

# Ionic conductivity in montmorillonite-doped silver iodide

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## Abstract

The ionic conductivity of AgI–montmorillonite composites was studied at a temperature ranging from 35 to 520 °C. Composites with montmorillonite as small as 0.89 w/o exhibited a maximum of about eight times the conductivity of the pure  $\beta$ -AgI at low temperatures. These results, which can be ascribed to the large surface area of the clay, may be qualitatively explained on the basis of a stabilisation of the low-temperature, higher-conducting metastable  $\gamma$ -phase of AgI.

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## 1. Introduction

Since the early work of Liang [1] and the subsequent one by Wagner [2] and Shahi and Wagner [3], it is known that heterogeneous doping with chemically inert and electrically insulating compounds can enhance the ionic conductivity of solid electrolytes. In this respect, particularly comprehensive has been the work later carried out by Maier on alumina-doped AgBr and AgCl [4,5]. In these papers, an explanation of this effect was proposed on the assumption that the inert surface acts as an attractive centre for silver cations, thus inducing an increase in the defect concentration at the AgBr–Al<sub>2</sub>O<sub>3</sub> interface. Particular is the case of AgI–alumina composites in which, according to recent comprehensive studies by Lee et al. [6,7], the surface effect leads to a structural reorganization of the AgI to give a layered disposition of  $\beta$ - and  $\gamma$ -AgI of much higher conductivity. In an earlier work from our laboratory [8], it was also suggested that the conductivity enhancement is associated with either the formation of a new phase or a strong interaction which stabilises the  $\gamma$ -form of AgI at the AgI/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> interface.

Montmorillonite clay due to its structure of high surface charged platelets was considered a possible heterogeneous dopant. In fact, a previous communication [9] showed a

remarkable increase of conductivity in montmorillonite-doped AgBr. The present paper regards the effect of variable amounts of Ag-exchanged montmorillonite on the ionic conductivity of AgI in a wide range of temperatures.

## 2. Experimental

AgI–montmorillonite samples were prepared by precipitation of AgI directly on aqueous suspensions of Ag-exchanged montmorillonite clay by dropwise addition of 0.5 M solutions of AgNO<sub>3</sub> and KI, keeping an excess of AgNO<sub>3</sub>. This procedure allows montmorillonite to exhibit its maximal specific surface area of about 800 m<sup>2</sup>/g [10] and an optimal contact between AgI and montmorillonite is thus achieved. The product was washed, dried, and ground to powder. Pure AgI powder was prepared in the same way. Details of the procedure are given elsewhere [9]. Several mixtures ranging from 0.3 to 1.5 w/o in montmorillonite were prepared. Structural characterisation of the samples was made by TEM and X-ray diffraction.

For the conductivity measurements, the powder samples were pressed at about 4000 kg cm<sup>−2</sup> to obtain pellets approximately 0.3 cm thick and of 0.6 cm in diameter. These pellets were kept between two silver electrodes under a slight pressure, inside a furnace with temperature control to  $\pm 1$  °C. The cell was maintained under nitrogen at 520 °C for 2 h in order to eliminate any residual water, to sinter the electrolyte compact, and to obtain a good

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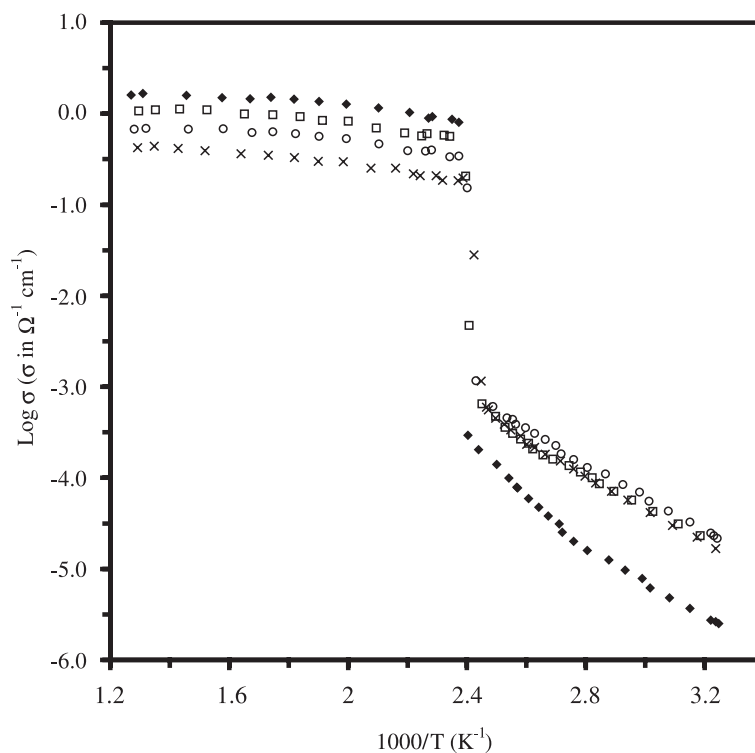


Fig. 1. Arrhenius plot for AgI–montmorillonite composites, (◆) pure AgI, (□) 0.6 w/o, (○) 0.89 w/o, (×) 1.2 w/o.

electrode contact. The measurements were performed in darkness under nitrogen atmosphere by means of an IM5d (and/or IM6e) Zahner-elektrik impedance analyser. The

electrolyte resistance was obtained from Nyquist plots in the frequency range from 1 Hz to 1 MHz. Measurements started at 520 °C and then the sample was cooled stepwise

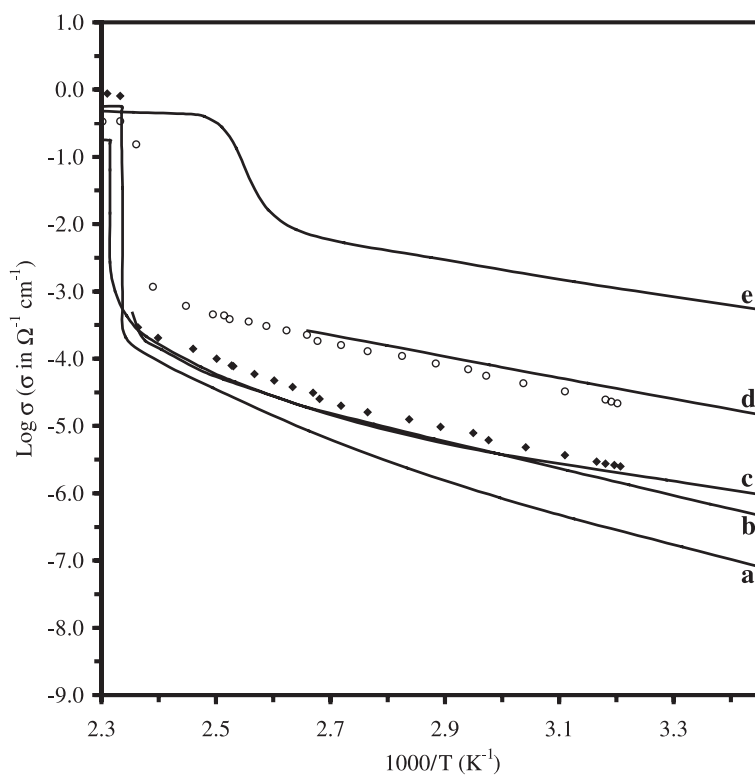


Fig. 2. Arrhenius plot for AgI samples from different authors, (◆) pure AgI, (○) 0.89 w/o; (a) Type I Ref. [12], (b) β-AgI Ref. [11], (c) Type II Poly Ref. [12], (d) γ-AgI form Ref. [11], (e) AgI/γAl<sub>2</sub>O<sub>3</sub> Ref. [7].

to about 35 °C with a holding time not shorter than 3 h before each measurement. After this, two heating and cooling cycles were performed in the same way. The conductivity values were calculated from the geometrical parameters of specimens.

An X-ray diffractometer, Rigaku Dmax III C with Cu K $\alpha$  radiation and graphite monochromator was used in order to determine the phase composition of pure AgI and its composites as powder at room temperature before and after heating to 520 °C. TEM images of composites were obtained with a JEOL 100CX electron microscope, point to point resolution 6 Å, accelerating voltage 80 kV, magnification 20000–40000  $\times$  before and after thermal treatment.

### 3. Results and discussion

Fig. 1 shows the Arrhenius-type plot corresponding to the conductivity data obtained for synthesized montmoril-

lonite–AgI samples as well as pure AgI. Since high temperature  $\alpha$ -AgI is a well-known superionic conductor, the promoting doping effect is evident only in the low-temperature region. The fact that the conductivity of montmorillonite composites above the transition temperature is lower than that of the pure AgI may be explained by the blocking effect of the internal boundaries with respect to the superionic conductivity of the bulk. Similarly as in AgI/ $\gamma$ -Al $_2$ O $_3$  composites [7], Fig. 1 shows that the conductivity decreases as montmorillonite content increases. Below the phase transition temperature, the enhancement on conductivity exhibits a maximum at 0.89 w/o. In contrast to AgI/ $\gamma$ -Al $_2$ O $_3$  [3,6,7], no thermal hysteresis except for that usually observed at the  $\alpha$ – $\beta$  transition of pure AgI was found when the measurements were carried out on heating and cooling cycles.

It is also worth comparing the conductivity data obtained below the phase transition with those reported in the

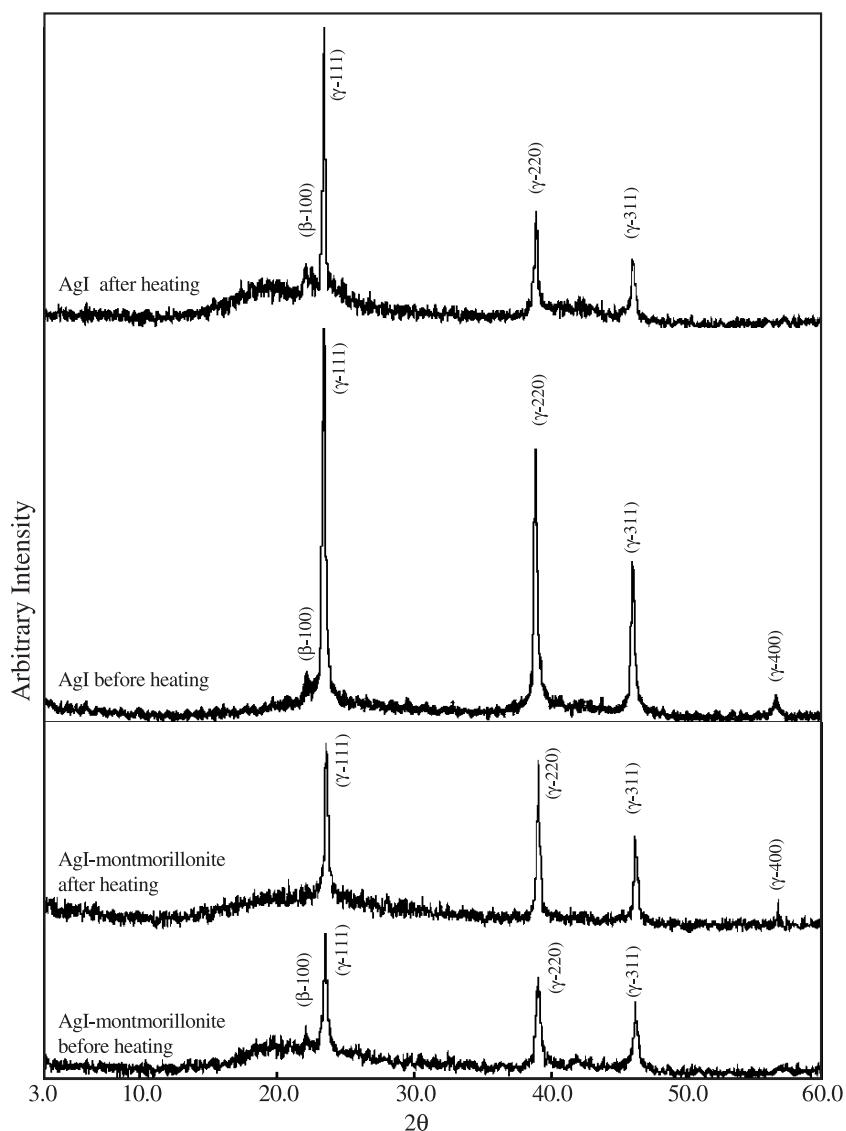


Fig. 3. XRD for pure AgI and 0.89 w/o AgI–montmorillonite composite, before and after heating at 520 °C in nitrogen.

literature for different structural forms of AgI, as shown in Fig. 2. The conductivity values for pure AgI are similar to those reported by Takahashi et al. [11] of a ‘ $\beta$ -AgI’ or by Lee et al. [12] of a ‘Type II Poly’ AgI. In turn, the conductivity values with the 0.89 w/o montmorillonite sample are close to those of a ‘ $\gamma$ -AgI’ [11]. It is also evident that the AgI–montmorillonite composites do not exhibit the thermal hysteresis nor the extreme enhancement, consistent with no formation of 7H polytype or heterostructure in nanoscale as in AgI/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> composites [7]. From the slopes of the Arrhenius plots, activation energies from 0.36 eV for  $\beta$ -AgI to 0.31 eV for the composite with the maximal conductivity were obtained. These values agree with those reported in the literature for both  $\beta$ -AgI and AgI/Al<sub>2</sub>O<sub>3</sub> composites [3]. In particular, the value of 0.31 eV found for the composite which exhibits the maximal conductivity agrees with the ones reported for ‘ $\gamma$ -AgI’ [11] and ‘Type II Poly’ AgI [12].

Fig. 3 shows X-ray powder diffraction pattern for pure AgI and 0.89 w/o AgI–montmorillonite composite at room temperature before and after heating at 520 °C in nitrogen. Before heating, the diffraction pattern for pure AgI shows the three main reflections of  $\gamma$ -AgI, together with a low line at  $2\theta=22.3^\circ$ , which can be identified as a  $\beta$ -AgI reflection on (100) plane. After heating, pure AgI shows an increase of the (100) reflection but no other signal corresponding to  $\beta$ -AgI is found. Thus, pure AgI after heating in this work may be considered  $\gamma$ -AgI mixed with  $\beta$ -AgI, similar to ‘Type II Poly’ AgI. On the other hand, the diffractogram of the composite after the heating cycle prior to the conductivity measurements only exhibits reflections corresponding to  $\gamma$ -form. It is clear that the technique used to prepare pure AgI under Ag-excess promotes the formation of  $\gamma$ -AgI, which upon heating is

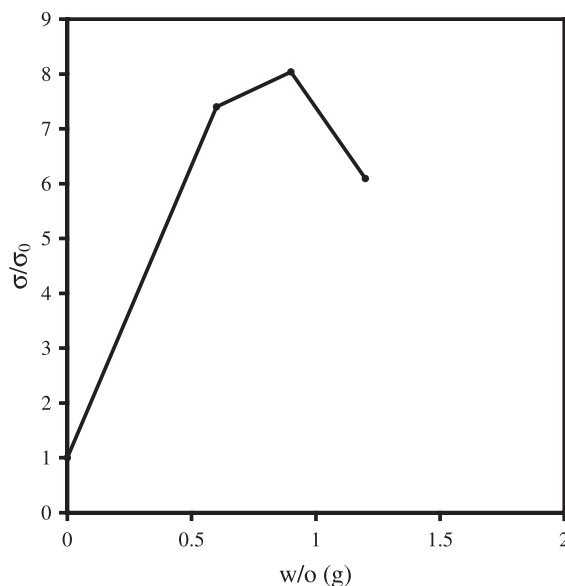


Fig. 5. Conductivity against composition for AgI–montmorillonite composites at 40 °C,  $\sigma_0$  is the conductivity of pure AgI. Composition is expressed in weight percent dopant.

partially transformed into  $\beta$ -AgI. On the contrary, the composite exhibits no such transformation. This could be indicative of a stabilisation of the  $\gamma$ -AgI by interaction with the montmorillonite, a trend already observed in conductivity measurements. Fig. 4 shows a TEM image of 0.89 w/o montmorillonite composites after heating at 520 °C, which confirms a uniform distribution of the clay platelets of about 0.5–1  $\mu$ m. AgI is shown as dark particles partially reduced by the electron beam. It is observed that this reduction takes place more rapidly for samples without thermal treatment. The observation further

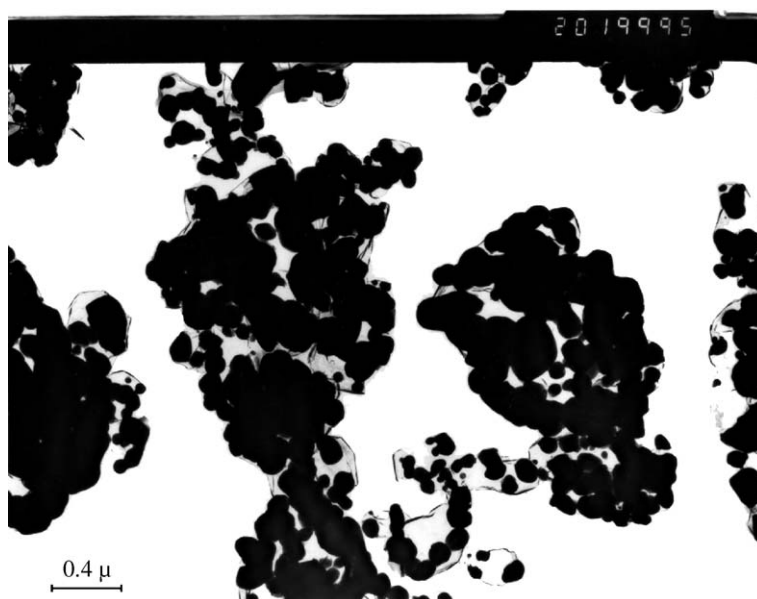


Fig. 4. TEM image of 0.89 w/o montmorillonite after heating at 520 °C in nitrogen.

indicates the stabilisation of the  $\gamma$ -AgI by an interaction between AgI and the clay platelets on heating.

Fig. 5 shows the conductivity as a function of montmorillonite content at constant temperature. The composites exhibit a maximum at about 0.89 w/o of montmorillonite, with a conductivity approximately eight times higher than the pure electrolyte. This optimal amount could be interpreted as a compromise between the increase in conductivity and the blocking effect on the conduction pathways as the amount of dopant augments. It is worth noting that in this case, the amount of heterogeneous dopant needed for reaching the maximum conductivity is considerably lower than that for the AgI–Al<sub>2</sub>O<sub>3</sub> system, namely 15.6 w/o (30 mol.%) [7]. This could be explained by considering that  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with a particle size of 0.06  $\mu$ m has a surface area of 80 m<sup>2</sup>/g [13], whereas the specific surface of montmorillonite as used here is reported to be 800 m<sup>2</sup>/g [10]. Finally, no measurable electronic contribution was found by applying the Wagner–Hebb technique.

#### 4. Conclusions

It has been demonstrated that montmorillonite clay can be a very effective heterogeneous dopant for solid silver iodide due to its large surface area. A considerable enhancement of the ionic conductivity was found. Such enhancement could be explained as resulting from the stabilisation of  $\gamma$ -AgI by the montmorillonite, which is confirmed by X-ray diffraction measurements.

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