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IMPEDANCE SPECTROSCOPY STUDIES OF Ag_2BI_4 (B=Cd, Hg) FAST IONIC CONDUCTORS

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INTRODUCTION

Superionic solids (solid electrolytes) represent a specific class of condensed matter, exhibiting anomalously high values of ionic conductivity, compared to those of liquid electrolytes. Generally, superionic conductivity results from the large number of intrinsic defects and the low values of activation energy for the hopping movement of ions [1]. One of the most intensively studied solid electrolyte ever is silver iodide, AgI, which is known to undergo a phase transition from non-superionic β-phase to the disordered superionic α-phase at 420 K [2–4]. Much effort has also been put by different workers into the investigation of the family of its ternary derivatives – $AgI–BI_2$ systems [5]. These compounds are obtained by the replacement of two Ag^+ cations in AgI lattice by single B^{2+} cation, where B=Hg, Cd, Pb, Zn.

Ag_2HgI_4 and Ag_2CdI_4 fast ionic conductors are attracting interest first of all as model objects for studying of the phase transitions into a superionic state. A lot of electrical conductivity studies have been reported up to now for the $AgI-HgI_2$ system [6–10], while only a limited number of works deal with the electrical properties of Ag_2CdI_2 [11,12]. In Ag_2HgI_4 the phase transition into the state with high ionic conductivity takes place at the fixed temperature [8], whereas in Ag_2CdI_4 one may observe the sequence of transitions upon heating from room temperature [13].

One of the most powerful techniques used for the electrical characterization of the fast ionic conducting systems is impedance spectroscopy. Impedance spectroscopy techniques are widely applied to polycrystalline solid electrolytes for identification of different physical and chemical processes involved [14]. Various parameters like transport numbers, concentrations of charge carrying species, electronic and ionic defects mobility etc. could be determined through analysis of impedance spectra.

Impedance spectra for Ag_2HgI_4 have been reported in limited frequency/temperature range and were found to be strongly influenced by preparation conditions and different physical factors. To our knowledge, no detailed investigations of temperature dependence of Ag_2CdI_4 impedance spectra have been carried out. Therefore this paper presents the results of impedance studies performed for both of these silver iodide-based superionic compounds in the wide range of temperatures and frequencies.

EXPERIMENTAL DETAILS

Ag_2CdI_4 and Ag_2HgI_4 solid electrolytes were obtained in the bulk polycrystalline form, using solid state chemical reactions. For this purpose a pressed fine-grained dispersed mixture of AgI and CdI_2 (HgI_2) with the stoichiometric ratio 2:1 was annealed at temperatures, lower than peritectical ones during more than 240 hours. Due to the peritectic type of Ag_2CdI_4 crystallization in case of this compound this is the only possible way of synthesis. For the electrical measurements cylindrical pellets (diameter $d \approx 8$ mm, thickness $h \approx 3$ mm) were formed under the pressure of 10^6 Pa.

Impedance measurements were made with impedance gain–phase analyzer Shlumberger 1260, providing the range of impedances measured from 10 Ω to 10 MΩ [15]. Spectra were recorded for the frequencies, ranging from 10 Hz up to 1 MHz in the temperature region of 290 to 400 K for Ag_2HgI_4 and 290 to 450 K for Ag_2CdI_4. ZView 2 Demo software package was for the equivalent circuit modeling and simulations.

RESULTS AND DISCUSSION

Frequency dependencies of real and imaginary parts of complex impedance measured for the Ag_2CdI_4 and Ag_2HgI_4 show typical behavior for both investigated samples (Fig. 1). Frequencies of the peaks observed in Im $Z\,(f)$ curves shift towards higher values at elevating temperatures. In terms of characteristic time constant, taking into consideration hopping model of ionic transport [3], this means that average time between two consecutive jumps of the mobile ion decreases upon heating.

Complex impedance plots for both compounds are shown in Fig. 2. At higher temperatures and lower frequencies, spectra are strongly influenced by the electrode processes represented by the 45 degree line at the complex plane [14].

Excluding the very-low frequency part, the typical impedance spectrum of Ag_2CdI_4 within the temperature range of measurements can be satisfactorily reproduced by the semicircle, displaced below the real axis. Such form of the spectra corresponds to the equivalent circuit, illustrated at Fig 3, *a*. Here R_{bulk} denotes a bulk resistance while Constant Phase Element (CPE), impedance of which is defined as follows

$$Z_{\text{CPE}} = \frac{1}{A(j\omega)^N},$$

characterizes bulk capacitance and non-homogeneity of charge distribution. The resistance connected in series implies that impedance arc does not pass through the origin. The circuit at Fig 3, *a* is completely described by four parameters, which are listed in the table 1. Due to the relatively small values of R_S the error of its determination is substantial. Errors in estimation of A, R_{bulk} and N do not exceed 10 %, 4% and 1% from the respective absolute values.

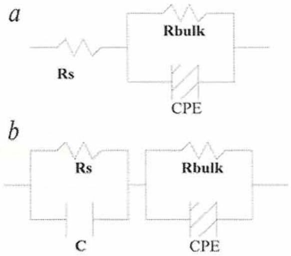

Figure 3. Equivalent circuits used for modeling of Ag_2CdI_4 (*a*) and Ag_2HgI_4 (*b*) impedance spectra.

Table 1. Ohmic parameters of Ag_2CdI_4 as determined from non-linear least squares fit of the measured impedance spectra at different temperatures.

T, K	R_S, Ohm	R_{bulk}, Ohm	$A\times10^{-11}$, F	N
332	3000	1459100	0,67	0,96
342	2700	968060	0,73	0,96
352	1100	315320	1,61	0,91
362	2360	157720	1,62	0,92
372	3350	72752	1,70	0,92
382	3480	27925	2,34	0,92
392	2750	11525	5,89	0,88
402	2090	5255	24,94	0,81

Despite the fact that investigated compounds are isostructural, the same circuit can not be used for the correct fitting in case of Ag_2CdI_4 and Ag_2HgI_4.

One may suggest the spectrum, obtained for the AgI-HgI_2 superionic system at given temperature, contains two partially overlapping semicircles. One of these arcs, slightly depressed below the real axis, taking into consideration the preparation method, should be ascribed to the bulk properties of the material. Other semicircle in this case is probably a manifestation of grain boundary effects. The equivalent circuit shown at Fig 3, *b* was used for fitting the experimental data. Evaluated ohmic parameters are presented in table 2.

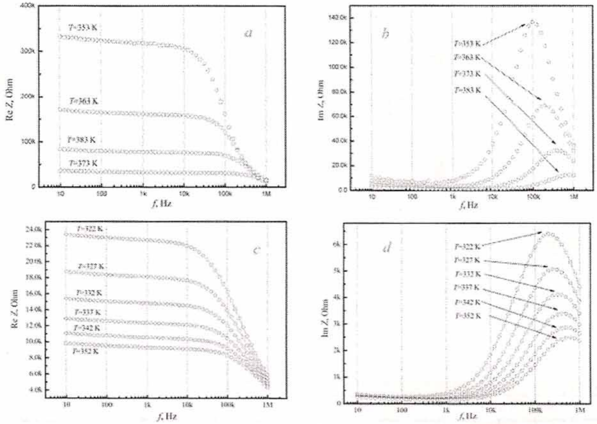

Figure 1. Plots of real and imaginary parts of complex impedance versus frequency for two superionic compounds at different temperatures: *a*, *b* – Ag_2CdI_4, *b, c* – Ag_2HgI_4.

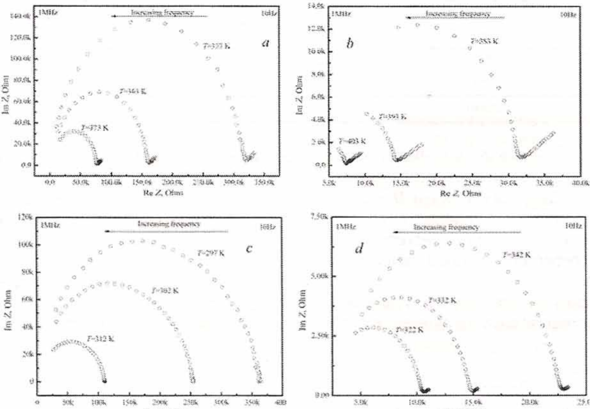

Figure 2. Complex impedance plots for Ag_2CdI_4 (*a*, *b*) and Ag_2HgI_4 (*c*, *d*) superionic compounds at different temperatures.

Table 2. Ohmic parameters of Ag_2CdI_4 as determined from non-linear least squares fit of the measured impedance spectra at different temperatures.

T, K	R_S, Ohm	$C\times10^{-12}$, F	R_{bulk}	$A\times10^{-10}$, F	N
297	59329	7,85	308440	6,4	0,67
302	33412	1,05	224970	7,7	0,66
307	14582	1,73	160730	9,45	0,64
312	5835	1,60	108130	11,54	0,64
317	5925	3,15	45777	21,33	0,66
322	4194	3,11	19014	83,93	0,60
327	3367	3,12	15083	80,74	0,60
332	2774	3,13	12267	77,35	0,61
337	2361	3,11	10111	72,02	0,61
342	2028	3,08	8570	68,14	0,62
347	1802	2,99	7520	64,08	0,62
352	1654	2,85	6573	53,00	0,63
357	1512	2,73	5606	40,22	0,64
362	1396	2,59	4815	27,21	0,66
367	1264	2,51	4094	15,25	0,68

The listed values of R_S and C should be treated as tentative ones, especially at lower temperatures, where the relative error reaches up to 30%. The parameters corresponding to the bulk properties are determined more precisely and the relative errors are not larger than 5% for pseudo capacitance and 3% for resistance.

For both investigated systems, calculated values of bulk ionic conductivity (which is reciprocal bulk resistance with taking into account geometric factor) show typical superionic behaviour. In case of Ag_2HgI_4 the superionic phase transition can be clearly identified to take place within the region of 317 – 322 K, while due to the electrode processes at higher temperatures only pretransitional changes in conductivity, starting from nearly 380 K was observed. These results are in good agreement with previously published [13, 16].

Element R_s, involved in both equivalent circuits one should refer to intergrain resistance, which in Ag_2CdI_4 is remarkably lower than that of the Ag_2HgI_4. Considering values of grain boundary capacitance observed in Ag_2Hg_4 being of order 10^{-12} F, one should expect it to be smaller or even negligible in Ag_2CdI_4. This clarifies the absence of C element in the equivalent circuit of AgI–CdI_2 system.

Strong distinction between values of N is noticeable. To explain this one should take into consideration the presence of pure AgI phase in the studied samples. The amount of this phase increases as the temperature approaches to that of the superionic transition. Thus in our case non-homogeneity is more apparent for Ag_2HgI_4, which transition temperature is lower.

CONCLUSIONS

Two isostructural superionic compounds, Ag_2HgI_4 and Ag_2CdI_4 have been synthesized and their impedance spectra have been measured for the wide range of frequencies and temperatures. Electrode processes were found to take place at frequencies below 100 Hz. An equivalent circuit analysis for each of obtained spectrum has been carried out. Ohmic parameters, elstimated for different temperatures, point on the two main conduction mechanisms which can be clearly separated. Temperature dependencies of the bulk ionic conductivity for both systems reflect the complex character of the superionic phase transitions in these materials.

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