Mechano-chemical synthesis of crystalline superionic conductors CsAg₄Br₃₋ₓI₂₊ₓ (0<x<1) and their silver-conducting properties

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Abstract. Silver ion conductive materials attract numerous interest of research nowadays, due to their high potentiality in the solid electrolyte ion source (SEIS) intended for the application in the ionic thruster. In the work, mechano-chemical synthesis of crystalline superionic conductors CsAg₄Br₃₋ₓI₂₊ₓ (0<x<1) was performed by means of high-energy ball milling for the first time. The structure, morphology, and elemental composition were investigated and the effects of iodine content on these properties were studied. Silver-conducting properties were characterized based on the generation of Ag⁺ ion beams. The ion current of about 15 nA was obtained at 152°C and 15 kV.

1. Introduction
Superionic conductors, also called solid electrolytes (SEs), are a class of solid-state materials that have high values of ionic conductivity (>10⁻⁴ S/cm) and low values of activation energy (~10⁻¹ eV) [1]. Since the discovery of crystalline MAg₄I₅ (M=K, Rb, and NH₄) in the 1960s [2], the silver-conducting SEs are widely applied in electrochemistry (solid-state batteries and supercapacitors), electric device, and ion emission device [3-9]. Among them, RbAg₄I₅ (silver-rubidium pentaiodide) solid electrolyte possessing one of the highest room-temperature ionic conductivity (0.26 S/cm) is inclined to degradation at this temperature, especially in the environmental conditions [10]. Apart from the silver-conducting MAg₄I₅, numerous superionic conductors have been found, for example, sodium-conducting β-alumina [11] and copper-conducting Rb₄Cu₁₀IrCl₁₃ compounds [12]. However, it still attracts much interests to search for novel superionic conductors.
Mechanochemical processing is a powerful technique for powder synthesis, which is often exploited in the preparations of metals and alloys, amorphous phases, and micro(nano) composites [13-15]. Among them, the application in superionic conductor synthesis just starts recently, and to the best of our knowledge, only a few studies are reported on crystalline SEs prepared by high-energy ball-milling [9]. In the present work, the crystalline CsAg₄Br₃₋ₓI₂₊ₓ (0<x<1) was prepared by the
mechano-chemical synthesis and the effect of I-doping content on the structure, morphology, and ionic conducting properties was studied.

2. Experimental details

2.1. Mechano-chemical processing and characterizations
In the work, the raw materials silver iodide $\beta$-AgI ($\geq 99\%$), cesium iodide CsI ($\geq 99.999\%$) and silver bromide AgBr ($\geq 99.9\%$) powder (Sigma-Aldrich) were weighted according to the intended molar ratio of CsI:AgI:AgBr = 1: (1+$x$): (3-$x$), where $x$ is within the range of 0 to 1. The powders were mixed in an agate mortar for 5 minutes beforehand. Then, the well-mixed powder was put in an agate milling container with agate balls ($\Phi \sim 6$ mm). High-energy ball-milling was conducted under dry argon atmosphere using a planetary ball-milling apparatus (Nanjing, QM-QX2).

The prepared samples were characterized by X-ray diffraction (XRD, Bruker D8 Advance), energy dispersive X-ray spectroscopy (EDS), and scanning electron microscope (SEM, Zeiss Sigma). Cu $k_{\alpha}$ radiation ($\lambda=0.154184$ nm) was used for the measurements of XRD spectra.

2.2. Test setup for Silver-conducting properties
To examine the silver-conducting properties of the synthesized solid electrolytes CsAg$_4$Br$_3$$_x$I$_{2+x}$, Ag$^+$ ion emitters were fabricated using the method described in [9]. An overview of the setup for ion emission measurements is shown in figure 1. The test setup consists of an emitter, ion collector (Faraday cup), and high voltage supply. The ion emitter is made of a silver tip covered by CsAg$_4$Br$_3$$_x$I$_{2+x}$ coatings. In principle, the generation of Ag$^+$ ion beam follows three successive processes: (i) transformation of Ag atoms into mobile ions via an electrochemical reaction occurring at the interface between silver metal and electrolyte film under an influence of the applied electric field, (ii) moving/migration of Ag$^+$ ions along the fast ion-transport channels existing insides the CsAg$_4$Br$_3$$_x$I$_{2+x}$ film towards the surface, and (iii) overcoming the surface potential barrier and field-stimulated emission into vacuum.

![Figure 1. Schematic diagram of the silver ion emission test setup.](image)

3. Results and discussions

3.1. Structure, morphology, and elemental composition of CsAg$_4$Br$_3$$_x$I$_{2+x}$
In our previous work [9], the optimal conditions for mechano-chemical synthesis of CsAg$_4$Br$_{2.68}$I$_{2.32}$ powder were found to be at 450 rpm for at least 3 hours. In the present work, various crystalline superionic conductors CsAg$_4$Br$_3$$_x$I$_{2+x}$ with $x$ values from 0 to 1 are prepared by means of high-energy ball milling at rotation rate of 450 rpm for 3 hours. XRD spectra of the prepared powder are shown in figure 2, where the order from up to bottom corresponds to the samples of $x=0$ to 1. All diffraction peaks can be indexed to the high-conductive CsAg$_4$Br$_{3.4}$I$_{2.8}$ phase except for small contributions of impurities CsAgBr$_2$ and Ag(Br,I) in the $x=0$ sample. All CsAg$_4$Br$_3$$_x$I$_{2+x}$ (0<$x$<1) crystals belong to MAg$_4$I$_5$ families having a simple cubic lattice. The $(hkl)$ indices of all diffraction peaks are indicated. The strongest characteristic peaks are assigned to be (3 1 1) plane and present a left shift in the XRD
spectra with an increasing of $x$ values, indicating an expanding of lattice. The lattice constant $a$ is related to the inter-plane spacing $d$ and the corresponding Miller index $(hkl)$:

$$d = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$$

(1)

Figure 2. XRD spectra of the ball-milled samples with $x$ value of 0 to 1 from up to bottom.

Figure 3. Lattice constant $a$ as a function of $x$ value.

The calculated values of lattice constant are plotted as a function of $x$-value in figure 3. It is observed that the lattice constant $a$ shows a roughly linear increase with the $x$-value due to the bigger atomic radius of iodine than that of bromine. Hence, it is reasonable to conclude that the CsAg$_{4}$Br$_{3-x}$I$_{2+x}$ lattice expands with the increase of iodine content. The grain size can be estimated from the Scherrer equation:
Where $\lambda$ is the wavelength of X-ray, $\beta$ and $\theta$ indicate the FWHM and diffraction angle of the corresponding ($hkl$) peaks. The estimated values of grain size $D$ for various crystalline CsAg$_4$Br$_{3-x}$I$_{2+x}$ are listed in table 1.

Figure 4 presents the SEM images of the CsAg$_4$Br$_{3-x}$I$_{2+x}$ powder, where the grain structure with the size of 0.2-1 $\mu$m is clearly observed. The average grain size is estimated for each sample using the ImageJ software, as listed in table 1. It is investigated that the grain grows with the increase of the iodine content resulting from the expanding of lattice, which is consistent with the analysis of XRD spectra. The EDS spectrum of CsAg$_4$Br$_3$I$_2$ powder is shown in figure 4(f), where the peaks at about 1.5 keV, 3.0 keV, 3.9 keV, and 4.25 keV are ascribed to Br, Ag, I, and Cs elements, respectively. The EDS spectra of the other samples are similar to figure 4(f) and therefore, not involved in the paper. The elemental compositions of CsAg$_4$Br$_{3-x}$I$_{2+x}$ crystals obtained from the analysis of EDS spectra are listed in table 1. The atomic ratio of Cs, Ag, and (Br+I) elements in all samples is rather close to the intended value of 1:4:5, revealing a successful synthesis of superionic conductors CsAg$_4$Br$_{3-x}$I$_{2+x}$ (0<x<1) by the method of mechano-chemical processing.

![Figure 4](image_url)

**Figure 4.** (a)-(e): SEM images of crystalline CsAg$_4$Br$_{3-x}$I$_{2+x}$ powder with $x$ value of 0 to 1, respectively. (f) EDS spectrum of the CsAg$_4$Br$_3$I$_2$ ($x=0$) sample.

**Table 1.** Elemental composition and grain size for CsAg$_4$Br$_{3-x}$I$_{2+x}$ powder.

| Sample | Composition (at%) | Grain size (nm) |
|--------|-------------------|-----------------|
|        | Cs    | Ag    | Br    | I     | SEM $^a$ | XRD $^b$ |
| x=0    | 10.81 | 39.31 | 33.99 | 15.89 | 360    | 90     |
| x=0.25 | 8.3   | 40.53 | 25.93 | 25.24 | 408    | 91     |
| x=0.50 | 12.26 | 39.48 | 26.01 | 22.25 | 425    | 94     |
| x=0.75 | 10.91 | 42.53 | 24.36 | 22.20 | 437    | 97     |
| x=1    | 10.76 | 41.73 | 20.63 | 26.88 | 700    | 119    |

$^a$ Estimation from SEM images by ImageJ software.

$^b$ Calculation from XRD ($hkl$) peaks by Scherrer equation.

3.2. Silver-conducting properties of CsAg$_4$Br$_{3.5}$I$_{2.5}$
In practice, ionic conductivty of solid electrolyte can be measured by electrochemical impedance spectroscopy (EIS). Hereby, the silver-conducting properties of CsAg$_4$Br$_2$I$_2.5$ are characterized using the setup shown in figure 1 based on the Ag$^+$ ion beams generation. The collected ion current is proportional to the temperature-dependent ionic conductivity of solid electrolyte and the potential applied on the apex of emitter [16]. In the section, ion current as functions of working temperature and accelerating voltage are recorded, as shown in figures 5(a) and 5(b). The current increases with the temperature following the Arrhenius equation:

$$I = I_0 e^{-\frac{Q}{k_B T}}$$

where $Q$ indicates the surface potential barrier. A threshold feature is observed at the temperature of 150$^\circ$C, which is close to the melting point of CsAg$_4$Br$_2$I$_2.5$. The threshold character can be attributed to the quasi-liquid film occurring on the surface of SE resulting in a formation of Taylor cone [17].

![Figure 5.](image1.png)

**Figure 5.** Ion current ($I$) versus (a) working temperature ($T$) obtained at 15 kV and (b) accelerating voltage ($U_{acc}$) at 168$^\circ$C.

![Figure 6.](image2.png)

**Figure 6.** The ion emission current recorded at 152$^\circ$C and 15 kV for about 2 hours.

The applied voltage on the emitter is also able to enhance the ion emission, seen in figure 5(b) due
to the Schottky effect, i.e. the applied field lowers the surface potential barrier for ion emission [18].

Figure 6 presents the stability of ion emission current for a long term (ca. 2 hours), where the 15 nA current is obtained at 15 kV and 152°C using CsAg₄Br₂.5I₂.5 film. The red line is the obtained current using RbAg₄I₅ film. It is found that using CsAg₄Br₂.5I₂.5 film results in stronger ion emission than RbAg₄I₅ film, which demonstrates that the silver-conducting capacity of CsAg₄Br₂.5I₂.5 can be higher than that of RbAg₄I₅.

4. Conclusions
In the present work, superionic conductors CsAg₄Br₃₋ₓI₂₊ₓ (0 < x < 1) were successfully synthesized by means of high-energy ball milling at rotation rate of 450 rpm for 3 hours. The expand of lattice and the grow of grain were observed with an increase of iodine content. The grain size of CsAg₄Br₃₋ₓI₂₊ₓ was distributed in the range of 0.2 - 1 μm. The silver-conducting properties of superionic conductor CsAg₄Br₂.5I₂.5 were characterized based on the generation of Ag⁺ ion beams. The ion current of 15 nA was obtained at a temperature of 152°C and accelerating voltage of 15 kV. It was demonstrated that CsAg₄Br₂.5I₂.5 can possess higher ion-conducting capacity than RbAg₄I₅.

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