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Chemical reactions and transport processes in lead iodide single crystals

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Résumé. — Le mouvement ionique anisotrope et les propriétés de dipôle (K⁺-V⁻), de l'ion du potassium et la vacance de l'ion d'iode, ont été étudiés en mesurant la d.c. conductivité ionique, la perte diélectrique (DL) et le thermocourant ionique (ITC). Les énergies migratoires de la V⁻ par l'application du champ électrique parallèle (cas I) ou perpendiculaire (cas II) à l'axe c des cristaux se sont révélées être la même valeur 0,26 eV dans les échantillons dopés K⁺ ions. D'autre part, l'énergie migratoire de la vacance des ions de plomb dans les cristaux dopés telle que 0,58 eV dans le cas I et 0,35 eV dans le cas II. Le maximum de DL près de 1,3 x 10³ Hz se sont révélés être à 402 K. D'après les mesures d'ITC deux courants maximaux près de 167 et 185 K ont été observés. Les résultats des mesures de DL et d'ITC ont été examinés en tenant compte des facteurs préexponentiels et de l'énergie d'activation pour le saut de V⁻, du dipôle. Il a été trouvé que le relâchement du dipôle se compose de deux degrés.

Abstract. — An anisotropic ionic motion and properties of potassium ion and iodine ion vacancy dipole (K⁺-V⁻) have been studied by measuring d.c. ionic conductivity, dielectric losses (DL) and ionic thermocurrent (ITC). The migration energy of V⁻ by the application of the electric field parallel (case I) or perpendicular (case II) to c-axis of crystals were found to be the same value of 0.26 eV in K⁺-doped crystals. On the other hand, the migration energy of Pb⁺⁺ ion vacancy in Bi⁺⁺⁺-doped crystals for cases I and II were 0.58 and 0.35 eV, respectively. The DL peak near at 1.3 x 10³ Hz was found at 402 K. From ITC measurements two current maxima at 167 and 185 K have been observed. The results from DL and ITC measurements were examined with respect to the preexponential factors and the activation energies for jump of V⁻ of dipoles. It is found that the relaxation process of dipole is composed of two stages.

1. Introduction. — In the field of material science the properties of lead iodide have been investigated extensively by many authors so far. There have, for example, been publications on the ionic conductivity [1, 2], photoconductivity [3], thermostimulated current [4] and the structure and/or phase-transition of crystals [5, 6]. But, the transport processes and chemical reactions of point defects in PbI₂ crystals have not been well established. Then, the information as to defect behaviour in PbI₂ crystals has been becoming essential.

The purposes of the present report are (a) to study an anisotropic transport process of anion and cation vacancies and (b) to investigate the properties of potassium ion and iodine ion vacancy dipole by using the dielectric loss (DL) measurements as well as the ionic thermocurrent (ITC) techniques.

2. Experimental procedure. — A purification by vacuum distillation at about 10⁻⁴ torr was carried out at around 630 K. Single crystallizations were performed in iodine vapour by using the Bridgman method. The introduction of K⁺ or Bi⁺⁺⁺ ions were done by adding an appropriate amount of KI or BiI₃, respectively, to purified PbI₂ powder. The crystals of type 12 R belonging to a hexagonal space group were obtained, which do not change its structure up to near melting point. The crystal slabs of 10 x 10 x 0.5 mm³ for measurements were arranged by cleaving with a thin blade (perpendicular to crystallographic c-axis) as well as by cutting with carbon-random disc blade cutter (parallel to crystallographic c-axis). The measurements for d.c. conductivity were done by using an electrometer having a sensitivity of 1.0 x 10⁻¹⁵ A. For DL measurements a model TR-1C dielectric loss measurement system which can cover all the frequency range from 30 Hz to 5 MHz was used. Moreover, to study the detailed behaviour of K⁺-V⁻ dipole the ITC were measured with a specially designed cryostat and a model TR-84M vibrating reed electrometer whose current detection limit was 1.0 x 10⁻¹⁷ A. The specimen was polarised in a static electric field of 5.0 x 10² V/cm and then cooled down to 120 K, after which the field was switched off. The specimen was warmed up to at the nearly constant rate of 0.1 K/s.

3. Results and discussion. — On the assumption that K⁺ and Bi⁺⁺⁺ ions in PbI₂ crystals are located substitutionally to Pb⁺⁺ ion sites, from the charge neutrality requirement, following two chemical reactions are considered:

K I → K⁺ + e⁻ + I⁻ + V⁻
and

\[ 2 \text{BiF}_3 \rightarrow 2 \text{Bi}^{4+} + 6 \text{I}^- + \text{V}_{\text{Pb}}^{-} \],

where \( K^{+} \) and \( V_{\text{I}}^{-} \) mean the potassium ion at lead ion site and the vacancy at iodine ion site, respectively. Consequently, by doping with \( K^{+} \) and \( \text{Bi}^{4+} \) ions we can examine the properties of cation and anion vacancies as well as the impurity-vacancy dipole. To study an anisotropic transport of isolated \( \text{I}^- \) and \( \text{Pb}^{2+} \) ion vacancy in crystals d.c. conductivity was measured for both cases where the applied electric field is parallel to \( c \)-axis (case I) and perpendicular to \( c \)-axis (case II). As for \( K^{+} - V_{\text{I}}^{-} \) dipole the measurements of DL and ITC were performed.

Consequently, by doping with \( 0.30 \) and \( 2.7 \) mol\% \( K^{+} \) ions were obtained to be 0.41 and 0.50 eV, respectively. Then, the averaged \( E_{\text{av}} \) is to be

\[ 0.41 + 0.50 = 0.91 \text{ eV} \]

Figure 1 shows the typical example for the d.c. conductivity of \( \text{Pbl}_2 \) single crystals where the electric field \( (E) \) is parallel to \( c \)-axis \( (E \parallel c) \) and perpendicular to \( c \)-axis \( (E \perp c) \).

![Figure 1](image)

Figure 2. — The anisotropic migration of iodine and lead ion vacancy in \( \text{Pbl}_2 \) crystals. Vacancies are shown by dotted circles.

![Diagram](image)

The frequency dependence of loss \( \tan \delta \) of specimens doped with \( 0.30 \) and \( 2.7 \) mol\% \( K^{+} \) ions are shown in figure 4. In these curves remarkable humps are observed near at \( 3 \times 10^2 \) and \( 2 \times 10^3 \) Hz. By raising temperature of specimens these humps shift to high frequency side, e.g., \( 1.26 \) kHz at 402 K and 2.5 kHz at 423 K. The existence of the relaxation of Debye type at 1.25 kHz was confirmed by analysing the Cole-Cole plots [9]. From the Arrhenius plots of peak frequencies of loss \( \tan \delta \) [10] the activation energy \( (E_{\text{ac}}) \) for the crystals doped with \( 0.30 \) and \( 2.7 \) mol\% \( K^{+} \) ions were obtained to be 0.41 and 0.50 eV, respectively. Then, the averaged \( E_{\text{ac}} \) is to be

\[ 0.41 + 0.50 = 0.91 \text{ eV} \]
0.46 eV, which is closely related to the energy of $V_1^-$, that is required for jumping at another iodine ion site as shown in Figure 5(a). Moreover, the characteristic relaxation time $\tau_0$ in $\tau = \tau_0 \exp(E_a/kT)$ was calculated to be $9.2 \times 10^{-10}$ s at 402 K [11]. Nevertheless, we could not detect any humps in dielectric loss $\text{tg} \delta$ in specimens for case II and in the pure crystals. Another details as to dipoles were obtained from ITC measurements.

As shown in Figure 6, the ITC in specimens doped with 0.30 mol % K$^+$ ions was found to be composed of two peaks appearing at 167 and 185 K. The peak at 167 K was uniquely observed under operating the polarisation at 168 K. The magnitudes of both peaks increased in proportion to the strength of the applied field up to 600 V/cm. Regarding two peaks, $E_a$ and $\tau_0$ for orientation of dipoles were $0.24 \pm 0.04$ eV; $2.4 \times 10^{-5}$ s (peak at 167 K) and $0.42 \pm 0.06$ eV; $5.2 \times 10^{-10}$ s (peak at 185 K), respectively [12, 13].

The activation energy and $\tau_0$ obtained from DL are in good agreement with those from ITC peak appearing at 185 K. Hence, it is considered that this coincidence comes from the same relaxation process of dipoles. Therefore, we propose a tentative model as shown in Figure 5(b). The ITC peak at 185 K may be caused by the relaxation of stage 2 while that for 167 K may be attributed to the relaxation through stage 1. The process of stage 2 is substantially the same process as that supposed from DL measure-
ments as shown in figure 5(a). On the other hand, the relaxation in stage 1 may be justified by considering the migration energy, 0.26 eV, of V₁ moving between the nearest neighbouring iodine layers as shown in figure 2(a). No discussion about the relaxation time with respect to stage 1 is given since there has not been other reports to compare with the present results.

Acknowledgment. — The authors are very much indebted to Prof. Dr. M. Ikeya for making a specially designed cryostat for ITC measurements.

DISCUSSION

Question. — Z. Morlin.

In your conductivity diagram the conductivity of the pure PbI₂ did not change in a large temperature interval. Why?

Reply. — T. Hagihara.

The measurements as to the same specimen after quenching from about 530 K to room temperature suggested that iodine ion vacancies, a dominant charge carrier in this temperature range, were trapped by the lead ion vacancies introduced during a zone-refining treatment.

References