

Short Communication

Alpha-phase Stabilization in Silver and Copper Halide Solid Electrolytes

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Silver and copper iodides undergo a phase transition at 145 and 405 °C, respectively, to form a high, ionically conducting α -phase. Statements are often made that this high temperature α -phase can be stabilized at room temperature by the addition of dopant materials [1 - 5], producing electrolytes of high ionic conductivity. It is not immediately apparent whether this merely means that the high conductivity is maintained or also that structural similarity is preserved.

We have studied some of these electrolytes (Table 1) using Debye-Scherrer and Guinier X-ray powder photography, high- and low temperature

TABLE 1

Electrolyte	Mol%	Decomposition temperature (°C)	Conductivity in $S\ m^{-1}$
$(CH_3)_4NI/AgI$	14:86	184	4.6
$(C_2H_5)_4Ni/AgI$	15:85	146	2.5
$(CH_3)_3SI/AgI$	16:84	198	1
$(CH_3)_2S(CH_2)_3S(CH_3)_2I/AgI$	7:93	146	1
$(CH_3)_2S(CH_2)_4S(CH_3)_2I/AgI$	8:92	148	2×10^{-1}
$\text{□}S-(CH_2)_3-S\text{□} \ 2I/AgI$	8:92	160	1×10^{-2}
$(C_2H_5)_3SI/CuI$	15:85	84	2.7×10^{-1}
$\text{◇}S \cdot CH_3I/CuI$	15:85	110	1.2×10^{-1}
$O\text{◇}S \cdot CH_3I/CuI$	16:84	152	1.3×10^{-1}
$\text{□}S \cdot (CH_2)_3 \cdot S\text{□} \ 2I/CuI$	15:85	144	4×10^{-4}
$(CH_3)_2S(CH_2)_4S(CH_3)_2I/CuI$	15:85	147	2.3×10^{-5}

diffraction, and differential thermal analysis (d.t.a.). Silver iodide does not give well-defined X-ray powder photographs; it has high absorption of, and shows discolouration on exposure to, X-rays, and exists as two phases,

β and γ , at room temperature. Regardless of the method of preparation, a mixture of β - and γ -AgI will be formed on standing for a few hours.

On investigation, all Table 1 electrolytes showed diffractometer peaks due to the room temperature form of AgI or CuI; none was missing and no peaks corresponded to the parent dopant material, but small extra peaks were present, Fig. 1. The peaks expected for α -AgI or α -CuI were always absent. Regardless of the method of preparation [6], the onset of high ionic conductivity coincided with the appearance of the extra peaks.

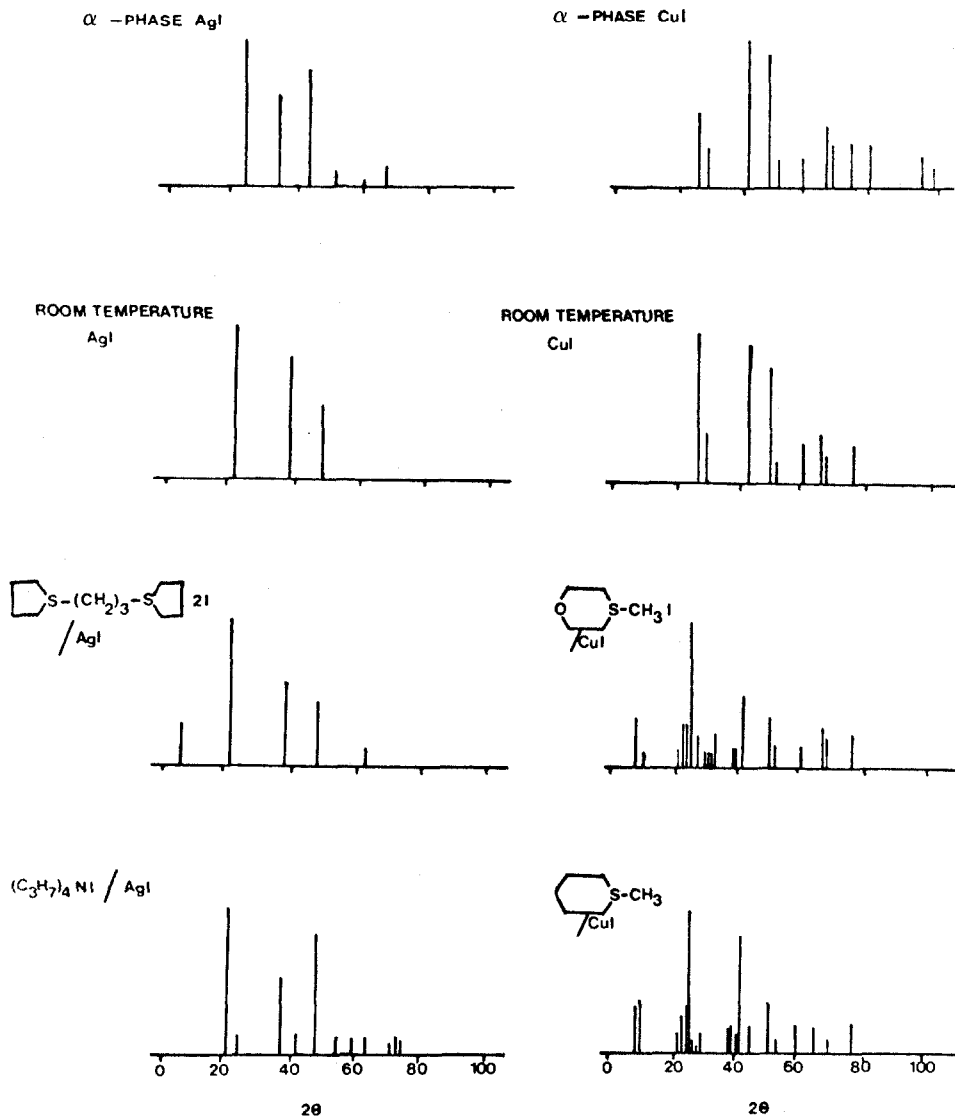


Fig. 1. Diffractometer traces of AgI and CuI electrolytes.

The absence of the $\beta \rightarrow \alpha$ transition, as detected by d.t.a. and high temperature Guinier X-ray photography, is an indication that compound formation has occurred. Unfortunately, these techniques cannot be carried out on all the electrolytes in Table 1 because of the low decomposition temperature of the organic dopant, and none can survive to the transition temperature of CuI. Two AgI-based electrolytes were studied, $(\text{CH}_3)_3\text{SI}/\text{AgI}$ and $(\text{CH}_3)_4\text{NI}/\text{AgI}$ and in these the $\beta \rightarrow \alpha$ transition at 145°C was completely absent, Fig. 2.

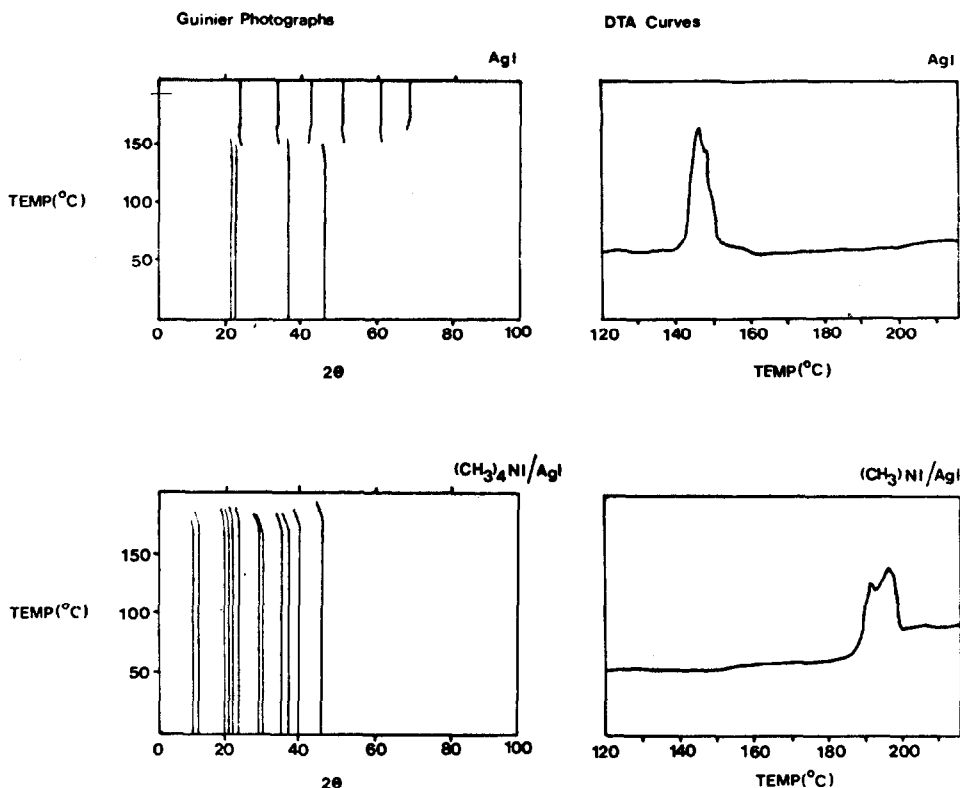


Fig. 2. High temperature Guinier X-ray data and d.t.a. curves for AgI, showing the $\beta \rightarrow \alpha$ transition, and $(\text{CH}_3)_4\text{NI}/\text{AgI}$, where the $\beta \rightarrow \alpha$ transition is absent.

Single crystals of compounds with the same stoichiometry as some of these electrolytes have been prepared [7] and full crystal structures determined. Unfortunately, to date, the results of conductivity measurements on these single crystals have not been published. Comparison of the powder diffraction data reported here with the single crystal studies of $|(\text{CH}_3)_4\text{N}|_2/\text{Ag}_{13}\text{I}_{15}$, [6], showed that the former are compatible with the electrolyte structure found for the single crystal.

From the above evidence, together with d.t.a. and Guinier photography, it seems that for $|(\text{CH}_3)_3\text{N}|_2/\text{Ag}_{13}\text{I}_{15}$, compound formation has occurred, but

that the compound has a similar structure to room temperature AgI, not α -AgI. The same is likely to be true for the other AgI- and CuI-based electrolytes in Table 1. X-ray powder diffraction evidence for compound formation rests therefore on the appearance of new peaks, not on the shift of original AgI or CuI peaks.

We conclude that the intention behind the statement that the α -phase is stabilized in copper- and silver halide electrolytes is that conductivity commensurate with that of the α -form is achieved; no structural implication is permissible.

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