

INFLUENCE OF Cs-DOPING ON THE CONDUCTIVITY OF THE SOLID ELECTROLYTE SILVER BROMIDE

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Abstract

A considerable enhancement of the conductivity of solid Silver Bromide by homogeneous doping with Cesium Bromide is reported. The results are explained on the assumption of an increase of the Frenkel defects, due to a lowering of their formation energy resulting from a "lattice loosening" caused by the introduction of the bigger guest cation.

Resumen

Se informa sobre un notable aumento de la conductividad del bromuro de plata sólido obtenido por introducción de iones cesio en la red. Esos resultados se interpretan sobre la base de un aumento en la concentración de defectos tipo Frenkel, asociado con una disminución de su energía de formación, debido a un ablandamiento de la red cristalina, ocasionado por la incorporación del catión huésped.

Introduction

Silver bromide is one of the best-known silver conducting solid electrolytes in which ionic conduction is due mainly to Frenkel defects, i.e. cationic vacancies associated with cations in interstitial sites [1]. Its conductivity follows Arrhenius-type dependence with temperature up to the melting point with activation energy of about 91 kJ/mol [1]. As with other conducting metallic halides, it seems worthy to study the effect of homogeneous doping upon the ionic conduction in AgBr for, in this way, either an improvement of the conductivity or a better understanding of the conduction mechanism may be obtained. In the present work, CsBr was used as dopant in view of the positive effect of caesium ion previously found on CuBr [2] as well as on CuI [3] and AgI [4]. To this purpose, conductivity measurements as well as DTA and X-ray diffraction studies were carried out.

Experimental

Samples of AgBr containing 0, 0.25, 0.50, 1.00, 2.00 and 4.00 mole percent CsBr were prepared by melting together the weighed amounts under pure nitrogen. The

chemicals used were Cerac Micropure (99.99 % purity). In each case, the resulting mixture was ground and pressed into pellets of 7 mm in diameter and thickness of about 3 mm. The conductivity data were obtained from resistance measurements, which were performed by means of a Zahner–elektrik Impedancemeter, and the sample dimensions. The working cell was made by pressing the sample pellet between high purity silver disk by means of stainless steel springs. The cell was located inside a glass furnace with temperature control to ± 2 K protected from light and maintained under purified, dried nitrogen. The temperature range covered between 400 K and 630 K and the measurements were carried out both in heating and cooling cycles. It was observed that for dopant amounts higher than 2 mol% the samples underwent considerable plastic deformation, which made it difficult to obtain sound conductivity values at temperatures higher than about 580 K. For the thermal analysis a Rigaku Thermoflex equipment was used, working at a heating rate of 10 K/min. The X-ray diffractograms were obtained by means of a PW3710 Philips equipment.

Results

The obtained conductivity data for all studied samples are represented in Figure 1 as $\log(\sigma T)$ in $\text{S cm}^{-1} \text{K}$ against $1/T$. The values corresponding to the pure compounds agree with those reported in the literature [1]. As for the doped samples, the Arrhenius-type plots show a change of behaviour at about 490 K. It can be seen that above that temperature the conductivity values increase up to about an order of magnitude with increasing dopant concentration. Besides, the slopes of the plots show that the activation energies decreases with increasing doping, going from 91 kJ/mol (0 mol% CsBr) down to 47 kJ/mol (4 mol% CsBr) as seen in Table I. Below 490 K no influence of Caesium on the conductivity values is detected. This points to the existence of a phase transition, which is absent in the pure compound. This finding agrees with the phase diagram for the system AgBr-CsBr reported by Bradley and Greene [5] which shows an isothermal line at about 480 K extending from about 5 mol% up to 33 mol% CsBr, the latter corresponding to the existence of the congruent melting compound CsAgBr_2 . Above that temperature a two-phase solid - liquid zone appears. It is to be remarked that the diagram published for these authors show no features at compositions lower than about 5 mol% CsBr.

Differential Thermal Analysis

The DTA measurements confirm, within experimental error, the temperature values for the solid - solid transition at about 490 K, as shown in Table 1, which presents the above mentioned results, including the melting temperatures and the activation energies found for the conductivity at the different sample compositions.

X-ray diffractograms. Figure 2 shows diffractograms taken at 470 K for samples containing 1, 2 and 4 mol% CsBr. No peaks corresponding to CsAgBr_2 are observed, which are clearly observed in the diffractograms taken at room temperature (not shown here). This finding, together with the fact that in order to close the phase diagram the solubility must be zero at the melting point of AgBr, allows it to assume solubility values

ranging from about 4 mol% to about 1 mol% in the range of the conductivity measurements, this is matter of further work.

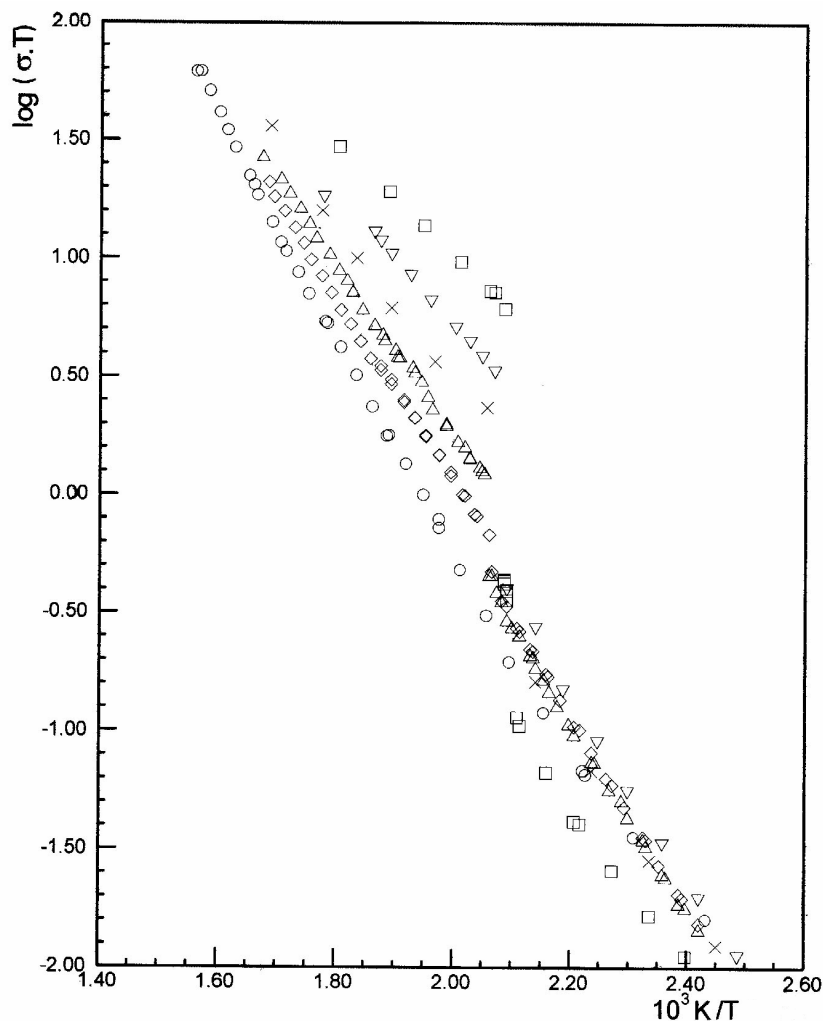


Figure 1: Conductivity times absolute temperature vs $1/T$ for different amounts of CsBr in mol%. \circ : 0.0; \diamond : 0.25; Δ : 0.50; \times : 1.0; ∇ : 2.0; \square : 4.0

Discussion

The observed decrease of activation energy with increasing dopant amount was found in other solid electrolytes in which the homogeneous doping was also carried out with homovalent cations, as in the systems $\text{CaBr}_2 - \text{MgBr}_2$ [6], $\text{AgBr} - \text{CuBr}$ [7] and $\text{AgI} - \text{CsI}$ [4]. It is worthy to recall that, in the case of solid electrolytes conducting via Frenkel-type defects, the activation energy for conductivity involves a kinetic as well as a thermodynamic term. The first is the migration activation energy, associated with the jumping of ions between defect sites, which is about 44 kJ/mol [8] and the second is taken as a half of the energy needed to form a pair of those defects which is about 100 kJ/mol [1]. The sum corresponds, within the experimental error, to the value given above.

Now, the value found in this work for the sample doped with 4 mol% is close to the mentioned value of the migration energy, thus indicating that the doping succeeded in decreasing the formation energy to a very low value.

As it was done in previous work on CsI-doped AgI [4] and CuI [2] the conductivity enhancement may be explained as arising from a "lattice loosening" resulting from the inclusion of the larger caesium ion. Thus, taking into account that the formation energy for Frenkel defects may be assumed as inversely proportional to the interionic distance [9], the decreasing in activation energy would result from an increase in the interionic distance. This effect of doping was indeed found in the present work, as can be seen from Figure 3, in which some data on the variation of the lattice constant with temperature and composition are shown.

Table 1: Transition and melting temperatures and activation energy for Cs-doped AgBr at high temperature.

mol % CsBr	T _{transition} /K		T _{melting} /K	E _α / kJ.mol ⁻¹
	Conduct.	DTA	DTA	
0.00	--	--	699	91.2
0.25	485	491	695	74.3
0.50	488	491	693	66.3
1.00	488	491	691	63.2
2.00	483	489	682	54.1
4.00	483	489	673	47.3

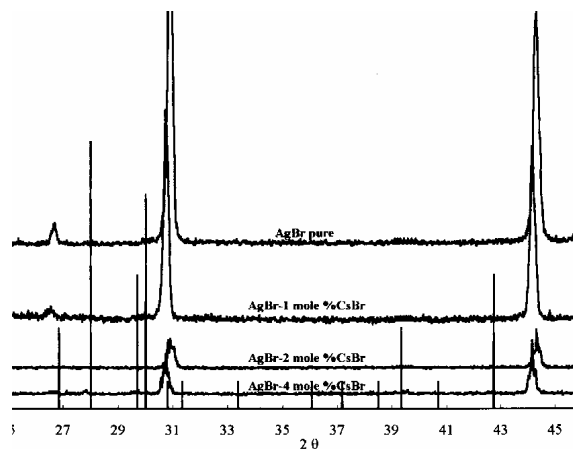


Figure 2: X-ray diffractograms at 470 K. Vertical drawn lines: AgCsBr₂.

It is also worth noting that the vacancy motion activation energy is about 44 kJ/mol, as reported by Teltow [8]. That is, the effect of the homogeneous doping has been to reduce the formation energy from about 50 kJ/mol down to about 6 kJ/mol.

In the present case, however, a second source of conductivity increment cannot be ruled out, arising from the fact that at temperatures higher than 490 K the samples under

study might be considered as a mixture of solid with a minor amount of the molten phase. This point is also supported by the above-mentioned increased plasticity of the samples. That is, the conductivity would increase at least partially due to the contribution of the more conducting molten component, which is probably present along the grain borders. This is at present difficult to quantify, but it can be said that the molten phase conductivity, having surely a much lower activation energy, would not contribute noticeably to the experimentally found total activation energy.

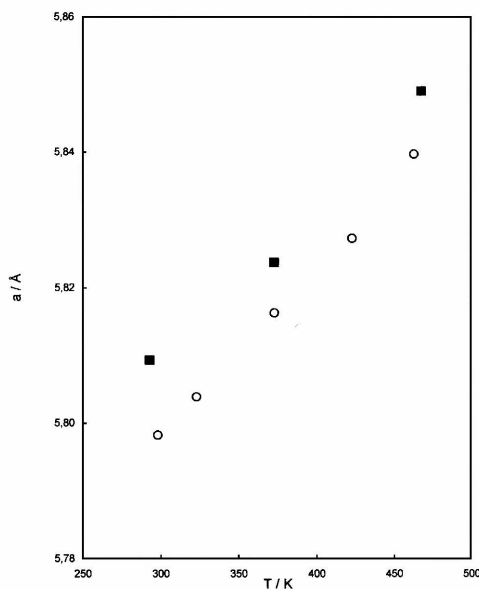


Figure 3: Lattice constants at different temperatures. ○ AgBr; ■ AgBr-2 mol%CsBr

Conclusions

The results obtained demonstrate that homogenous doping with Caesium ions could notably enhance the ionic conductivity of Silver Bromide. As in previously reported cases, this effect may be mainly attributed to an increase in the defects concentration caused by a softening of the halide lattice induced by the incorporation of the larger guest cation.

Acknowledgements

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