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UV-VIS Absorption Spectra of Molten AgCl and AgBr and of their Mixtures with Group I and II Halide Salts

Abstract: The UV-VIS absorption spectra of $(Ag_{1-X}[Li-Cs, Ba]_X)Cl$ and of $(Ag_{1-X}[Na, K, Cs]_X)Br$ at 823 K at the concentrations X = 0.0, 0.1, 0.2 have been measured. The findings show that on adding the respective halides to molten silver chloride and silver bromide, shifts of the fundamental absorption edge to shorter wavelengths result. A correlation between the observed shifts and the expansion of the silver sub-lattice is found, which is valid for both silver halide systems studied in this work.

Keywords: Molten; Silver Halides; UV-VIS.

1 Introduction

Measurements of the transport properties of pure and "doped" silver chloride melts were conducted [1, 2] in order to see if postulated covalent structures [3] are influenced by adding up to 20 mole% of strongly ionic chloride salts. Such influence could not be found, but instead it was observed that there was a colour shift when the silver chloride was doped [2]. The colour changed from the deep red of the pure melt to a lighter red or almost to yellow, depending on the concentration and type of salt added. A similar effect was reported by Sundheim and Greenberg, who worked on AgCl dissolved in a LiCl/KCl eutectic [4]. We concluded that because the degree of the colour change depended not only on the concentration but also on the nature of the added salt, this could not be a trivial dilution effect. The aim of this work is, therefore, to quantify our qualitative observations on the silver chloride systems and to extend these measurements to the silver bromide systems. Furthermore, we intend to search for a parameter, which correlates with the degree of colour change.

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2 Experimental

Absorption spectra were measured using a Perkin-Elmer UV-VIS spectrometer 557 (Perkin Elmer LAS GmbH, Rodgau, Germany). The spectrometer and its photomultiplier were separable and were placed 280 mm apart. The furnace had two windows of 0.5 mm thick quartz slide-glasses of optical quality and was placed in the optical path of the spectrometer and photomultiplier, being separated from these by short, water-cooled flanges. The quartz cuvette assembly is shown in Figure 1 and was used in all experiments. The cuvette itself, (B), had an optical path length of 1 mm and was made of the same type of quartz glass used for the windows of the furnace. It had both an argon inlet tube and a melt reservoir (A) connected to it which was sealed with a heat-resistant cell lid (C). The appropriate amount of silver halide was weighed into the melt reservoir, and the cuvette assembly was installed in the furnace. A steady stream of dry, oxygen-free argon was passed through the assembly to keep the melt out of the cuvette until the calibration had been performed at 823 K. Thereafter, the argon flow was interrupted, the melt flowed into the cuvette, and a scan of the pure silver halide was performed. The melt was then blown back into the reservoir in order to enable doping. Because the tube of the melt reservoir extended above the lid of the furnace, the halide dopants could be subsequently added to the melt without the furnace having to be opened. After thermal and chemical equilibrium was regained, the doped silver halides were scanned. The preparation of the chloride dopants has been described elsewhere [2, 5]. Silver bromide (Degussa) was zone refined, and the bromide dopants were thoroughly dried before use.

3 Results and Discussion

The absorption spectra of pure and doped AgCl and AgBr at 823 K are show in Figure 2 and 3, respectively. The absorption coefficient K was determined according to K = Absorbance/d, where d is the optical path length. Because in the liquid silver halides the density of states of both valence band and conduction band smear out into the band gap, a long exponential low energy tail appears in their absorption spectra [6]. Upon reaching the absorption edge, there is a sharp transition from partial absorption
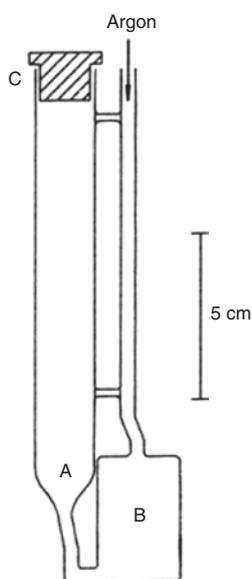
Figure 1: Cuvette assembly: A = melt reservoir, B = cuvette, C = lid.

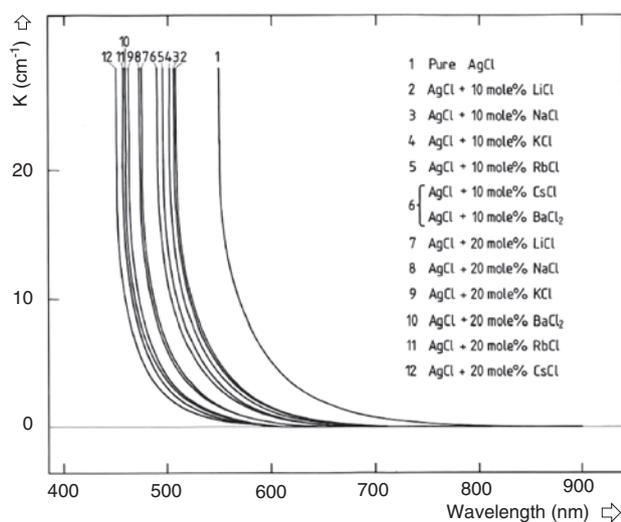**Figure 2:** UV-VIS spectra of pure and doped AgCl at 823 K.

Figure 3: UV-VIS spectra of pure and doped AgBr at 823 K.

to complete absorption, leading to almost vertical spectra. This almost vertical part of the spectrum (also called the Urbach edge) can be taken to be the wavelength λ_0 of the transition between absorption and transmission [4]. The λ_0 values reported in this work were determined at an absorption coefficient of K of 25 cm^{-1}. The reproducibility of the repeatedly determined absorption wavelengths λ_0 of the pure silver halides was very high, so that the overall reproducibility of the measured systems was estimated to be better than ±2.5 nm. Because all substances were carefully weighed and the dopants were added in such a way that they were completely mixed into the silver halides, a concentration error of at most ±1.0% can be estimated,
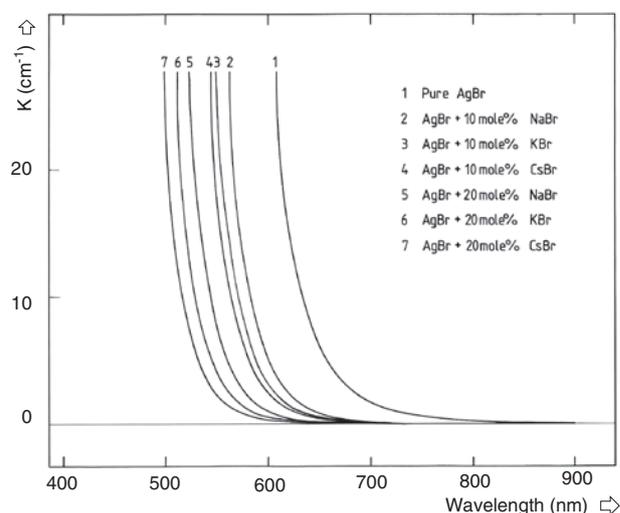
which would equally apply to the determined shift in the absorption edge.

The λ_0 of the AgCl and AgBr spectra at 823 K were determined to be 549 nm and 606 nm, respectively. Sundheim and Greenberg [4] obtained a value of 570 nm for AgCl at 823 K, whereas the value determined from a diagram in a publication by Iseki et al. [7] is approximately 550 nm at 823 K.

The results show that the reported visual observation of different colour changes on adding varying chloride salts to silver chloride are confirmed spectroscopically (Fig. 2). When doped with 10 mole% of any of the chlorides used in this work, the λ_0 is significantly blue shifted. The larger the cation of the added salt, the greater is the shift. Silver chloride doped with 20% behaves similarly, the shift only being larger. The same effect was observed when AgBr was doped with alkali metal bromides (Fig. 3).

The molar volumes of binary silver halide-alkali halide melts depend similarly on the dopant cation radii as shown in Table 1 using data from previous publications [1, 2, 8, 9].

Both for AgCl and for AgBr, the molar volume of the binary systems at a given concentration increases from the lithium to the caesium system. A plot of the absorption shift from the pure to the doped silver halide against the molar volume at a given dopant concentration does not lead to a correlation of the data. If one considers the addition of the dopant to have expanded the silver halide sublattice – the alkali metal cations otherwise having no effect on the absorption process at the absorption edge of the binary silver chloride melt – and plots the resulting absorption shift against the calculated relative molar volume of the silver halide sublattice, a correlation can be found. Figure 4 shows the correlation between the molar

Table 1: Absorption edge (λ_0), molar volumes, and Ag-ion sublattice dilation.

System	Absorption edge (nm)	Molar volume ($10^{-6} m^3$)	Molar volume of Ag-ion sublattice	Ag-ion sublattice dilation factor	Shift of absorption edge (nm)	Ag-ion sublattice dilation (%)
AgCl	549	29.83	29.83	1.0000	0	0.00
AgCl + 10 mole% LiCl	507	29.68	32.98	1.1055	42	10.55
AgCl + 20 mole% LiCl	475	29.41	36.76	1.2324	74	23.24
AgCl + 10 mole% NaCl	506	30.4	33.78	1.1323	43	13.23
AgCl + 20 mole% NaCl	473	30.08	37.60	1.2605	76	26.05
AgCl + 10 mole% KCl	501	31.48	34.98	1.1726	48	17.26
AgCl + 20 mole% KCl	462	33.17	41.46	1.3900	87	39.00
AgCl + 10 mole% RbCl	495	32.04	35.60	1.1934	54	19.34
AgCl + 20 mole% RbCl	456	34.39	42.99	1.4411	93	44.11
AgCl + 10 mole% CsCl	491	32.86	36.51	1.2240	58	22.40
AgCl + 20 mole% CsCl	450	35.92	44.90	1.5052	99	50.52
AgCl + 10 mole% BaCl$_2$	489	32.88	36.53	1.2247	60	22.47
AgBr	606	34.42	34.42	1.0000	0	0.00
AgBr + 10 mole% NaBr	561	34.94	38.82	1.1279	45	12.79
AgBr + 20 mole% NaBr	524	35.63	44.54	1.2939	82	29.39
AgBr + 10 mole% KBr	549	36.12	40.13	1.1660	57	16.60
AgBr + 20 mole% KBr	511	37.95	47.44	1.3782	95	37.82
AgBr + 10 mole% CsBr	545	37.72	41.91	1.2176	61	21.76
AgBr + 20 mole% CsBr	499	41.33	51.66	1.5009	107	50.09
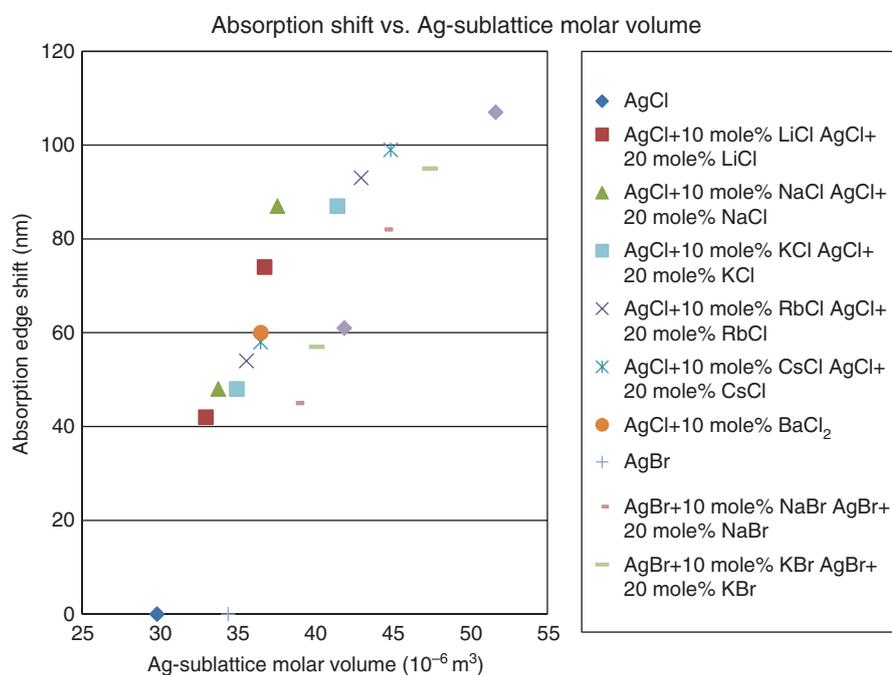
Figure 4: Absorption edge shift vs. Ag-sublattice molar volume.

volume of the silver chloride and silver bromide sublattices (determined by dividing the molar volume of the binary melt, by the molar fraction of the silver halide in the melt) and the change of λ_0.

An even better correlation can be achieved, if the dilation of the silver ion sublattices (calculated as the percentage of increase of the silver halide sublattice compared to the pure silver halide melt) is compared to the change of λ_0 (see Fig. 5). This correlation indicates that for a given melt temperature, the expansion of the silver ion sublattice through the addition of dopants is a factor that leads to a corresponding shift of the absorption edge λ_0.

A possible explanation for this observation is based on the mechanism of absorption. In a simple picture, the
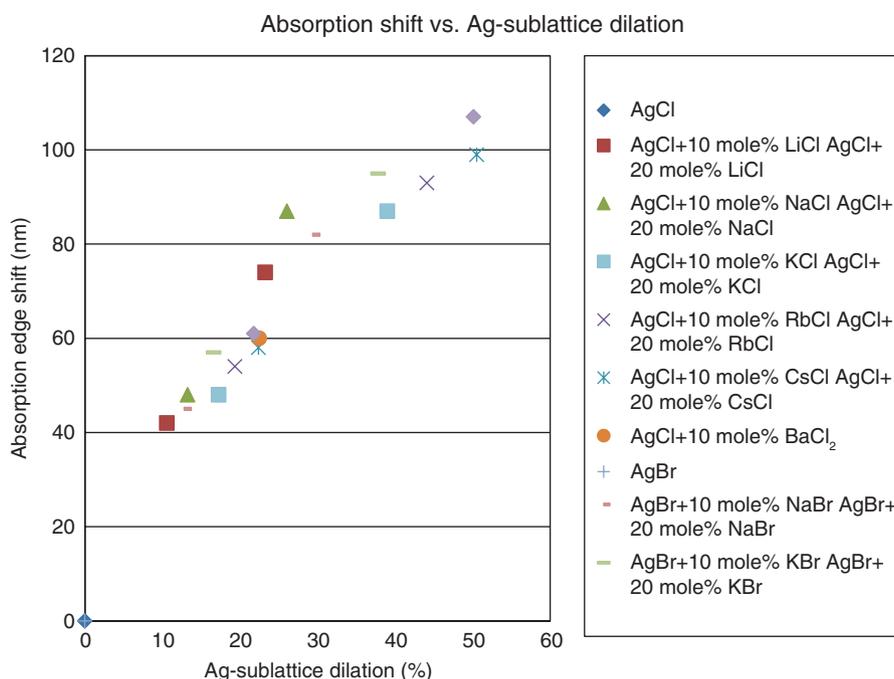
Figure 5: Absorption edge shift vs. Ag-sublattice dilation.

full p-orbitals of the halide ions of the AgCl-melt constitute the valence band, whereas the silver ions with their empty s-orbitals are the conduction band. The absorption of light occurs by exciting electrons from the halide ion valence band to the silver ion conduction band. The addition of halide salts to the silver halide melts does not lead to a significant change in the valence band, because the halide ion density remains largely unchanged. In the case of the valence band, cations are added, which are significantly less electronegative than silver ions. The weaker electronegativity of the dopant cations leads to their conduction bands being at a higher energy level than that of the silver ions, so that on excitation of the mixture, the electrons from the halide ions continue to move to the silver ion conduction band.

The width of the conduction band depends on the degree of overlap of the orbitals [10]. The more the orbitals overlap, the wider the conduction band. If the silver sublattice is expanded, the overlap deteriorates, which leads to the conduction band becoming narrower. Assuming that the centre of the conduction band remains unchanged, the distance between the upper edge of the halide ion valence band and the lower edge of the silver ion conduction band increases. This leads to a higher energy requirement to excite electrons and thus results in a shift of the absorption edge to shorter wavelengths.

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