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New $Ag(F_{1-x}Cl_x)$ phases for energy storage applications

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This work is dedicated to Professor Michael Grätzel at his 70th birthday.

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ABSTRACT

Several types of mixed-anion fluoride–chloride phases of silver(I) (with stoichiometries close to $AgF_{0.5}Cl_{0.5}$ and $AgF_{0.75}Cl_{0.25}$) have been synthesized for the first time in reactions between AgF (or AgF₂, respectively) and AgCl. The products crystallize in the rock salt unit cell, similarly to the pristine AgF and AgCl phases. The members of the $Ag(F_{1-x}Cl_x)$ series exhibit an almost linear relationship of the cubic cell vector with the composition parameter, *x*, which indicates that AgF and AgCl form a solid solution with a disordered anionic sublattice. The $AgF_{0.5}Cl_{0.5}$ phase exhibits quite a low melting point of 307 °C (as compared with 435 °C for AgF and 455 °C for AgCl), and small entropy change at melting, some 10 J (mol K)⁻¹ (as compared to 23.6 J (mol K)⁻¹ for AgF, and 18.1 J (mol K)⁻¹ for AgCl), indicative of high disorder and large absolute entropy of $AgF_{0.5}Cl_{0.5}$ solid. Despite that, the $Ag(F_{1-x}Cl_x)$ phases show smaller specific electric conductance than the end members of the series, AgCl and AgF. Parent AgF turns out to have rather high specific conductance of 3×10^{-2} mS cm⁻¹ at a room temperature and rather small activation energy for conductivity (29.2 kJ mol⁻¹) which suggest the presence of high concentration of defects and substantial electron doping to the conduction band.

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1. Introduction

Silver(II) is a powerful one-electron oxidizer, which is stabilized in the solid state in over one hundred compounds [1]. Nearly all of them contain fluoride anions or complex fluorine-rich anions. Presence of fluorine in these compounds is not coincidental: F^- is the most difficult to oxidize among all common inorganic anions. Thermodynamic stabilization of fluoride Ag(II) salts in F^- rich ligand environment originates from the fact that the value of the standard redox potential, E^0 , for the Ag(II)/Ag(I) redox pair (+1.98 V vs. normal hydrogen electrode [2,3]) is much less positive than that for the F_2 , $2H^+/2HF$ redox pair (+3.05 V¹ [2]) which prevents F_2 evolution. Still, great majority of Ag(II)-based systems are considered to be very strong oxidizers. Not surprisingly, therefore, AgF₂ may be used in conjunction with Li as a component of

(W. Grochala).

high-voltage power sources with the discharge voltage reaching 3.4 V [4], and even a Li-free $Ag_{(s)}|AgF_{(aHF)}|AgF_{2(s)}|(Pt)$ electrochemical cell has an appreciable electromotive force exceeding 1.38 V [5]. However, aHF (anhydrous hydrogen fluoride) solvent is volatile (T_{boil} = 19.5 °C) and "an unlikely choice for a model solvent system, given its reactivity towards the usual materials for construction of scientific equipment" [6]. Having practical applications in mind, and taking into account environmental concerns, one should take advantage of the oxidizing power of Ag(II) using either a common, cheap, non-volatile, and fluorine-free solvent [3], or a solid electrolyte.

AgF, which like all silver(I) halides easily forms defects of its crystal lattice [7–9], is a straightforward candidate for solid electrolyte for the $Ag_{(s)}|AgF_{(s)}|AgF_{2(s)}|(Pt)$ electrochemical cell [10]. An alternative use of silver fluorides in batteries is that in electrochemical cells based on fluoride ion shuttle, $M|F^-_{(sol)}|M'F_x$ [11] (*e.g.* M' = Ag, x = 1 or 2). Excellent ionic conductivity for both Ag(I) cations and halide anions – which in fact enabled the appearance of photography in the first half of the XIX century – is an inherent feature of defected silver halides and AgX-based composite materials [12]. The nature of defects and ionic conductivity in silver(I) halides are intensely studied these days

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¹ The redox potential is rather weakly dependent on proton activity, and the E^0 values for the (F₂, H⁺/HF₂⁻) and (F₂/2F⁻) redox pairs are +2.98 V and +2.87 V, respectively (www.webelements.com).

not just in conjuction with photographic process [13] and in diverse pressure-temperature conditions [14] but also due to fast development of infrared fiber optics [15], compact electrochemical cells [16] as well as of quantum devices [17]. Theoretical studies have also been conducted to understand the energetics of defect formation [18], ionic conductivity [19] as well as anomalous melting features of some of these solids [20], and elastic properties of these phases [21].

AgF, the lightest member in the silver(I) halides series, is photosensitive just like all other Ag(I) halides², but it also shows marked differences of physicochemical properties from its heavier congeners. First, it is the only water-soluble silver(I) halide. Second, despite more ionic nature of AgF its direct (4.63 eV [7]) and indirect (2.8 eV [7]) electronic band gaps are smaller than the corresponding ones for AgCl (5.15 eV and 3.25 eV, respectively [7]). As a consequence, the freshly obtained AgF is dark yellow, while pure AgCl is colourless. Indeed, the standard density functional theory (DFT) calculations fail to correctly predict the electronic band structure of AgF and they yield the closure of the indirect band gap [7]. The third anomalous property is that AgF shows lower melting point (435 °C) than AgCl (455 °C) despite the larger lattice energy for the former compound.

In an attempt to generate Ag(I) halide with substantial amount of defects of anionic sublattice, and possibly exhibiting an improved ionic conductivity suitable for energy storage applications, we have explored the formation of solid solutions of AgF and AgCl and we have characterized the products with elemental combustion and classical titration analysis, powder x-ray diffraction (PXD), thermal analysis combined with evolved gas analysis (TGA/DSC/EGA) as well as electric impedance spectroscopy (EIS). Selected samples were also studied using x-ray photoelectron spectroscopy (XPS). We have also performed the state-of-the-art quantum mechanical electronic band structure calculations in order to reproduce the direct and indirect band gap of AgF at the Fermi level.

2. Materials and methodology

2.1. Synthesis

Two types of samples were prepared, with stoichiometries similar to (**A**) AgF_{0.75}Cl_{0.25} and (**B**) AgF_{0.5}Cl_{0.5}.

To obtain phase **A**, AgF₂ and AgCl in 1:1 molar ratio have been ground in ZrO₂ mill ($N \times 5$ s with 1 min breaks for mill cooling, N = 3-9). After pre-homogenization the reagents were heated to 200 °C for 2 h inside a sealed PTFE reactor. Pressure increase has been observed due to evolution of an unidentified gas (see Section 3.2). The best quality samples are obtained when using of the sealed reactor and allowing for pressure increase; non-homogenous (two-phase) samples are obtained when the PTFE reactor is open during the progress of reaction. To obtain phase **B**, AgF and AgCl in 1:1 molar ratio have been heated to 400 °C for 30 min in a Pt boat leading to their *co*-melting. All procedures were carried out inside Ar-filled glovebox from MBraun.

Syntheses involving AgF and $Cl_{2(1)}$ or $Cl_{2(g)}$ have also been attempted but they did not proceed.

2.2. Elemental contents

Determination of atomic composition was performed using elemental combustion analysis for fluorine and chlorine (at Institute of Organic Chemistry Polish Academy of Sciences, Warsaw), or classical titration analysis (Ag₂CrO₄) for silver (Mohr method [22]). Results from these two methods were combined in order to calculate stoichiometry of a compound. The results were compared to crude elemental analysis based on x-ray photoelectron spectroscopy, which tends to show large abundance of C and O (as typical of surface-sensitive XPS spectra), but still yields reasonable Ag:F:Cl ratios. Only the results of classical wet analyses are quoted below.

2.3. XPS

The x-ray photoelectron spectra were measured using a custom-designed system made by SPECS which allows for loading of the samples in inert atmosphere of Ar gas. The spectra were recorded using Al $K\alpha$ radiation of XR50 M x-ray source (1486.74 eV, 400 W), a single crystal quartz mirror monochromator, the Phoibos 100 hemispherical analyser (with 100 mm mean radius), and a delayline electron detection system (DLD 3636). The electron flood gun FG 15/40 was used for the charge compensation. The instrument settings corresponded to the spectra accumulated from the spot of *ca.* 2 mm radius. For more details of XPS experimental setup see [23].

2.4. Thermal analysis

Netzsch STA 409 PC Luxx was used for thermogravimetriccalorimetric-evolved gas analysis (TGA/DSC/EGA) measurements. All measurements were conducted in a stream of flowing Ar gas (6 N) using Pt or Al₂O₃ crucibles. To measure the progress of thermally-induced AgF₂ + AgCl reaction the substrates were manually pre-homogenized in a mortar and heated from 30 °C to 200 °C with the rate of 4 K min⁻¹ and then kept for 2 h at 200 °C. To obtain phase **B** several experiments using different molar ratios (AgF:AgCl-1:4, 2:3, 1:1, 3:2, 4:1) were conducted. After homogenizing substrates in a mortar, each sample was heated from 25 °C to 280 °C (10 K min⁻¹), then stabilized isothermally for 1 h, next it was heated to 350 °C (0.5 K min⁻¹) and then stabilized isothermally for 1 h, followed by cooling to 25 °C (at 1.5 K min⁻¹). Three more measurements were conducted for 1:1 stoichiometry to get better statistics and extract the values of temperature and entropy of melting/crystallization. These 1:1 samples were heated from 30 °C to 350 °C at 1 K min⁻¹ and after 2 h of isothermal stabilization they were cooled to 30 °C at 1 K min⁻¹.

2.5. PXD and structural refinement

Powder x-ray diffraction patterns of all samples sealed under argon inside 0.3 mm thick quartz capillaries were measured using Bruker D8 Discover diffractometer (parallel beam; the $CuK_{\alpha 1}$ and $CuK_{\alpha 2}$ radiation intensity ratio of *ca.* 2:1). The LeBail refinement of the recorded diffraction patterns has been performed using Jana 2006 [24]. The NaCl-type $Fm\bar{3}m$ structure was used as the initial structure model and the cubic lattice vector was refined.

2.6. Electric impedance spectroscopy

(EIS) is often used to determine conductivity of fluoride-ionrich solids and solid electrolytes [25–28]. The AC impedance measurements were carried out by using a Solartron 1260 Frequency Response Analyzer and if needed a 1296A Dielectric Interface System. The spectra were collected within the frequency range from 10^7 to 10^{-2} Hz and AC amplitude within the range 10 mV–1 V. Each sample (<20 mg) was embedded inside a stainless steel or silver cell of a novel design [29,30] equipped with two parallel electrodes with a working surface area of 0.785 cm². Two types of electrodes were used: hardened steel and silver (see Section 3.4). Thickness of the layer of a solid was usually close to d = 0.1 mm and it was measured individually for each

² Yellow AgF turns brown when irradiated with sunlight. The commercial samples are also brown-yellow.

sample. The sample holder was equipped with a water jacket; the temperature was controlled within the range from -50 to +60 °C (± 0.01 °C) with a LAUDA RE 1050 thermostat (LAUDA DR. R. WOBSER GMBH & CO. KG, Germany). The cell was loaded with sample under argon gas. Impedance measurements were carried out after stabilization of temperature for each temperature point (typically after 1 h). Freshly prepared phases **A** and **B** or commercially available silver halides of high purity (99.99% AgCl, 99.9% AgF, 99.5% AgF₂ from Sigma-Aldrich) were used for impedance measurements.

2.7. DFT calculations

The periodic DFT calculations were done with the Vienna ab initio simulation package (VASP) [31] and using the hybrid HSE06 (Heyd–Scuseria–Ernzerhof) functional calculations [32]. HSE06 functional uses an error function screened Coulomb potential to calculate the exchange portion of the energy in order to improve computationally efficiency, especially for metallic systems; it tends to yield very similar thermochemistry as the PBEO functional, but converges more rapidly with respect to the number of k-points. In all cases we have used the projector-augmented wave method (PAW) [33]. For both GGA and HSE06 we have applied PBEsol exchange-correlation functional revised for solids [34]. Parameters for full geometry optimization and for electronic band structure calculations were: SCF convergence criterion 10⁻⁷ eV, ionic convergence 10^{-5} eV, k-point spacing of 0.3 Å^{-1} (using the Monkhorst–Pack scheme [35]), valence electrons were described by plane waves with kinetic energy cutoff of 500 eV providing good energy convergence. The calculations correspond formally to pressure of 0 GPa and T = 0 K. The lattice constant of AgF was reproduced with excellent accuracy (theory: 4.892 Å, experiment at room temperature: 4.92 Å [1]).

3. Results and discussion

3.1. Electronic structure of AgF from hybrid DFT

The calculated electronic band structure is shown in Fig. 1 and the computed direct and indirect band gaps are listed in Table 1. The calculation within the generalized gradient approximation (GGA) using PBEsol functional tends to severely Table 1

Electronic band gaps of AgF: comparison of experiment and theory.

Band gaps (eV)	GGA	HSE06	Experiment [7]
Direct	0.97	2.86	4.63
Indirect	-0.70	+0.89	2.80

underestimate the band gaps and leads to closure of the indirect band gap, similarly to what was reported in the literature [7]. However, use of the hybrid DFT (HSE06/PBEsol) leads to the indirect band gap opening.

Although the use of hybrid DFT method has led to correct qualitative assessment of the direct and indirect band gaps of AgF [36], which constitutes a substantial improvement over the results reported so far, the quantitative agreement is far from satisfactory. The calculated direct band gap of 2.86 eV constitutes only 62% of the experimental value, while the indirect one of 0.89 eV is a mere 32% of the experimental one. The agreement between theory and experiment could likely be improved in the future by varying the parameters of the HSE06 exchange–correlation functional, in particular the percent of the exact exchange and the screening parameter [37].Let us now see how the properties of rock salt AgF may be modified by introducing disorder in anionic sublattice.

3.2. Composition and crystal structure of the Ag(F,Cl) phases

The thermally induced reaction between AgF_2 and AgCl commences at temperature as low as 110 °C according to TGA/ DSC/EGA analysis (not showed); only Cl_2 is easily detected by mass spectroscopy in gases evolved. The ability of Ag(II) to facile oxidation of chloride anions, as well as covalently bound Cl atoms, has been noticed before by Malinowski et al. [38] and Grzybowska et al. [39]. Malinowski et al. have observed that an intensely orange solid forms when AgF_2 reacts violently at a room temperature with SiCl₄ liquid [38]; Grzybowska et al. have seen formation of a similar product when AgF_2 was reacted with perchlorobenzene, C_6Cl_6 , upon heating to 150 °C [39]. Moreover, Malinowski et al. have determined that the orange residue crystallized in rock salt structure with the lattice constant intermediate between those of AgF and AgCl [38].



Fig. 1. The calculated electronic band structure of AgF: GGA/PBEsol calculation (left) and hybrid DFT HSE06/PBEsol calculation (right).



Fig. 2. The measured PXD patterns of samples A and B as compared to patterns generated from crystal structures for two reference samples: AgF and AgCl. The CuK_α radiation source was used.

Table 2

Elemental analysis of three different A samples from combustion (F, Cl) and titration (Ag) analyses. To obtain the nominal stoichiometry, the molar contents of silver has always been scaled up to unity.

Sample	A1 [*]		A2		A3	
Combustion analysis (% mas) Titration analysis (% mas)	F 10.69% Cl 7.07% Ag 74.71%	AgF _{0.81} Cl _{0.29}	F 11.05% Cl 4.98% Ag 78.8%	AgF _{0.8} Cl _{0.19}	F 10.48% Cl 6.65% Ag 79.6%	AgF _{0.75} Cl _{0.25}

* Halide contents substantially exceeds unity for this sample, this will be reflected in Fig. 3.

The product of the AgF₂/AgCl reaction is canary-yellow/deep orange and thus different from both AgF (brown-yellow) and AgCl (colorless). Its PXD (Fig. 2) shows the absence of unreacted substrates and the presence of a single crystalline phase with the lattice constant close to 5.1 Å (slightly varying from sample to sample), thus intermediate between those of AgF (4.92 Å) and AgCl (5.55 Å). This result suggests that the reaction does not proceed according to the reaction equation:

$$1/2\text{AgF}_2 + 1/2\text{AgCl} \rightarrow \text{AgF} + 1/4\text{Cl}_2 \uparrow \tag{1}$$

but rather some Cl is preserved in the solid product. The elemental analysis of three different **A** samples (Table 2) indicates that the composition of the product is close to $AgF_{0.75}Cl_{0.25}$, and thus the simplified reaction equation might be written as:

$$1/2AgF_2 + 1/2AgCl \rightarrow AgF_{0.75}Cl_{0.25}(phaseA) + 1/4"ClF" \uparrow$$
 (2)

It is not assumed in Eq. (2) that CIF is the only gaseous product but rather that the composition of the evolved gases (CI:F) must be close to of 1:1. One possible scenario is the evolution of a higher fluoride of chlorine and elemental chlorine gas, *e.g.*:

$$ClF \leftrightarrow 1/3ClF_3 + 1/3Cl_2 \tag{3}$$

with some ClF₃ presumably fluorinating the quartz capillary which joins the TGA/DSC apparatus and the quadruple mass spectrometer. This could explain why only Cl₂ has been detected in the gases evolved. It is also reasonable to assume that the *in situ* evolved ClF₃ reacts with as yet unreacted AgCl as reaction progresses, while leading to Cl \leftrightarrow F exchange; this would explain why the fate of the AgF₂/AgCl reaction depends on the overpressure of the evolved gas (see Section 2).

Phase **B**, obtained from *co*-melting of two Ag(I) halide precursors at 1:1 stoichiometric ratio:

$$1/2AgF + 1/2AgCl \rightarrow AgF_{0.5}Cl_{0.5}(phaseB)$$
(4)

is dark brown-yellow; no gas is evolved during formation of this product. The solid's PXD (Fig. 2) shows the absence of substrates

and the presence of a single face-centered cubic phase with the lattice constant of 5.25 Å. Such lattice constant suggests that the product is more rich in chlorine than the phase **A** which is obviously to be expected judging from the elemental composition of the substrate mixture. The estimated mean grain size of phases **A** and **B** – as calculated from broadness of the diffraction reflections using Topas [40] – is 28 nm and 23 nm, respectively; thus, they are much smaller than those of AgF (75 nm) and AgCl (82 nm) substrates.

It turns out that a close-to-linear correlation exists between the chlorine contents and the lattice constant of the $AgF_{1-x}Cl_x$ phases (Fig. 3). This is no surprise considering that the $AgF_{1-x}Cl_x$ phases are solid solutions of isostructural AgF and AgCl phases. The ionic radii of hexa-coordinated halide anions are not very far from each other (1.19 Å for fluoride and 1.67 Å for chloride) and formation of solid solution is facile.

While the reaction described by Eq. (2), regardless of the reaction conditions yields only samples with composition close to x = 0.25, that described by Eq. (4) seems to be more universal and could in principle allow formation of AgF_{1-x}Cl_x phases with any Cl content. However, it has been found that this is not the case, and when the ratios of reagents depart from 1:1, mixtures of two different AgF_{1-x}Cl_x phases result. Nevertheless, the linear dependence showed in Fig. 3 is very useful for estimation of the composition of these phases³.

³ For example, reaction between AgCl and AgF using substrate ratio of 3:1 leads to formation of a phase with lattice constant of 5.455(8) Å and corresponding to the composition of *ca*. AgF_{0.15}Cl_{0.85} as well as a phase with lattice constant of 5.357(8) Å and corresponding to the composition of *ca*. AgF_{0.31}Cl_{0.69}; the ratio of both phases is close to 1:2. On the other hand, the substrate ratio of 1:3 leads to formation of *a*. AgF_{0.77}Cl_{0.23} as well as a phase with lattice constant of 5.064(7) Å and corresponding to the composition of *ca*. AgF_{0.77}Cl_{0.23} as well as a phase with lattice constant of 5.129(7) Å and corresponding to the composition of *ca*. AgF_{0.67}Cl_{0.33}; the ratio of both phases is close to 4:1. The fact that the 1:1 phase does not form in these conditions suggests that it does not correspond to the most stable eutectic composition. As the referee reminded us, the phases obtained at rather low temperatures not exceeding 200 °C using AgF₂ precursor likely correspond to non-equilibrium conditions as this exceenting expendence.



Fig. 3. Correlation of the cubic lattice constant of $AgF_{1-x}Cl_x$ phases with the chlorine content (*x*). Three different samples of phase **A** were shown. Entry A1* is based on the nominal amount of chlorine, A1** on that of fluorine (*cf.* Table 2). Linear interpolation is shown between *x* = 0 and *x* = 1.0 compositions.



Fig. 4. The fragment (200-550 min) of the DSC profiles for two consecutive heating-cooling cycles of the AgF + AgCl (1:1) pre-ground mixture.

3.3. Thermal properties of the Ag(F,Cl) phases

The insight into formation and selected properties of Ag(F,Cl) phases have been gained using thermal analysis. The prehomogenized 1:1 mixture of AgF & AgCl (Fig. 4), as well as preprepared phase **B** (Table 3), have been studied with TGA/DSC.

The finely ground AgF:AgCl 1:1 mixture melts at *ca*. 350 °C⁴ (the related DSC peak is broad, noisy and structured, Fig. 4). The onset temperature of crystallization of this melt is *ca*. 307 °C; the DSC signal is now much narrower since after a two-hour-long isothermal stabilization the melt is quite homogenous. The much lower temperature of crystallization than that of melting is associated with the fact that the composite which was undergoing the first melting process was not a homogenous phase, but rather a conglomerate of two phases, AgF and AgCl, albeit with a small grain size. Re-melting of the so-obtained solid takes place at *ca*. 310 °C.

These results are confirmed in a separate TGA–DSC experiment (result not shown) for a larger amount of phase **B** which was preprepared using the Pt boat (and not *in situ* using the TGA crucible). Phase **B** melts at 312 °C (onset 309 °C) and it crystallizes at 307 °C (onset 304 °C) with an associated evolved heat of 5.8 kJ mol⁻¹ Ag. The melting point for phase **B** of 307 °C (at peak) is very low compared to those for substrates (Table 3). Moreover, the heat of melting is also much smaller for phase **B** – by a factor of 2–3 – than those for the binary halides (Table 3). This altogether suggests that AgF and AgCl form an eutectic mixture; however, the composition of $AgF_{0.5}Cl_{0.5}$ is unlikely to correspond precisely to the eutectic one⁵.

One may determine the change of entropy at melting, ΔS_m , from the condition of thermodynamic equilibrium:

$$\Delta S_m = \frac{\Delta H_m}{T_m} \tag{5}$$

The value of 10.0 J (mol K)⁻¹ obtained for phase **B** is again much smaller than the corresponding values for pristine AgF (23.6 J (mol K)⁻¹) and AgCl (18.1 J (mol K)⁻¹). This implies that phase **B** in the solid state has substantial absolute entropy which may be linked to structural disorder of the anionic sublattice. This in turn is related to the presence of soft phonon modes of the crystal lattice, since vibrational entropy constitutes nearly all absolute entropy of a semiconducting solid. In view of these results it is interesting whether one might obtain an Ag(I) compound

 $^{^4\,}$ Melting of this mixture is a complex process since a smaller endothermic peak at ca. 318 $^\circ C$ may also be seen.

 $^{^5}$ For some samples which composition is not precisely known the melting point was even as low as 299 $^\circ C$ (onset).

Table 3

Results from TGA/DSC measurements for phase \mathbf{B} (AgF_{0.5}Cl_{0.5}) as compared to the corresponding values for AgCl and AgF precursors.

Compound	AgF	AgCl	AgF _{0.50} Cl _{0.50} (phase B)
Melting point (°C)	435	455	307
Heat of melting (kJ mol ⁻¹)	16.7	13.2	5.8
Entropy change at melting $(J(mol K)^{-1})$	23.6	18.1	10.0

which would be *liquid at a room temperature*, for example using an eutectic mixture of Ag(I) salts with low-melting points and small heats of melting, such as for example fluorosulfate ($T_m = 156 \degree$ C) [41] or trinitromethanide ($T_m = 98 \degree$ C) [42].

3.4. Ionic conductivity of the Ag(F,Cl) phases as well as AgF and AgCl precursors

The impedance spectroscopy using the special-design cell [29] has been utilized to evaluate the ionic conductivity of the novel phases (Fig. 5) as compared to the AgF and AgCl limiting compositions. For sake of consistency, AgF_2 substrate was also studied.

Fig. 5 shows complex plane plot of impedance spectra registered in the hardened steel cell. In this experimental setup two semicircles or one deformed semicircle were observed for each samples. For some samples (AgCl) semicircles are followed by

a Warburg impedance (line tilted at 45°) at lower frequencies related to the charge accumulation at blocking electrodes. The arc is identified as a bulk property from the fact that it passes through the Z'-Z'' origin, and from the associated capacitance. The first semicircle was ascribed to conductivity of the silver halides grain interior whereas second semicircle to the conductivity of grain boundaries and reactions with electrode material in the low frequency range. This assignment was confirmed by impedance measurements using the cell equipped with silver electrodes. Disadvantage of these electrodes is that one can use only a moderate pressures up to 200 MPa to compress the sample in between electrodes; hence the powders are much less compact as compared to those measured using hardened steel electrodes (which provide pressures up to 2000 MPa), and the associated resistances are usually higher. However, silver electrodes are more resistant to oxidation than steel and they are not blocking for silver ions. Indeed, with the setup using Ag electrodes we have observed only one semicircle in the complex plane plot (Fig. 6). This observation confirms that the second semicircle or the low frequency deformation seen in the spectra measured using steel electrodes are both related to the (electro)chemical reactions with the electrode material (steel); this is obviously expected based on redox potentials of Ag(I)/Ag(0) and Fe(II)/Fe(0) redox pairs (silver is more noble metal than iron). The observation of single semicircle and thus finite resistance at very low frequencies ($\omega \rightarrow 0$) *i.e.* under DC conditions indicate also that these are predominantly silver cations which are responsible for the charge transport in these



Fig. 5. Complex resistivity spectra for silver halides samples registered at 25 °C using hardened steel electrodes; AgF_{0.75}Cl_{0.25} = phase **A**, AgF_{0.5}Cl_{0.5} = phase **B**. Equivalent circuit used for fitting of impedance response is showed at bottom right corner.



Fig. 6. Complex resistivity spectra for two selected silver halide samples registered at 25 °C using silver electrodes; AgF_{0.75}Cl_{0.25} = phase A.

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The values of dimensionless parameter, *P*, as well as charge carrier densities, *N*, for three silver halide samples at 25 °C (*cf.* Eq. (6)); $AgF_{0.5}CI_{0.5} = phase B$.

Compound	P(1)	<i>N</i> (cm ⁻³)
AgF AgCl AgF _{0.5} Cl _{0.5}	$\begin{array}{c} 2.4 \pm 0.5 \\ 1.9 \pm 0.3 \\ 1.6 \pm 0.5 \end{array}$	2.01E+21 1.92E+21 6.37E+21

materials. In other words, phases **A** and **B** constitute ionic conductors, just like their parent AgF and AgCl precursors.

The impedance response was fitted with the equivalent circuit, in which dielectric relaxation was included. For this purpose a Cole-Cole relaxation was assumed, which can be represented in the equivalent circuit by a capacitor with capacitance $C_{\infty} = (\varepsilon_0 \times \varepsilon_{\infty} \times A)/d$, connected in parallel to a series connection of constant phase element and a capacitor with the capacity equal to $C_{C} = (\varepsilon_{0} \times \Delta \varepsilon \times A)/d$ (Fig. 5). By using this approach it is possible to take into account the characteristic change in the relative dielectric constant between the high frequency value ε_{∞} related to instantaneous sample polarization and the low frequency value $\varepsilon = \varepsilon_{\infty} + \Delta \varepsilon$ related to slow dipolar relaxation and ionic conductivity [28]. It should be noticed that $\Delta \varepsilon$ can be purely related to ionic conductivity and not involve the bulk dielectric effects at all. Empirical relation introduced by Barton, Nakajima and Namikawa (known as the BNN relation [43-45]) correlates the electrical conductivity σ_0 to the dielectric strength $\Delta \varepsilon$ of the low frequency polarization mechanism through:

$$\sigma_0 = P \varepsilon_0 \Delta \varepsilon \,\omega_{\rm max} \tag{6}$$

where ω_{max} is the angular frequency which corresponds to the maximum value of the dielectric losses and P is a dimensionless parameter which typically falls between 1 and 2 for ionic conductors [28]. The calculated values of this parameter are collected in Table 4 together with charge carrier densities, *N*, determined by method described in [28]. Indeed, the value of *P* slightly exceeds 2 only for AgF and it falls in the 1–2 range for both AgCl and phase **B**. Remarkably, phase **B** is characterized by charge carrier density which is three times larger than those for pristine AgF and AgCl, which suggests the presence of substantial share of defects in the crystal structure.

It turns out the radius of the semicircle seen in the complex plane plot of impedance spectra is strongly dependent on the temperature. Fig. 7 shows the temperature dependence of the bulk ionic conductivity for all silver halide samples studied. AgF – with its predominant silver ion conductivity – turns out to exhibit quite high conductivity of 3×10^{-2} mS cm⁻¹ at room temperature. This



Fig. 7. An overview of temperature-dependent conductivity of silver halides (Arrhenius plot). The values of the activation energies for ionic conductivity, $E^{#}$, are given for each sample.

value is actually two orders of magnitude short of the "superionic limit" of 1 mS cm⁻¹ but still comparable to the ionic conductivity of BaSnF₄ or KSn₂F₅ at room temperature [26] (these compounds are known as ones of the best fluoride ion conductors). This result suggests that pristine AgF could indeed be used as solid ionic conductor in the silver fluoride batteries, for example: $Ag_{(s)}|AgF_{(s)}|AgF_{2(s)}|(Pt)$. On the other hand, AgF_2 is a very poor ionic conductor and it is likely to be a major source of internal resistance of the electrochemical cell [46].

Interestingly, both new mixed-halide phases $AgF_{0.5}Cl_{0.5}$ and AgF_{0.75}Cl_{0.25} are characterized by markedly smaller electronic conductivity than the parent AgF and AgCl. For example, the $x \approx 1/2$ 2 sample shows conductivity ca. 8000 times smaller than that of AgF (at room temperature). This results is surprising considering that Ag(F,Cl) phases are characterized by (i) substantial disorder of the anionic sublattice (see Section 3.3), (ii) larger density of charge carriers than that of AgF, as discussed above, (iii) as well as by smaller grain size of 23–28 nm as compared to 75–82 nm for AgCl and AgF (Section 3.2)—note that decrease of the grain size usually leads to conductivity increase [27]. The seeming discrepancy is explained by analysis of the activation energy for conductivity, $E^{\#}$. It turns out that the value of $E^{\#}$ of 52.7 kJ mol⁻¹ for Ag(F_{1/2}Cl_{1/2}) is over twice as large than those of 22-24 kJ mol⁻¹ measured here for AgF and AgCl [47]. This result suggests that - despite the increased disorder of anionic sublattice - the Ag⁺ cations are more strongly bound in the lattice and they are less labile in the mixedhalide phases than for parent AgF and AgCl. Because of higher activation energy of both new mixed-halide phases theirs conductivities can be higher than conductivities of AgF and AgCl at higher temperature.

4. Conclusions

We have prepared and characterized two types of new mixed-halide phases of silver(I), notably AgF_{0.5}Cl_{0.5} and $AgF_{0.75}Cl_{0.25}$. These phases crystallize in the rock salt structure $(Fm\bar{3}m)$; the as-prepared samples show small grain size of 23-28 nm. They also exhibit low melting point, small melting heat and atypically small entropy change at melting as compared to native AgF and AgCl, indicative of substantial disorder of the anionic sublattice. However, analysis of the thermally-induced changes of the ionic conductivity shows that they exhibit significantly higher activation energy for ionic conductivity than pristine AgF and AgCl, likely due to stronger binding of the Ag⁺ cations in the lattice. AgF, which itself is a nonstoichiometric and quite photosensitive compound, turns out to be a superior lowresistivity Ag(I) ion conductor, which could serve as a membrane material in energy storage applications. AgF₂ exhibits much higher resistivity than AgF; attempts are being carried out to introduce defects into the crystal structure of the former compound in order to obtain new anode materials showing enhanced ionic conductivity. We have been able to qualitatively reproduce the most important features of the electronic band structure of this compound (*i.e.* its semiconducting and indirect bandgap character) from the state-of-the-art hybrid DFT calculations.

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