High Br^- Ionic Conductivity for $(1\text{-}x)PbBr_2 \cdot xKBr$ System

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The electrical conductivity of $(1\text{-}x)PbBr_2 \cdot xKBr$ solid electrolytes enhanced with increasing x up to x=0.02, where 2.7×10^{-6} $S \cdot cm^{-1}$ at 298 K was obtained. The carrier ion for this system was Br^-, as determined by the Tubandt's method.

Anion conductors have been investigated for applications in gas sensors and fuel cells. A high conductivity at room temperature has been obtained for the monovalent F^- or Cl^- carrier ion. Tubandt reported that $PbCl_2$ is a pure Cl^- ion conductor,[1] and its conductivity is greatly increased by doping MCl (M=Na, K, etc.) to give $(1\text{-}x)PbCl_2 \cdot xMCl$.[2] The formation of anion vacancies with M^+ doping is very effective for obtaining high Cl^- ion conductivity. For a Br^- conducting electrolyte, however, high conductivity at room temperature has not been reported.[3] It is commonly accepted that Br^- ions are too large to migrate in a solid electrolyte. This paper describes a high Br^- ionic conductivity for $(1\text{-}x)PbBr_2 \cdot xKBr$ solid solutions.

The stoichiometric mixture of $PbBr_2$ (99.99%) and KBr (>99%) was dried at 573 K for 1 h in a glass tube, which was then evacuated and sealed, followed by melting the mixture to give solid solution at 773 K for 1 h. The sample was then ground and pressed into a pellet (13mm diameter and ca. 1mm thickness) at a pressure of 1×10^8 Pa. Gold electrodes were deposited on both surfaces of the pellet using an Ion Coater (Shimadzu IC-50). The electrical conductivity was determined by means of a complex impedance method (100~1M Hz) using Hewlett-Packard Model 4276A and 4277A impedance analyzers. Before measurements, the pellet was heated to 523 K in a stream of dried N_2 to eliminate adsorbed water.

Figure 1 presents the temperature dependence of the conductivity for the $(1\text{-}x)PbBr_2 \cdot xKBr$ system. Although pure $PbBr_2$ shows low conductivity, the conductivity is greatly enhanced by the KBr doping. The conductivity enhancement occurs even at x=0.0001. The maximum conductivity was obtained for x=0.02, which gave 2.7×10^{-6} $S \cdot cm^{-1}$ at 298 K.

The carrier ions were determined using the Tubandt's method for the sample illustrated in Fig. 2.[1] Electrolyte I, II, and III had the same composition of $0.98PbBr_2 \cdot 0.02KBr$, and superposed upon each other. Gold as a cathode electrode was sputtered on the surface of electrolyte III, while a Pb metal anode was pressed on electrolyte I. The samples were heated to 473 K for 2 h in a stream of dried N_2 before the measurements, and then electrolyzed at 10 μA for 453 h at 413 K. Theoretical weight changes of the three electrolytes expected for the transport by a given species alone are also shown in Fig. 2. It was found that the weight changes in our experiments were close to the theoretical weight change for Br^- ion migration. DC conductivity of the sample with Au electrodes also suggests that the transport number of electrons was less than 10^{-3}, which will be published in future.

In conclusion, a high Br^- conductivity was obtained at room temperature for the $0.98PbBr_2 \cdot 0.02KBr$ solid solution.

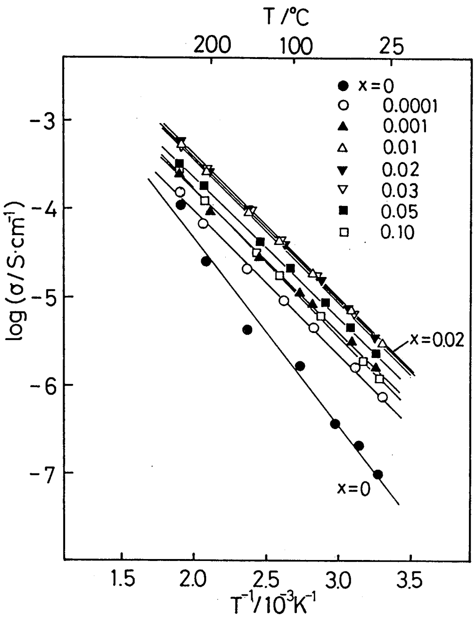
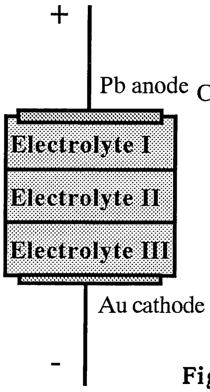


Figure 1. Temperature dependence of the electrical conductivity for the $(1\text{-}x)PbBr_2\text{-}xKBr$ system.



Carrier	Theoretical weight change (mg) Electron	K^+	Pb^{2+}	Br^-	Experimental Result (mg)
I	±0	-6.6	-17.5	+13.5	**+13.6**
II	±0	±0	±0	±0	**-0.4**
III	±0	+6.6	+17.5	-13.5	**-12.3**

Figure 2. Tubant's method

References and Notes

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