thermoelectric properties.

Pb_2CrO_5 is a photo-active dielectric material with band-gap energy of 2.1 - 2.3 eV.[14] The photoconductive properties have been studied on ceramic pellets and thin films, showing application potentiality for photovoltaic and optoelectronic devices.[14–17] However, there is a lack of investigations on the optical and electrical transport properties of single-crystal Pb_2CrO_5. In this paper, we report the temperature variations of the transport properties of Pb_2CrO_5 single crystals in dark and also demonstrate the photo-Seebeck effect as a function of photon flux density at fixed temperatures. The temperature-dependent thermoelectric transport in dark reveals a crossover from high-temperature insulating to low-temperature metallic transport regime across a characteristic temperature, which is ascribed to a degenerate-carriers conduction in a donor level. In the low-temperature range, the light illumination on the crystal induces a nontrivial photo-Seebeck effect where we find that the Seebeck coefficient and the conductivity both increase with increasing photon flux density. This result cannot be understood in terms of conventional one-carrier photo-doping effect in an intrinsic semiconductor. The observed phenomena are rather explained by considering bipolar contribution of photo-excited carriers to the Seebeck effect.

II. EXPERIMENTS

The single crystals of Pb_2CrO_5 were made by a self-flux method.[18] High-purity PbO (5N) and Cr_2O_3 (5N) oxide powders were mixed in 3:1 ratio and put in an alumina crucible. The crucible was heated up to 1223 K in an electrical furnace with a heating rate of 200 K/h. After confirming complete melting of the mixture, the furnace was cooled down slowly with a cooling rate of 1 K/h, and at 1181 K the electrical power of the furnace was switched off. This method results in red translucent single crystals as displayed in the inset of Fig. 1. We measured σ and S as functions of temperature and photon flux density. To avoid photo-chemical reactions, all the measurements were done in vacuum (2.5×10^{-4} Pa) with a home-made experimental setup. The light emitting diode (LED) with the photon energy of $\hbar\omega = 2.6$ eV was used for light illumination and the intensity of illumination was controlled by changing LED excitation current. The photon flux density of the incident light was obtained from the measured illuminance using an illuminance meter. To check the photo-induced heating effect, we have illuminated the thermometer directly and confirmed that the heating is negligible in the present temperature range.

In Fig. 1, we show the absorbance spectrum of a Pb_2CrO_5 single crystal measured with a grating spectrometer at 300 K. The band-gap energy estimated from the absorbance data is $E_g = 2.15$ eV, well consistent with the earlier report.[14] Above E_g, the transmittance rapidly decreases and becomes almost zero owing to its large crystal thickness, making it difficult to precisely measure the absorbance above E_g, in contrast to the thin-film experiments.[14] Due to the large band gap, Pb_2CrO_5 possesses a very low electrical conductivity in dark ($\sigma \sim 10^{-6}\ \Omega^{-1}\text{cm}^{-1}$ at $T = 300$ K). Therefore, instead of conventional open-circuit voltage measurement technique, we utilized a current measurement method to obtain the Seebeck coefficient by exploiting the Boltzmann equation $J = \sigma E + \sigma S(-\nabla T)$, where J, E, and ∇T are the current density, electric field, and temperature gradient, respectively.[12] Firstly, we measured the electrical current with applying electric field under no temperature gradient, and obtain the conductivity $\sigma = J/E$. The linearity in the J-E curves was checked for confirming negligible Joule heating effect. We then measured the current under ∇T without applying electric field in order to evaluate $S = J/(-\sigma\nabla T)$. These transport coefficient were measured at each photon flux density. To eliminate the unavoidable offset contri-

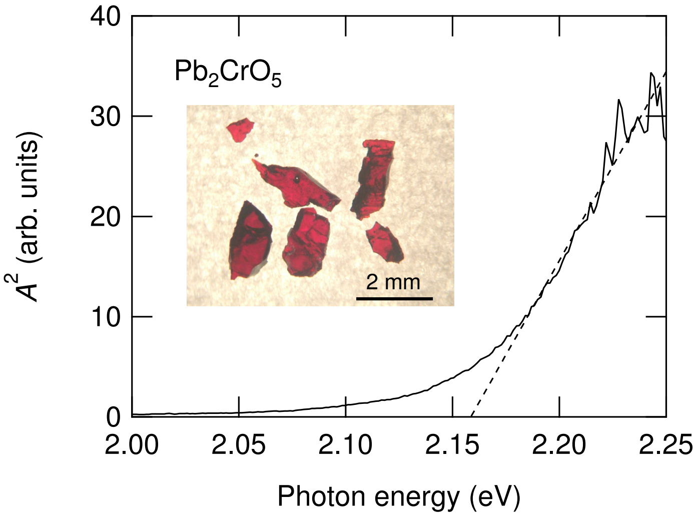

FIG. 1. (color online) The photon energy dependence of the square of the absorbance A measured at 300 K. The dashed line represents a linear fitting function for estimating the band-gap energy. The inset shows a photograph of the single crystals.

butions into the Seebeck coefficient, we evaluated S from the slope in J/σ-∇T curves by applying four different values of ∇T.

III. RESULTS AND DISCUSSION

The temperature variations of the electrical conductivity σ and the Seebeck coefficient S of Pb_2CrO_5 single crystal measured in dark are displayed in Figs. 2(a) and 2(b), respectively. The conductivity exhibits an activation-type insulating behavior as seen in the inset of Fig. 2(a). The energy gap of $E_a = 0.9$ eV is estimated from the activation formula $\sigma \propto \exp(-E_a/2k_BT)$. This gap value is smaller than $E_g = 2.15$ eV obtained from the absorbance measurements. The band calculation on this material shows that the direct band-gap energy is almost the same as the indirect one.[20] Then the discrepancy in these gap energies implies an activation-type hopping transport with a mobility gap or an existence of a deep impurity level. We note that the present conductivity value is 10^4 times larger than that of the polycrystalline samples at 500 K.[19] This implies a significant suppression of the mobility in the polycrystalline samples probably due to a grain-boundary scattering as well as the difference of the impurity density between the polycrystalline and the present single-crystal samples.

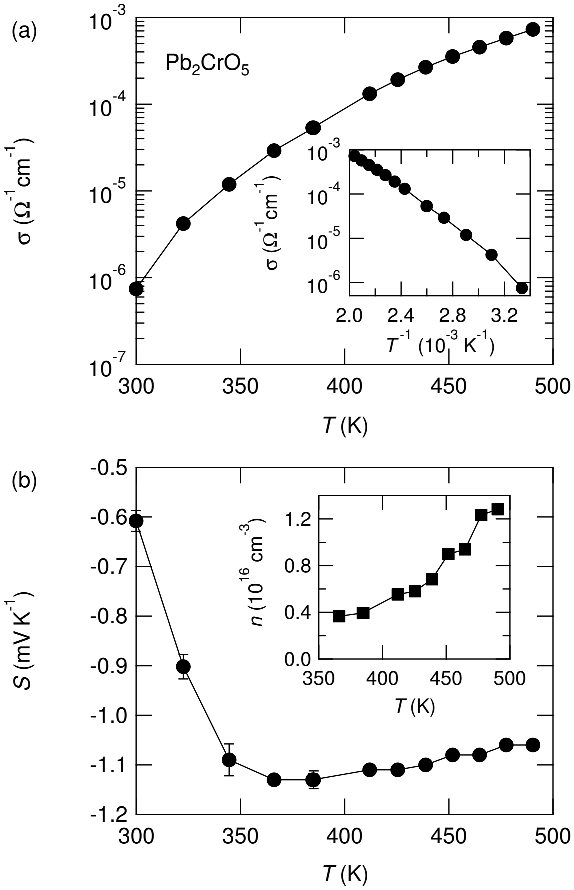

FIG. 2. Temperature variations of (a) the electrical conductivity σ and (b) the Seebeck coefficient S of Pb_2CrO_5 single crystal measured in dark. The inset of (a) shows the electrical conductivity σ as a function of $1/T$. The inset of (b) displays the temperature dependence of the carrier concentration n above 350 K.

As seen in Fig. 2(b), the Seebeck coefficient exhibits negative values in the present temperature range. This n-type conduction might be attributed to oxygen vacancies created during the crystal-growth process,[19] which turn some of Cr^{6+} (d^0) into Cr^{3+} (d^3), acting as an electron doping. In contrast to the conductivity, the temperature dependence of S is non-monotonic. With decreasing temperature the absolute value of S increases like an insulator, and then turns to decrease through a maximum at around 370 K. Such a crossover behavior has been observed widely in doped semiconductors such as silicon,[21] CdSb,[22] and potential thermoelectric compound $CoSb_3$.[23] In the high-temperature non-degenerate range above 370 K, $|S|$ decreases with increasing temperature as the thermally-excited minority-carrier contribution increases. In the low-temperature range below 370 K, on the other hand, the thermal excitation across the band gap becomes inactive and degenerate

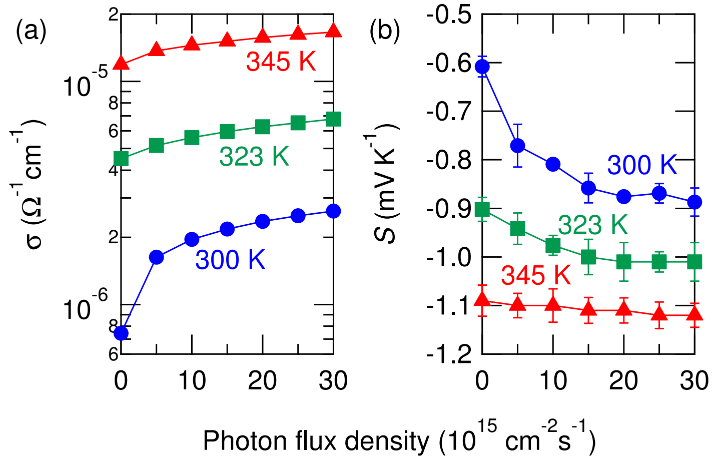

FIG. 3. (color online) (a) The electrical conductivity and (b) the Seebeck coefficient as a function of photon flux density measured at several temperatures. The photon energy of incident light is $\hbar\omega = 2.6$ eV.

carriers in a donor level dominantly contribute to the transport properties. Such degenerate carriers usually lead to a metallic or temperature-independent conductivity in high-mobility compounds,[22] while the observed conductivity is still insulating at the lower temperatures. This indicates that a low-mobility hopping transport is realized at low temperatures in the present system. Also note that similar transport behavior has been reported in the oxide double-perovskite compounds.[24]

We have evaluated the carrier concentration n in the high-temperature range using a non-degenerate formula for the Seebeck coefficient expressed by

$$S = \frac{k_B}{e}\left[\ln\frac{n}{N_c} - \left(r + \frac{5}{2}\right)\right], \quad (1)$$

where $N_c = 2(2\pi m^* k_B T/h^2)^{3/2}$, m^* is the effective mass, and r is a scattering parameter.[25] Here we used $m^* = m_0$ and $r = 3/2$ for an impurity scattering. The calculated temperature variation of the carrier concentration is shown in the inset of Fig. 2(b). Indeed, the carrier concentration is as low as the order of 10^{16} cm^{-3}. The mobility $\mu = \sigma/ne$ is estimated to be 0.4 cm^2/Vs at 500 K, but decreases to a low value of 1.6×10^{-2} cm^2/Vs at 350 K. This low mobility also implies that a hopping transport becomes dominant with decreasing temperature as discussed above. Such a conduction may originate from the unique crystal structure consisting of isolated CrO_4 tetrahedra.[26]

Now we examine the photo response in this compound. Figures 3(a) and 3(b) show the photo-induced transport properties under light illumination with the photon energy $\hbar\omega = 2.6$ eV measured at fixed temperatures, $T = 300$, 323, and 345 K. In this temperature range, both the con-

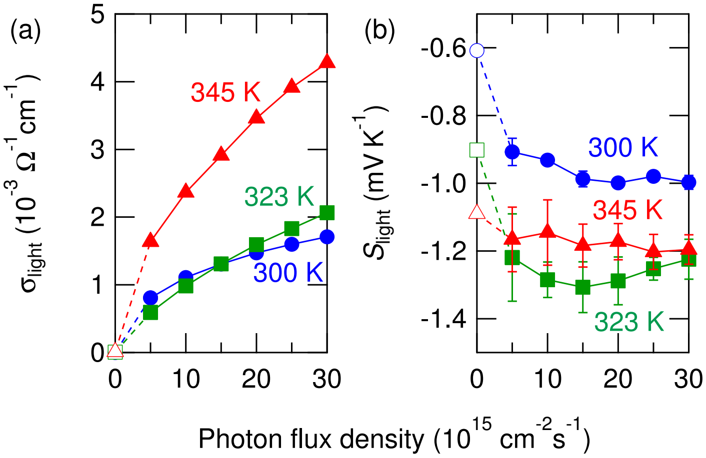

FIG. 4. (color online) (a) The photo-induced conductivity $\sigma_{\rm light}$ and (b) the photo-induced Seebeck coefficient $S_{\rm light}$ as a function of photon flux density. Open symbols show the conductivity and the Seebeck coefficient measured in dark.

ductivity and the Seebeck coefficient increase in magnitude under light illumination with photon energy larger than the band-gap energy. This behavior seems incompatible with conventional photo-doping effect on the thermoelectric property, by which the conductivity increases but the Seebeck coefficient decreases in magnitude.[11,12]

To extract the photo-transport properties of this material, we apply a simple parallel-circuit model composed of thin conducting and thick insulating layers.[11,12] Here the absorption coefficient of Pb_2CrO_5 is about 9×10^4 cm^{-1} at $\hbar\omega$ = 2.6 eV,[14] indicating that the illuminated light penetrates into a thin region ($\lambda \sim 110$ nm) at the crystal surface. In this model, the measured electrical conductivity σ and Seebeck coefficient S are expressed by[27]

$$\sigma = \left(1 - \frac{\lambda}{d}\right)\sigma_{\rm dark} + \frac{\lambda}{d}\sigma_{\rm light}, \tag{2}$$

$$\sigma S = \left(1 - \frac{\lambda}{d}\right)\sigma_{\rm dark}S_{\rm dark} + \frac{\lambda}{d}\sigma_{\rm light}S_{\rm light}, \tag{3}$$

where d is the crystal thickness (0.1 mm) and λ is the penetration length (110 nm). Here $\sigma_{\rm dark}$ ($S_{\rm dark}$) and $\sigma_{\rm light}$ ($S_{\rm light}$) are the electrical conductivities (the Seebeck coefficients) measured in dark and induced by light illumination, respectively. Using $d \gg \lambda$, the photo-induced components $\sigma_{\rm light}$ and $S_{\rm light}$ are expressed as

$$\sigma_{\rm light} = \frac{d}{\lambda}\left(\sigma - \sigma_{\rm dark}\right), \tag{4}$$

$$S_{\text{light}} = \frac{\sigma S - \sigma_{\text{dark}} S_{\text{dark}}}{\sigma - \sigma_{\text{dark}}}. \tag{5}$$

Figures 4(a) and 4(b) show the photo-induced electrical conductivity σ_{light} and the photo-induced Seebeck coefficient S_{light} as a function of photon flux density. The photo-induced conductivity is not proportional to the irradiated flux density, implying that, in addition to an increase of the carrier concentration, the mobility is reduced by illumination as observed in photoconductors CdS and CdSe.[28] This result will be discussed later. We note that the evaluation of the number of the photo-induced electron-hole pairs is difficult because the value of the recombination time, which strongly depends on the sample quality in usual,[29,30] has not been determined in the present compound. The photo-induced Seebeck coefficient is still larger than the dark one in magnitude although there is a large error bar in the low-excitation range in which the photo-induced change in the measured transport quantities is relatively small.

We infer an origin of the observed nontrivial photo-Seebeck effect, although additional photo-Hall measurements might be required for more quantitative discussion. Here we consider a situation that the excess photo-induced electrons and holes exist in the conduction and the valence bands, respectively. Then, using a two-carrier model, the conductivity and the Seebeck coefficient of photo-induced carriers can be described as

$$\sigma_{\text{light}} = \sigma_e + \sigma_h = \sigma_e \left(1 + \frac{\sigma_h}{\sigma_e}\right), \tag{6}$$

$$S_{\text{light}} = \frac{\sigma_e S_e + \sigma_h S_h}{\sigma_e + \sigma_h} = \frac{S_e + \frac{\sigma_h}{\sigma_e} S_h}{1 + \frac{\sigma_h}{\sigma_e}}, \tag{7}$$

where $\sigma_e(S_e)$ and $\sigma_h(S_h)$ denote the electrical conductivity (the Seebeck coefficient) of the photo-excited electrons in the conduction band and of photo-excited holes in the valence band, respectively. Here, $S_e < 0$ and $S_h > 0$. Note that the contribution from the residual electrons in a donor level should be negligible under illumination because the dark conductivity is two orders of magnitude smaller than the photo-induced one.

In an ideal insulator, the light illumination creates the same number of electrons and holes, which should be involved in thermoelectric transport equally, resulting in no contribution to the Seebeck effect in total. To account for the present result that the Seebeck coefficient is enhanced with illumination, the negative contribution (S_e) in Eq. (7) should largely exceed the positive one ($\sigma_h S_h/\sigma_e$), as also discussed in two-carrier photo-Hall effect in semiconductors.[28] Such an enhancement of the negative contribution can be achieved by an increase of σ_e and by a decrease of σ_h under illumination. Here, as seen in Fig. 4(a), the total photo-induced conductivity σ_{light}

deviates downward from the linear function. This result indicates a drastic photo-induced suppression of the hole conductivity, and therefore the electron contribution to the Seebeck coefficient is relatively enhanced by illumination.

The origin of such a quenching of hole conductivity under illumination is, on the other hand, not clear at present. Some negatively-charged defects or impurities in Pb_2CrO_5, which should be clarified by more detailed spectroscopic measurements as a future study, may act as trapping centers for holes to reduce σ_h. We also note that the photon energy of the irradiated light (2.6 eV) is larger than the band-gap energy of Pb_2CrO_5 (2.15 eV), resulting in a non-equilibrium hot-electron state under illumination,[31] in which the carrier transport can occur in higher- and lower-energy bands in contrast to a thermally-activated conduction in an equilibrium condition.[32] If the hole mobility is reduced in such a photo-induced hot-electron state, like the suppression of the electron mobility in the hot-electron state in GaAs,[33] the conductivity ratio σ_h/σ_e is also decreased by light illumination, leading to a possible photo-enhancement of the negative Seebeck coefficient.

IV. CONCLUSION

In summary we have studied the electrical and thermoelectric transport properties including the photo-Seebeck effect in Pb_2CrO_5 single crystals. The Seebeck coefficient in dark shows a crossover from high-temperature insulating to low-temperature metallic transport regime across a characteristic temperature, as observed in doped semiconductors. In the low-temperature regime, both the Seebeck coefficient and the electrical conductivity are found to increase under light illumination, in high contrast to the conventional photo-Seebeck effect. To qualitatively explain the observed nontrivial phenomena, we have considered a photo-induced two-carrier model, in which a quenching of the hole conductivity might induce the photo-enhancement of the Seebeck coefficient.

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REFERENCES

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[1]G. D. Mahan, Solid State Phys. **51**, 81 (1998).

[2]G. J. Snyder and E. S. Toberer, Nature Mater. **7**, 105 (2008).

[3]*Thermoelectrics and its Energy Harvesting*, edited by D. M. Rowe (CRC Press, London, 2012).

[4]*Thermoelectric Nanomaterials; Materials Design and Applications*, edited by K. Koumoto and T. Mori (Springer, Heidelberg, 2013).

[5]S. Maekawa, H. Adachi, K. Uchida, J. Ieda, and E. Saitoh, J. Phys. Soc. Jpn. **82**, 102002 (2013).

[6]G. Benenti, G. Casati, T. Prosen, and K. Saito, arXiv:1311.4430 (2013).

[7]J. Tauc, Czech. J. Phys. **5**, 528 (1955).

[8]I. Terasaki, R. Okazaki, P. S. Mondal, and Y.-C. Hsieh, Mater. Renew. Sustain. Energy **3**, 29 (2014).

[9]J. G. Harper, H. E. Matthews, and R. H. Bube, J. Appl. Phys. **41**, 3182 (1970).

[10]H. B. Kwok and R. H. Bube, J. Appl. Phys. **44**, 138 (1973).

[11]R. Okazaki, A. Horikawa, Y. Yasui, and I. Terasaki, J. Phys. Soc. Jpn. **81**, 114722 (2012).

[12]P. S. Mondal, R. Okazaki, H. Taniguchi and I. Terasaki, J. Appl. Phys. **114**, 173710 (2013).

[13]J. G. Harper, H. E. Matthews, and R. H. Bube, J. Appl. Phys. **41**, 765 (1970).

[14]K. Toda and S. Morita, J. Appl. Phys. **57**, 5325 (1985).

[15]K. Toda and S. Morita, J. Appl. Phys. **55**, 210 (1984).

[16]K. Toda and S. Morita, Appl. Phys. A **33**, 231 (1984).

[17]K. Toda and S. Morita, J. Appl. Phys. **65**, 857 (1989).

[18]T. Negas, J. Am. Ceram. Soc. **51**, 716 (1968).

[19]B. Indovski, M. P. Singh, and F. S. Razavi, J. Magn. Magn. Mater. **331**, 72 (2013).

[20]Materials properties repository from high-throughput *ab-initio* calculation: http://www.aflowlib.org

[21]T. H. Geballe and G. W. Hull, Phys. Rev. **98**, 940 (1955).

[22]F. Ermanis and E. Miller, J. Electrochem. Soc. **108**, 1048 (1961).

[23]T. Caillat, A. Borshchevsky, and J.P. Fleurial, J. Appl. Phys. **80**, 4442 (1996).

[24]R. Takahashi, R. Okazaki, Y. Yasui, I. Terasaki, T. Sudayama, H. Nakao, Y. Yamasaki, J. Okamoto, Y. Murakami, and Y. Kitajima, J. Appl. Phys. **112**, 073714 (2012).

[25]G. S. Nolas, J. Sharp, and H. J. Goldsmid, *Thermoelectrics: Basic Principles and New Materials Developmemts* (Springer, Berlin, 2001).

[26]K. Toda and S. Morita, J. Appl. Phys. **55**, 2733 (1984).

[27]G. Homm, M. Piechotka, A. Kronenberger, A. Laufer, F. Gather, D. Hartung, C. Heiliger, B. K. Meyer, P. J. Klar, S. O. Steinmüller, and J. Janek, J. Electron. Mater. **39**, 1504 (2010).

[28]R. H. Bube and H. E. Macdonald, Phys. Rev. **121**, 473 (1961).

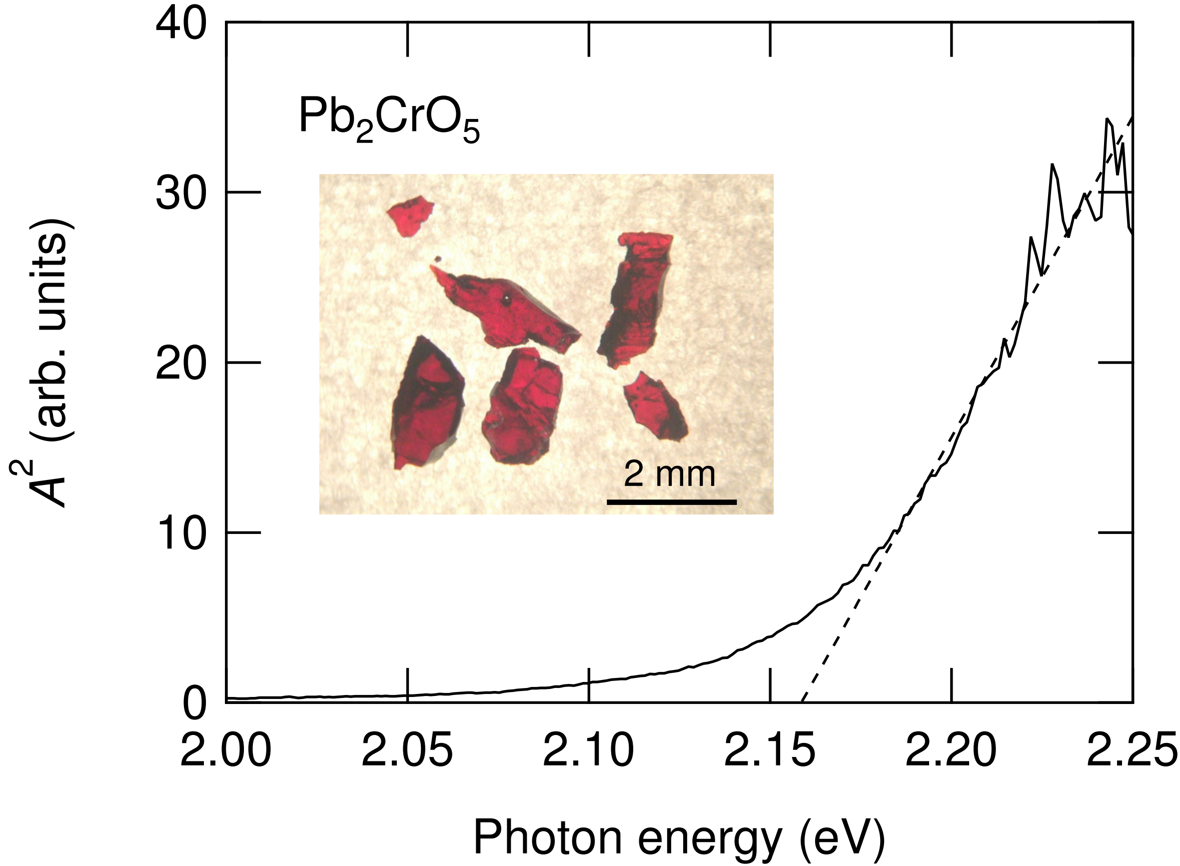
[29]S. A. Studenikin, N. Golego, and M. Cocivera, J. Appl. Phys. **83**, 2104 (1998).

[30]S. B. Zhang, S.-H. Wei, and A. Zunger, Phys. Rev. B **63**, 075205 (2001).

[31]K. Kempa, M. J. Naughton, Z. F. Ren, A. Herczynski, T. Kirkpatrick, J. Rybczynski, and Y. Gao, Appl. Phys. Lett. **95**, 233121 (2009).

[32]E. M. Conwell, Solid State Phys. Suppl. **9**, 81 (1967).

[33]B. K. Ridley and T. B. Watkins, Proc. Phys. Soc. **78**, 293 (1961).



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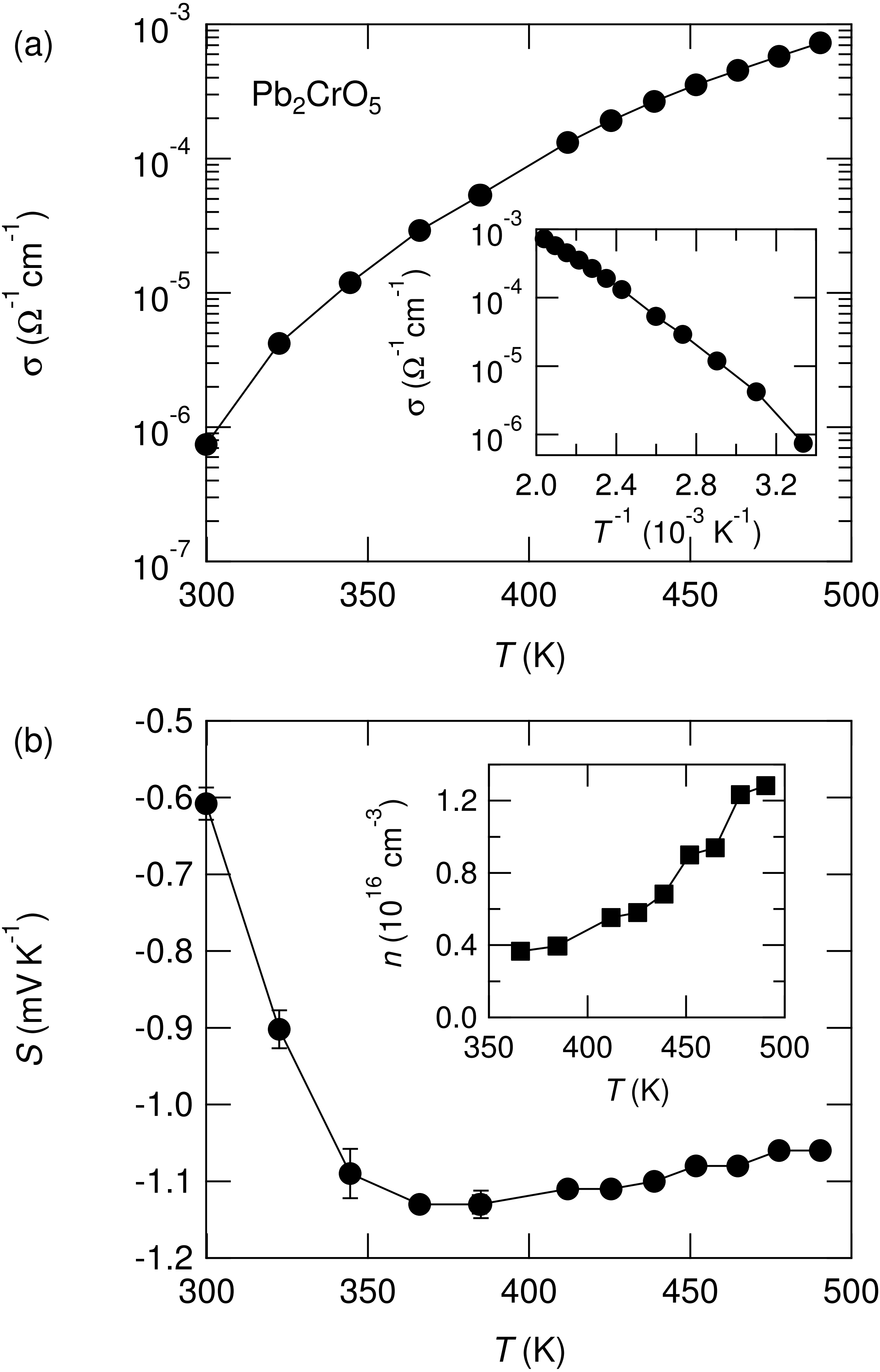
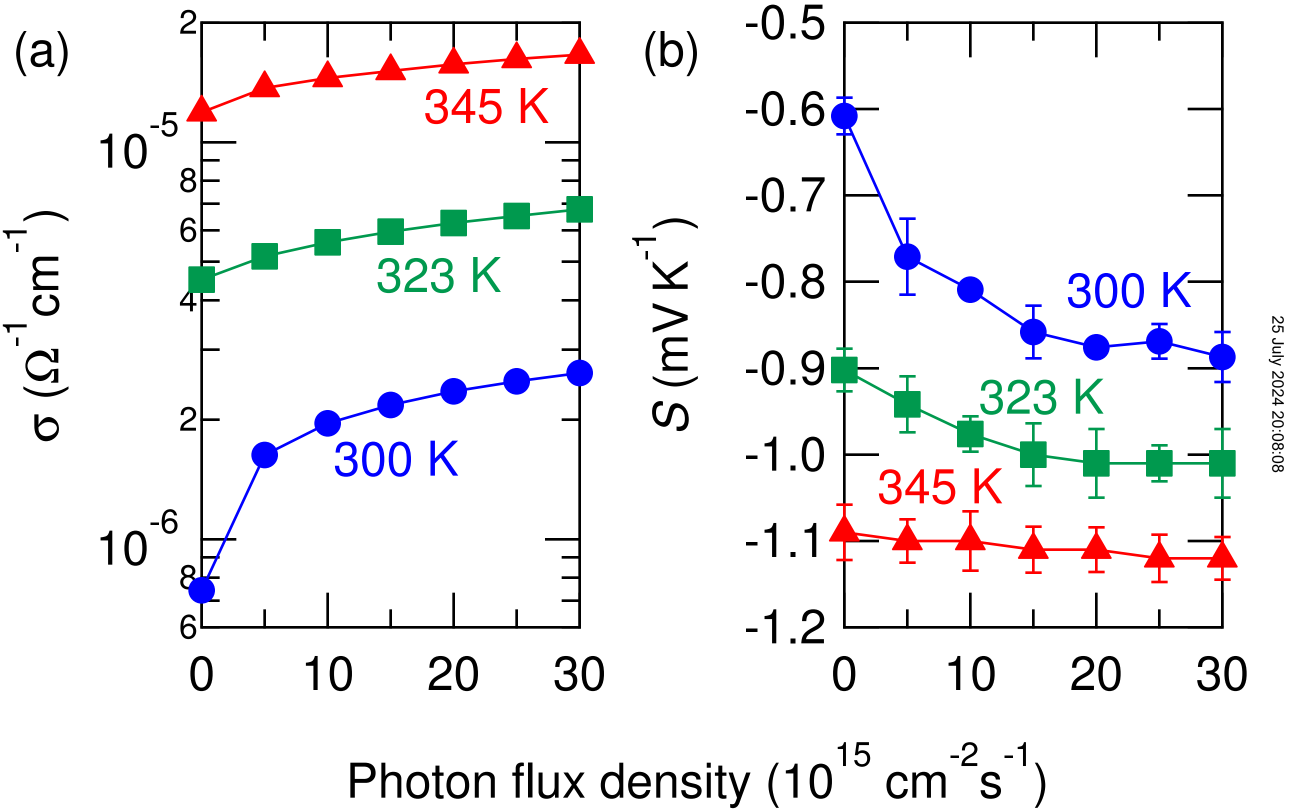


(a)
Pb2CrO5
σ (Ω-1 cm-1)
10-3
10-4
10-5
10-6
10-7
300
350
400
450
500
T (K)
2.0
2.4
2.8
3.2
T-1 (10-3 K-1)
(b)
S (mV K-1)
-0.5
-0.6
-0.7
-0.8
-0.9
-1.0
-1.1
-1.2
n (1016 cm-3)
0.0
0.4
0.8
1.2


(a)
(b)
σ (Ω⁻¹ cm⁻¹)
S (mV K⁻¹)
345 K
323 K
300 K
Photon flux density (10¹⁵ cm⁻² s⁻¹)
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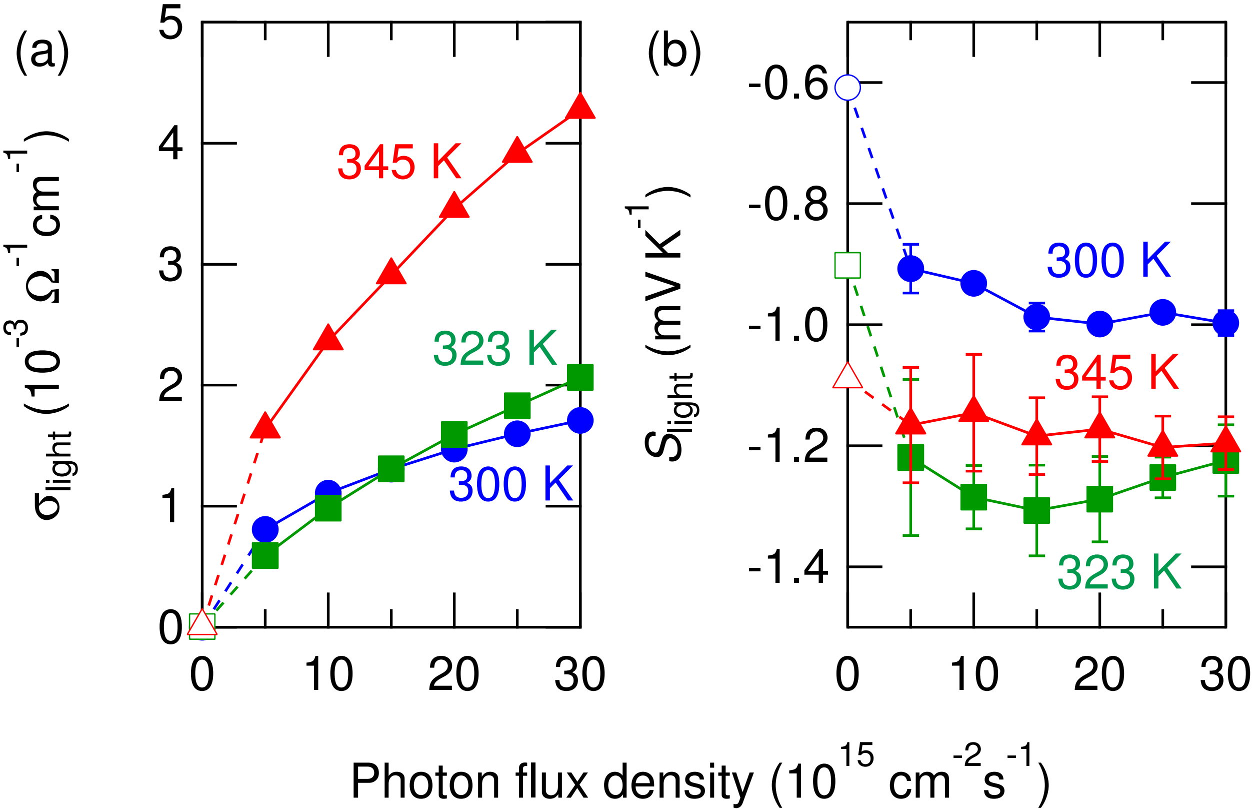

(a)
(b)
σ_{light} (10^{-3} Ω^{-1}cm^{-1})
S_{light} (mV K^{-1})
345 K
323 K
300 K
300 K
345 K
323 K
5
4
3
2
1
0
-0.6
-0.8
-1.0
-1.2
-1.4
0
10
20
30
0
10
20
30
Photon flux density (10^{15} cm^{-2}s^{-1})