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Investigations on Transport, Thermal, and Structural Properties of $(CuI)_{100-x}$–$(Ag_3PO_4)_x$ ($0 \leq x \leq 60$) Fast Ionic Conductors

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The silver orthophosphate–cuprous iodide (Ag_3PO_4–CuI) mixed system in the solid state has been thoroughly studied using ac impedance analysis, transport number measurements, differential scanning calorimetry (DSC), and X-ray diffraction (XRD). Polycrystalline samples having 12 different mol% Ag_3PO_4, viz., 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, and 60, have been synthesized by the melting process. The ac impedance analysis carried out on pellet specimens over the temperature range 293–403 K and in the frequency range 1 Hz–65.5 kHz has revealed that a composition of 50 mol% Ag_3PO_4–50 mol% CuI would possess a silver ionic conductivity as high as 1×10^{-2} S cm^{-1} at 303 K and a low activation energy of 0.14 eV for Ag^+ ion migration in the above temperature range. This result has been further confirmed by the measurement of the transport number of silver ions in this system which is found to be ≈ 1 (as determined by the emf method). Detailed XRD and DSC studies carried out on various compositions have indicated a crystal structure which may be favorable for fast ionic transport in these materials. The formation of fast ion conducting materials exhibiting high silver ionic conductivity in the above mixed system has been attributed to ion exchange chemical reactions which appear to occur in the molten state.

Introduction

Fast ion conducting materials in both polycrystalline and glassy forms are currently being extensively investigated in view of their potential applications in various technological areas, such as electrochemical power sources, sensors, optical devices, lasers, fuel cells, and double-layer capacitors (*1–6*).

In recent years, significant work has been carried out on AgI–silver oxysalts and some of these show glass-type structures with high ionic conductivity at ambient temperatures (*7–9*). From the practical point of view, many works concerning replacement of Ag^+ ions in AgI by Cu^+ ions have been published because of the fact that CuI possesses structural properties similar to AgI and is less expensive than AgI (*10–13*). Rivolta *et al.* (*14*) have reported that it is possible to obtain silver ion conductors in the CuI–Ag_3PO_4 system. Synthesis of amorphous fast ionic conductors using CuI is normally difficult due to its very unstable nature. However, by optimizing the processing and melting conditions, it is possible to avoid the decomposition of CuI while preparing polycrystalline fast ionic conductors. Hence, powder studies have been preferred for the present investigation, which has been undertaken with the primary objective of identifying the best conducting composition in the mixed system $(CuI)_{100-x}$ $(AgPO_4)_x$ ($0 \leq x \leq 60$) through detailed transport, structural, and thermal studies.

Experimental

Preparation of Samples

Ag_3PO_4 was prepared as a solid specimen following the method suggested by Takahashi *et al.* (*7*). Cuprous iodide was pre-

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pared using reagent grade copper sulfate and potassium iodide by the precipitation method in an aqueous medium. The iodine liberated during the process was removed by treating the precipitate with an aqueous solution of sodium thiosulfate. The precipitate was then washed several times with doubly distilled water before being dried in a vacuum oven. All the chemicals used were of research grade with high purity.

The $(CuI)_{100-x}$–$(AgPO_4)_x$ $(0 \leq x \leq 60)$ mixtures were prepared by taking appropriate mole percents of the two starting materials, namely CuI and Ag_3PO_4. The powder mixtures were ground thoroughly, sealed in Pyrex tubes under vacuum (10^{-5} Torr to avoid any iodine liberation), and annealed at 723 K for 20 hr to allow for complete melting. The resulting solidified material after fast quenching to room temperature was used for further studies.

Characterization Studies

Differential scanning calorimetry (DSC). Using a Perkin–Elmer model DSC7, in conjunction with a Perkin–Elmer 3700 data station, DSC measurements were carried out on all the various compositions in the mixed system CuI–Ag_3PO_4 over the temperature range 303–673 K at a heating rate of 10°/min, in order to determine the phase transition temperatures in these materials.

X-Ray diffraction (XRD). To determine the formation of any new high conducting material, a JEOL JDX-8030 X-ray diffraction system controlled by a NEC/PC 9801 VX computer was employed. The powder XRD data for all the samples have been collected using Cu K_α radiation (λ = 1.5418 Å).

Transport Studies

AC impedance analysis. Finely ground powder specimen of the various compositions pressed together with electrodes (silver + sample in the weight ratio 2 : 1) on either face under the pelletizing pressure of 4 ton/cm^2 to form circular pellets with 12 mm diameter were used for ac electrical conductivity studies. A Solartron model 1254 four-channel frequency response analyzer and a Solartron model 1286 electrochemical interface, in conjunction with a BBC model B$^+$ microcomputer, was used for the analysis in the frequency range 1 Hz–65.5 kHz, and over the temperature range 293–403 K. A chromel–alumel thermocouple was employed to record the sample temperature.

Transport number measurements. The silver ion transport number in the synthesized samples was determined by an emf method using the electrochemical cell.

$$(-)\text{Ag} + \text{E}\ (2:1)/\text{electrolyte}/\text{I}_2(+) \quad (1)$$

in which the overall cell reaction is

$$\text{Ag} + \tfrac{1}{2}\text{I}_2 \rightarrow \text{AgI}. \quad (2)$$

The transport number of Ag^+ ions is given by the ratio $t = E_0/E_t$, where E_0 is the observed emf and E_t the theoretical emf (in this case 687 mV) of the cell.

Results and Discussion

X-Ray Diffraction (XRD) and Differential Scanning Calorimetry Results

Figure 1 shows the typical XRD patterns obtained for three different compositions, viz. 45, 50, and 55 mol% of Ag_3PO_4, carried out at room temperature. Samples having higher CuI content in the range 70–90 mol% are found to show a gradual shift in *d*-spacing corresponding to the most intense lines. A systematic search for the identification of various peaks observed during the present investigation clearly suggests the presence of peaks corresponding to metallic silver for the composition from 30–60 mol% Ag_3PO_4 and peaks of silver iodide in both 40 and 45 mol% Ag_3PO_4. A few weak peaks of silver, silver iodide, and a series of unidentified peaks probably related to new phases have been noticed for the sample with a composition of 50 mol% Ag_3PO_4. It is clear from these observations that a new substance

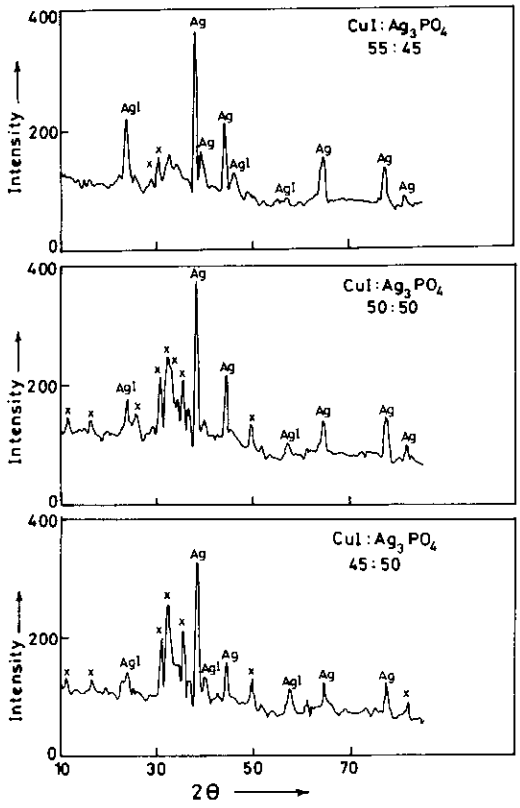

FIG. 1. XRD patterns of CuI–Ag_3PO_4 mixed system for three different compositions; viz., 45, 50, and 55 mol% Ag_3PO_4.

may be formed in the case of 50 mol% Ag_3PO_4 samples.

The DSC results for the various compositions of Ag_3PO_4 as presented in Table I reveal that all the samples except samples having compositions of 40 and 45 mol% Ag_3PO_4 exhibit an endothermic peak of melting at around ≈552 K, whereas these two samples possess endothermic peaks at 423 and 420 K, respectively, probably ascribable to the presence of silver iodide (*14*) ($\beta \rightarrow \alpha$ phase transition). The X-ray analysis has also confirmed the presence of silver iodide in these compositions. By correlating the results of XRD and DSC, the reaction between the two starting materials, namely Ag_3PO_4 and CuI, is found to be complete for the compositions 40, 45, and 50 mol% Ag_3PO_4.

AC Impedance Analysis

The bulk transport has been established from the ac impedance analysis by determining the bulk resistance of the electrolyte by appropriate extrapolations on the real axis of the complex impedance plots (Z' vs Z'') at higher frequencies. Complex impedance plots obtained for the composition 50 mol% CuI–50 mol% Ag_3PO_4 at four different temperatures, 303, 323, 333, and 363 K, are depicted in Fig. 2. A part of the depressed circular arc (DCA) with its center displaced below the real axis (Z') with a low-frequency spur inclined at an angle approximately 45° to the real axis is present. As per the general theory proposed by MacDonald (*15*) for solid electrolytes having parallel nonblocking electrodes, the point of intersection of the impedance plot on the real axis at high frequency range predominantly gives the bulk resistance of the sample, eliminating other effects like grain boundary, etc. In Fig. 2, a shift toward the origin, i.e., toward the high-frequency side, with an increase in temperature is evident. This clearly indicates that, at high temperatures, the bulk resistance of the sample decreases, resulting in the enhancement of electrical conductivity and thus obeying the Arrhenius law. The depressed circular arc is indicative of non-Debye behavior which has been commonly observed in real solid

TABLE I

DSC DATA FOR THE SYSTEM CuI–Ag_3PO_4

Mol% Ag_3PO_4	Endothermic peak position (°K)
5	552
10	552
15	526
20	550
25	552
30	548
35	559
40	423
45	420
50	552

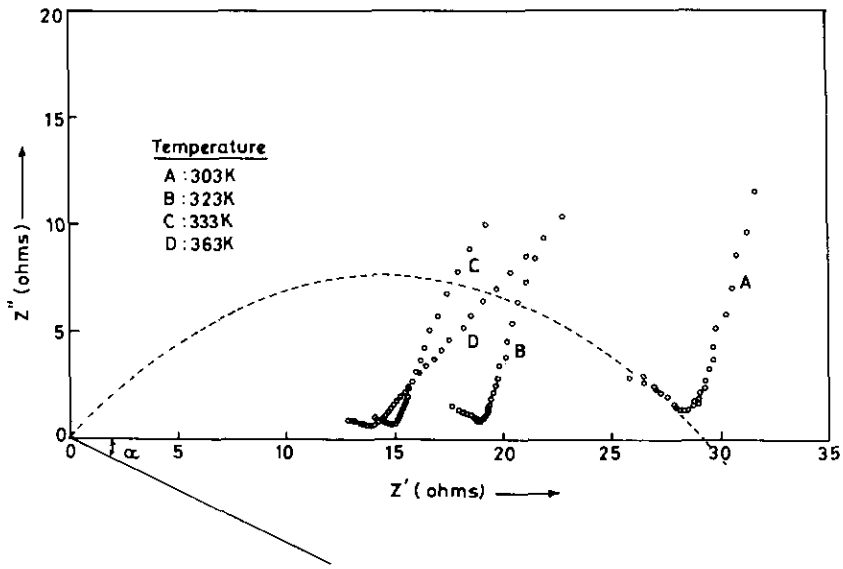

FIG. 2. Complex impedance plots for the composition 50 mol% CuI–50 mol% Ag_3PO_4 at various temperatures.

electrolytes (*16, 17*), while the low-frequency spur predominantly represents the electrode/electrolyte interfacial effects (*16, 18*) which have been present for almost all solid electrolytes with very high ionic conductivity (*19*).

Figure 3 shows the room temperature conductivity–composition curve of the CuI–Ag_3PO_4 system for a series of compositions. This curve shows a maximum conductivity of 8.3×10^{-3} S cm^{-1} for a composition of 50 mol% Ag_3PO_4. As this conductivity

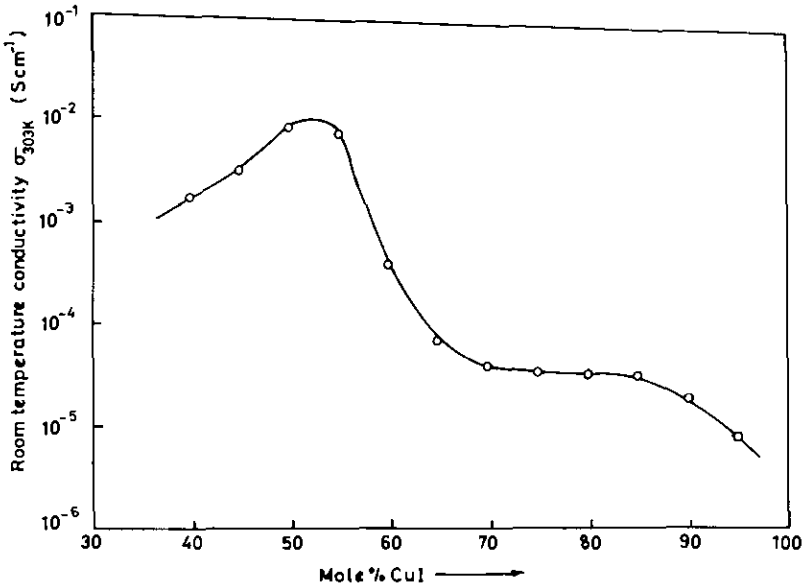

FIG. 3. Electrical conductivity variation in the system CuI–Ag_3PO_4 with the composition of Ag_3PO_4 at room temperature.

value is higher than that of the starting materials, i.e., Ag_3PO_4 and CuI, an indication of the possible formation of a new intermediate compound at this composition may be inferred. This result is further supported by the presence of unidentified peaks appearing in the XRD pattern of this particular composition.

All these results combined indicate that the system CuI–Ag_3PO_4, with 50 mol% each, acts as a fast ionic conductor having properties similar to those of a silver ion conducting solid electrolyte system like AgI–Ag_3PO_4.

The combination of Ag_3PO_4 and CuI has been observed to result in the formation of metallic silver, silver iodide, and a new phase which may be responsible for the high Ag^+ ionic conduction (Fig. 1). Therefore the following simplest scheme for this solid state reaction between Ag_3PO_4 and CuI may be proposed,

$$Ag_3PO_4 + CuI \rightarrow AgI + Ag + CuAgPO_4, \quad (3)$$

which is similar to the reaction proposed earlier by Rivolta *et al.* (*14*) for the system CuI–Ag_3AsO_4. Accordingly, $CuAgPO_4$, possibly a new compound formed with a disordered structure, may be responsible for the enhanced electrical conductivity of the sample having 50 mol% Ag_3PO_4. New phase formation different from the starting materials, i.e., Ag_3PO_4 and CuI, has already been revealed by the XRD pattern recorded for the sample. The absence of strong AgI peaks in the XRD pattern and of a specific endothermic peak around 423 K ($\beta \rightarrow \alpha$ phase transition of AgI) in the DSC trace also substantially shows the evidence that the proposed reaction (Eq. (3)) is complete and that the product must be a new compound with a disordered structure associated with fast ionic transport. To this date, no ASTM X-ray data file is available for the material $CuAgPO_4$. The fact that Eq. (3) represents the possible reaction products, and that the presence of AgI and Ag has been confirmed by XRD studies, suggests that $CuAgPO_4$ must be the unidentified reaction product. Hence, no attempt was made to synthesize and analyze $CuAgPO_4$ separately. For the sample with a composition of 40 mol% Ag_3PO_4, the peaks of AgI were predominant which is also reflected from its characteristic DSC endothermic peak around 423 K ($\beta \rightarrow \alpha$ transition). The observed conductivity value of the order of 10^{-4} S cm^{-1} for this composition also shows that it is mainly due to AgI. But in the case of a sample with the composition 45 mol% Ag_3PO_4, though the presence of AgI is seen from XRD and DSC results, an enhanced conductivity of the order of $\approx 10^{-3}$ S cm^{-1} is noted, indicating that the conductivity is partially due to AgI and a new compound. These results reveal that the proposed reaction (Eq. (3)) is complete and that the amount of the reaction product AgI is reduced by the increase of Ag_3PO_4 while the amount of high conducting compound $CuAgPO_4$ is increased. These results are in good agreement with the XRD results because of the fact that the XRD patterns for the compositions around 50 mol% Ag_3PO_4 contain only a few weak AgI and Ag peaks.

For the galvanic cells constructed as given in Eq. (1), the transport number values of the silver ion have been estimated to be in the range 0.92–0.98 for the samples with more than 25 mol% Ag_3PO_4, indicating that Ag^+ ions are the mobile species in these new materials and that the electronic contribution to the total conductivity is negligible. For the samples having Ag_3PO_4 content of less than 25 mol%, the conductivity is also very poor which is very well implied in Fig. 3. The effect of metallic silver present may be negligible as it may be dispersed highly in the bulk. A similar effect has been reported by Rivolta *et al.* (*14*) for the CuI–Ag_3AsO_4 system. From these data, the high conducting material with a composition of 50 mol% Ag_3PO_4 has been found to exhibit a silver ionic transport number of approximately unity, thus establishing the fact that it is a fast ionic conductor.

Figures 4a and 4b indicate the variation of electrical conductivity with temperature measured in the range 293–403 K for the

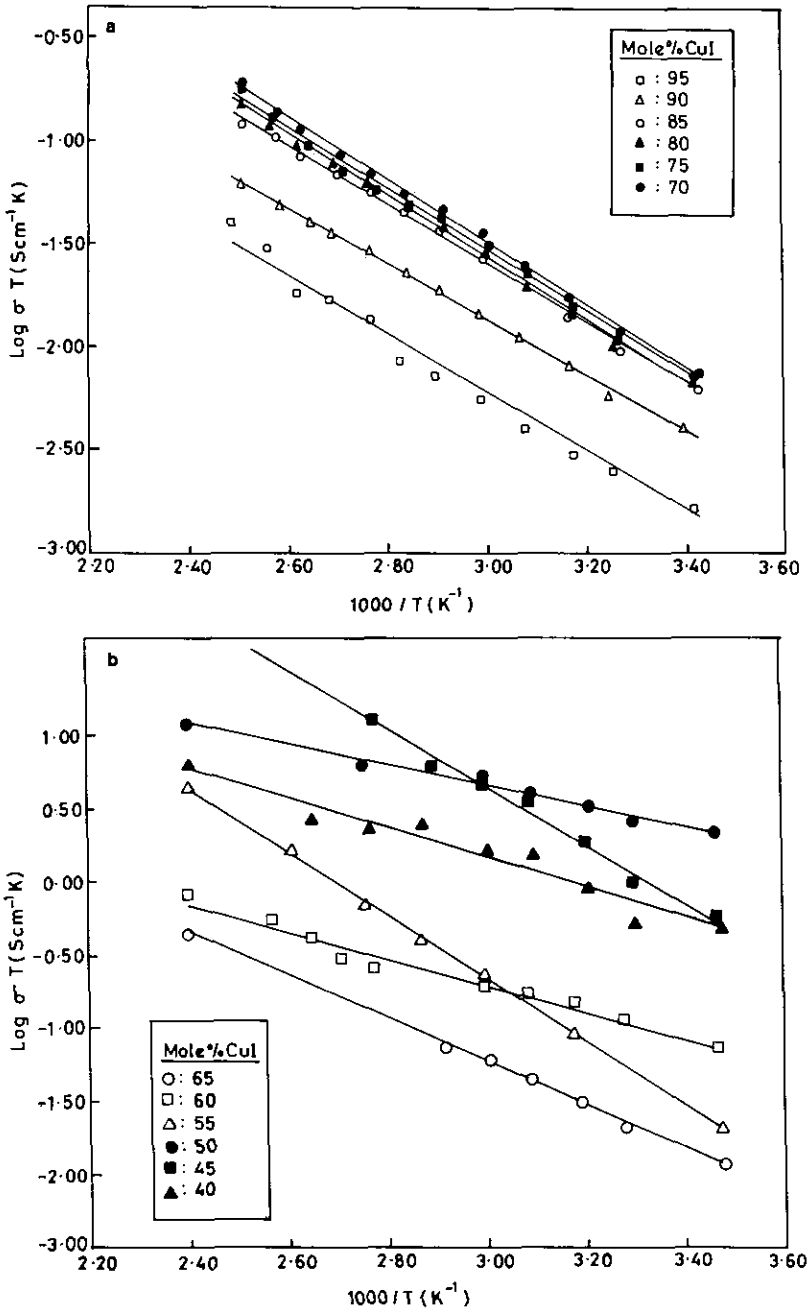

FIG. 4. (a)–(b), Arrhenius plots (log σT vs $1/T$) for different compositions in the system CuI–Ag_3PO_4.

samples containing 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, and 60 mol% Ag_3PO_4, respectively. All these plots obey Arrhenius behavior, satisfying the equation

$$\sigma T = \sigma_0 \exp(-E_a/kT), \qquad (4)$$

where σ_0 is the pre-exponential factor, T the absolute temperature, E_a the activation

TABLE 2

Sample	Composition Ag_3PO_4–CuI (mol%)	RTC σ_{RT} S cm^{-1}	E^* (eV)	DSC peaks (°C)	t_{ion}
1	5–95	7.92 E-6	0.28	279	0.25
2	10–90	1.89 E-6	0.27	279	0.49
3	15–85	3.18 E-5	0.30	253	0.45
4	20–80	3.22 E-5	0.28	276	0.85
5	25–75	3.48 E-5	0.29	279	0.92
6	30–70	3.94 E-5	0.30	274	0.95
7	35–65	6.71 E-5	0.30	286	0.98
8	40–60	3.76 E-4	0.18	150	0.98
9	45–55	7.05 E-3	0.43	147	0.97
10	50–50	8.26 E-3	0.14	279	0.97
11	55–45	3.17 E-3	0.40		0.98
12	60–40	1.71 E-3	0.20		0.97
13	100–0	>10 E-7	—	—	—

Note. E^* is Activation energy, t_{ion} is Ag^+ ionic transport number, and RTC is room temperature conductivity.

energy, and k the Boltzmann constant. The activation energy for the silver ion migration calculated from the plots ranges from 0.14–0.43 eV. The best conducting composition, as established by other studies, which has a composition of 50 mol% Ag_3PO_4, is found to have the lowest activation energy, 0.14 eV. This particular composition may therefore be suitable as a good candidate for electrochemical applications. The linearity shown in the log σT vs $1/T$ plots clearly indicates that the synthesized solid electrolyte materials are thermally stable from ambient to 403 K. The low activation energies for the materials having appreciably high ionic conductivity reflect that the electrical conductivity is less temperature dependent. Table II gives the summary of the experimental results obtained for the system CuI–Ag_3PO_4.

Ion-Exchange Chemical Reactions

The formation of a high silver ionic conducting material, by the reaction between Ag_3PO_4 and CuI, may be due to the ion exchange reaction. The exchange reaction is favored because of the effects of softness of the Lewis acids, and of silver and copper ions which are classified as soft by Pearson (*20*). From the rule proposed by Pearson, that "hard acids bind strongly to hard bases and soft acids bind strongly to soft bases," the reaction expected when CuI is mixed with the oxysalt Ag_3PO_4 is that a AgI or Ag^+ based compound may be formed (as I^- is also a soft base), depending on the CuI mol% present in the mixture CuI–Ag_3PO_4 during the melting process. Ion exchange has been reported for similar systems by Malugani *et al.* (*21*). Formation of AgI has also been noted in the case of the CuI–Ag_3AsO_4 mixed system by Rivolta *et al.* (*14*) and Sukeshini and Hariharan in the case of CuI–Ag_2O–MoO_3 (*22*). The present experimental results also support the presence of AgI in some of the compositions synthesized. This formalism further supports the proposed chemical reaction (Eq. (3)) between Ag_3PO_4 and CuI, resulting in the formation of a new high Ag^+ ion conducting material with 50 mol% Ag_3PO_4 and 50 mol% CuI.

Conclusions

This paper presents the study involving the synthesis and characterization of the mixed system Ag_3PO_4–CuI. The transport, thermal, and structural studies carried out have shown that the system with 50 mol% Ag_3PO_4–50 mol% CuI exhibits the highest Ag^+ ionic conductivity of 8.3×10^{-3} S cm^{-1} at room temperature, with an activation energy of 0.14 eV for Ag^+ ionic migration. These materials are found to be extremely stable in the temperature range 293–403 K, as well.

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