$Ag_{13}I_4(AsO_4)_3$: Synthesis, Crystal Structure and Ionic Conductivity

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Ruby-red single crystals of $Ag_{13}I_4(AsO_4)_3$ were prepared for the first time by reacting a stoichiometric mixture of Ag_2O, AgI and As_2O_3 at elevated oxygen pressure of 120 MPa and at a temperature of 350 °C. The polyhedral crystals belong to the monoclinic space group $P2_1/m$ with $a = 9.247(1)$, $b = 7.152(1)$, $c = 17.674(2)$ Å, $\beta = 91.492(2)°$, and $Z = 2$. The structure is fully ordered and was solved by Direct Methods, and refined on single crystal diffraction data (10376 observed reflections, $R1 = 3.28\,\%$). The crystal structure is built up of two two-dimensional interlocked partial structures, one consisting of silver and iodine ions, the other of silver and arsenate(V) ions. The slabs extend in the *ac* plane, and the Ag–I framework is linked to the $AsO_4{}^{3-}$ units by Ag–O contacts. The silver–oxygen interactions perturb the tetrahedron of the arsenate group, resulting in As–O distances ranging from 1.670 to 1.697 Å, and angles varying from 107.3 to 112.1°. Pure $Ag_{13}I_4(AsO_4)_3$ is a solid ion conductor with a r. t. conductivity of $6.4 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$ at 30 °C. The activation energy for silver ion conduction is 0.41 eV in the temperature range from 30 to 130 °C.

Key words: Silver, Iodine, Arsenate, Silver Ion Conductivity

Introduction

Silver iodide-containing materials exhibit exceptionally high silver ion conductivity in the solid state. Already at temperatures slightly above ambient conditions, their conductivities can reach values in the order of magnitude of $1\ \Omega^{-1}\ cm^{-1}$, which are comparable to those observed in molten salts. The most famous member in this class of electrolytes with a unique electrical performance is $RbAg_4I_5$ [1 – 3]. The impressive performance of silver ionic conductors has prompted efforts to expand this class of solid state electrolytes among others by combining silver iodide with silver oxyacid salts, resulting in *e. g.* AgI-$Ag_n(MO_4)$ (M = P, W, Se, Te, Cr) [4 – 10]. The structures and properties of these compounds have been studied thoroughly, in particular with respect to disorder and melting of the silver cation partial structures, and various special structural features have been discovered to occur, as there are extended arrays of interconnected metallocomplexes or new types of heteropolyanions of non-metals [8, 9]. For the AgI-$Ag_3(AsO_4)$ system, thus far only silver ion conducting glasses were reported [11 – 14]. In the course of our structural and related conductivity investigations on silver iodide-silver oxyacid salts we have now synthesized and characterized $Ag_{13}I_4(AsO_4)_3$, the first crystalline compound in this system.

Experimental Section

Synthesis

$Ag_{13}I_4(AsO_4)_3$ was prepared by reacting Ag_2O (freshly precipitated from $AgNO_3$ and KOH solutions), AgI (Fluka, p. a.) and As_2O_3 (Fluka, > 98 %) in stainless-steel autoclaves at elevated oxygen pressure and temperature. Stoichiometric amounts of the starting materials were intimately mixed and placed into gold tubes which were sealed on one side and mechanically closed on the other. In a typical experiment, $Ag_{13}I_4(AsO_4)_3$ was synthesized from a mixture of 104 mg Ag_2O (0.45 mmol), 94 mg AgI (0.4 mmol) and 30 mg As_2O_3 (0.15 mmol), which were reacted at $p(O_2)$ = 120 MPa and T = 350 °C for 50 h. In order to grow single crystals suitable for an X-ray diffraction analysis, 1.0 mL H_2O was added to the starting mixtures as a mineralizer. The crystalline product was filtered off, washed with deionized water and dried in air. The ruby-red crystals of $Ag_{13}I_4(AsO_4)_3$ are stable towards air and water.

X-Ray investigations

Powder samples were characterized by high-resolution X-ray powder diffraction (D8, Bruker, Cu$K_{\alpha 1}$ radiation from primary Ge(111) Johannson-type monochromator). The data

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Table 1. Experimental X-ray powder data for $Ag_{13}I_4(AsO_4)_3$ with $d > 1.58$ Å ($I > 1.5$ %).

d_{obs} (Å)	I (%)	h	k	l	d_{obs} (Å)	I (%)	h	k	l	d_{obs} (Å)	I (%)	h	k	l
5.4121	2.1	1	−1	−1	2.3341	9.8	3	2	0	1.9247	5.8	4	2	1
5.3622	4.5	1	1	1	2.3101	6.1	4	0	0	1.9113	3.8	4	0	5
3.9456	1.6	1	0	4	2.2929	29.6	3	0	5	1.9064	2.9	3	−1	−7
3.7580	2.6	0	1	4	2.2500	4.0	4	0	−2	1.8982	2.2	2	−2	−7
3.6827	2.6	2	0	−3	2.2369	4.9	1	−3	−2	1.8790	5.2	0	2	8
3.5907	4.8	2	0	3	2.2350	2.0	3	−1	−5	1.8528	1.7	0	3	6
3.4547	6.2	1	1	4	2.2254	7.3	2	−2	−5	1.8494	2.5	1	−2	−8
3.0488	5.3	3	0	−1	2.1834	1.7	3	1	5	1.8465	1.9	4	1	5
3.0186	7.1	1	−1	−5	2.1705	2.6	4	0	−3	1.8267	5.4	2	−3	−5
2.9756	2.5	1	1	5	2.1570	6.0	3	0	−6	1.8225	3.8	1	−3	−6
2.9447	5.1	0	0	6	2.1554	2.3	3	2	3	1.8190	2.8	5	0	−2
2.9331	14.7	3	0	−2	2.1444	4.4	1	3	3	1.8119	2.2	3	2	6
2.8904	35.3	1	2	3	2.1215	2.7	4	1	2	1.8110	2.4	1	3	6
2.8860	100.0	3	0	2	2.1186	1.6	2	3	0	1.7874	2.0	3	3	3
2.8300	27.9	3	1	0	2.1000	2.6	3	0	6	1.7852	2.2	5	−1	−1
2.8282	2.5	2	2	0	2.0807	3.0	3	−2	−4	1.7733	2.1	3	0	8
2.8271	12.8	1	0	−6	2.0698	4.4	4	0	−4	1.7675	2.5	2	−1	−9
2.7837	16.0	3	1	1	2.0658	3.6	2	−3	−2	1.7627	8.2	4	2	4
2.7597	2.7	3	0	−3	2.0547	5.7	2	3	2	1.7457	2.6	5	1	2
2.7200	12.9	0	1	6	2.0513	1.7	1	−3	−4	1.7269	5.2	4	0	−7
2.6811	5.8	2	2	2	2.0404	1.9	1	3	4	1.7101	2.8	2	3	6
2.6763	84.8	3	1	2	2.0260	4.1	4	0	4	1.6979	5.7	1	3	7
2.6736	4.7	1	−2	−4	2.0217	1.9	1	−2	−7	1.6548	3.3	4	−3	−1
2.6420	22.3	2	−1	−5	2.0035	3.5	1	2	7	1.6445	2.8	5	1	4
2.6291	51.6	1	−1	−6	2.0012	4.3	2	−3	−3	1.6414	1.8	2	−4	−2
2.5133	10.0	2	0	−6	1.9779	3.3	3	0	−7	1.6386	4.8	5	−2	−1
2.4967	3.0	3	0	4	1.9655	2.9	3	−2	−5	1.6364	3.3	3	0	9
2.4368	3.5	1	−2	−5	1.9575	6.1	4	0	−5	1.6133	2.6	2	3	7
2.3647	3.5	2	2	4	1.9493	2.5	4	1	4	1.6084	6.5	2	−4	−3
2.3625	4.1	0	3	1	1.9379	1.7	2	−1	−8	1.5844	2.7	5	0	−6

Table 2. Crystal structure data for $Ag_{13}I_4(AsO_4)_3$.

M_r	2326.67	T, K	296(2)
Cryst. size, mm^3	0.1×0.1×0.05	F(000), e	2036
Crystal system	monoclinic	hkl range	$-10 \leq h \leq +10$ $-8 \leq k \leq +8$ $-21 \leq l \leq +21$
Space group	$P2_1/m$	μ(MoK_α), mm^{-1}	20.3
a, Å	9.247(1)	Refl. measured	10376
b, Å	7.152(1)	Refl. unique	2227
c, Å	17.674(2)	R_{int}	2.80
β, deg	91.492(2)	Param. refined	170
V, Å^3	1168.3(3)	$R_1(F)^a$ (all reflections), %	3.28
		$wR_2(F^2)^a$ (all reflections), %	7.32
Z	2	GoF (F^2)	1.050
D_{calcd}, g cm^{-3}	6.61	$\Delta\rho_{fin}$ (max/min), e Å^{-3}	3.26 / −2.39

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

were recorded at r. t., covering the range of 5 to 90° in 2 θ. Experimental d values and relative intensities are given in Table 1. The single-crystal diffraction data were collected on a Bruker AXS Smart-CCD diffractometer (MoK_α radiation, graphite monochromator). The intensities were corrected for Lorentz and polarization effects, and a face-indexed absorption correction was applied. The structure was solved with Direct Methods using the program package SHELXS-97 [15] and refined by full-matrix least-squares techniques (SHELXL-97 [16]). All atoms were refined with anisotropic displacement parameters. For technical details of data acquisition and selected crystallographic data, see Tables 2 and 3.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-420671.

Impedance spectroscopy

Ionic conductivities of compact discs (diameter 6 mm, thickness 0.75 mm, pressed with 190 MPa) were measured by using ion-blocking gold electrodes. The samples were placed into a quartz glass cell [17], and measurements were performed under argon atmosphere. The temperature-dependent AC impedance spectra were recorded with a Novocontrol Alpha-A 4.2 Analyzer in combination with the impedance interface ZG 4 in a 2-wire arrangement in the frequency range of ν = 1.0 Hz to ν = 20 MHz. Measure-

Table 3. Atomic coordinates and equivalent isotropic displacement parameters U_{eq}[a] for $Ag_{13}I_4(AsO_4)_3$.

Atom	W.-position	x/a	y/b	z/c	U_{eq} (Å^2)
Ag(1)	2*e*	0.2957	1/4	0.3294	0.0313(2)
Ag(2)	2*e*	0.9491	3/4	0.3849	0.0293(2)
Ag(3)	4*f*	0.0222	0.5253	0.2421	0.0329(2)
Ag(4)	4*f*	0.6081	0.4686	0.3343	0.0413(3)
Ag(5)	4*f*	0.2286	0.4914	0.4770	0.0368(2)
Ag(6)	4*f*	0.3703	0.4889	0.1547	0.0602(3)
Ag(7)	2*e*	0.0887	3/4	0.0883	0.0527(4)
Ag(8)	4*f*	0.7356	0.5019	0.0670	0.0761(4)
I(1)	2*e*	0.7894	3/4	0.2197	0.0278(2)
I(2)	2*e*	0.4724	1/4	0.4575	0.0284(2)
I(3)	2*e*	0.6001	1/4	0.1949	0.0354(2)
I(4)	2*e*	0.4597	3/4	0.0463	0.0378(2)
As(1)	2*e*	0.3129	3/4	0.3216	0.0163(3)
As(2)	2*e*	0.0715	1/4	0.0737	0.0214(3)
As(3)	2*e*	0.9378	1/4	0.3940	0.0163(2)
O(1)	4*f*	0.2710	0.5549	0.2711	0.025(1)
O(2)	2*e*	0.2071	3/4	0.3992	0.024(2)
O(3)	2*e*	0.4899	3/4	0.3439	0.025(2)
O(4)	4*f*	0.1269	0.4423	0.1212	0.032(2)
O(5)	2*e*	0.1419	1/4	−0.0130	0.040(2)
O(6)	4*f*	0.8342	0.4465	0.3958	0.023(1)
O(7)	2*e*	0.0471	1/4	0.4709	0.026(2)
O(8)	2*e*	0.0361	1/4	0.3140	0.024(2)
O(9)	2*e*	0.8887	1/4	0.0633	0.051(3)

[a] $U_{eq} = \frac{1}{3}[U_{22} + 1/\sin^2\beta(U_{11} + U_{33} + 2U_{13}\cos\beta)]$.

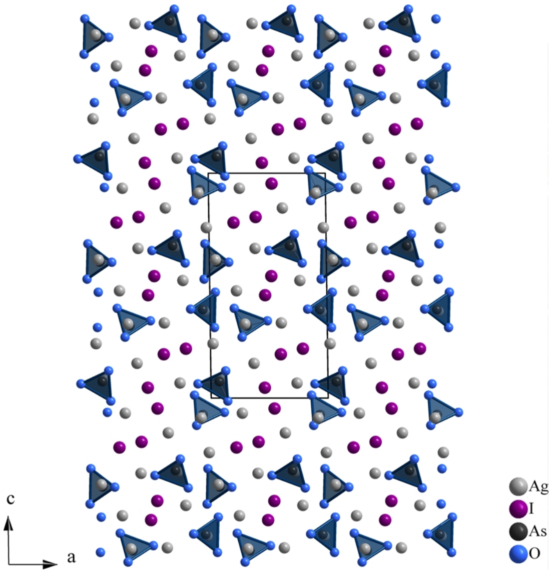

Fig. 1. Projection of the crystal structure of $Ag_{13}I_4(AsO_4)_3$ along [010]; unit cell marked by solid black lines.

ments and data recording were carried out with the program WINDETA [18]. The bulk conductivities were determined by non-linear mean squares deviation curve fitting of the impedance spectra using the program WINFIT [19].

Table 4. Selected interatomic distances (Å) and angles (deg) for $Ag_{13}I_4(AsO_4)_3$. Estimated standard deviations are given in parentheses.

Ag(1)–O(1)	2.411(6)	Ag(4)–O(6)	2.345(6)
Ag(1)–O(1)	2.411(6)	Ag(5)–O(2)	2.307(5)
Ag(1)–O(8)	2.404(8)	Ag(5)–O(6)	2.380(6)
Ag(2)–O(2)	2.389(8)	Ag(5)–O(7)	2.399(6)
Ag(2)–O(6)	2.412(6)	Ag(6)–O(1)	2.320(6)
Ag(2)–O(6)	2.412(6)	Ag(6)–O(4)	2.337(6)
Ag(2)–O(7)	2.559(8)	Ag(7)–O(4)	2.290(6)
Ag(3)–O(1)	2.353(6)	Ag(7)–O(4)	2.290(6)
Ag(3)–O(4)	2.437(6)	Ag(7)–O(5)	2.496(11)
Ag(3)–O(8)	2.339(4)	Ag(8)–O(5)	2.309(6)
Ag(4)–O(3)	2.287(4)	Ag(8)–O(9)	2.281(7)
Ag(1)–I(2)	2.780(2)	As(1)–O(1)	1.694(6)
Ag(2)–I(1)	3.264(2)	As(1)–O(1)	1.694(6)
Ag(3)–I(1)	2.701(1)	As(1)–O(2)	1.697(7)
Ag(4)–I(1)	3.321(1)	As(1)–O(3)	1.670(8)
Ag(4)–I(2)	2.972(1)	As(2)–O(4)	1.682(6)
Ag(4)–I(3)	2.923(2)	As(2)–O(4)	1.682(6)
Ag(5)–I(2)	2.853(1)	As(2)–O(5)	1.677(9)
Ag(6)–I(3)	2.800(2)	As(2)–O(9)	1.693(11)
Ag(6)–I(4)	2.805(2)	As(3)–O(6)	1.693(6)
Ag(8)–I(1)	3.266(2)	As(3)–O(6)	1.693(6)
Ag(8)–I(3)	3.162(2)	As(3)–O(7)	1.686(8)
Ag(8)–I(4)	3.223(2)	As(3)–O(8)	1.694(8)
Ag(8)–I(4)	3.112(2)		
O(1)–As(1)–O(1)	110.0(4)	O(5)–As(2)–O(4)	110.0(3)
O(1)–As(1)–O(2)	107.5(2)	O(5)–As(2)–O(4)	110.0(3)
O(1)–As(1)–O(2)	107.5(2)	O(5)–As(2)–O(9)	107.3(6)
O(3)–As(1)–O(1)	109.9(2)	O(6)–As(3)–O(6)	111.2(4)
O(3)–As(1)–O(1)	109.9(2)	O(6)–As(3)–O(8)	108.9(2)
O(3)–As(1)–O(2)	112.1(4)	O(6)–As(3)–O(8)	108.9(2)
O(4)–As(2)–O(4)	108.7(4)	O(7)–As(3)–O(6)	108.4(2)
O(4)–As(2)–O(9)	110.4(3)	O(7)–As(3)–O(6)	108.4(2)
O(4)–As(2)–O(9)	110.4(3)	O(7)–As(3)–O(8)	111.0(4)

Results and Discussion

Crystal structure

The synthesis of $Ag_{13}I_4(AsO_4)_3$ was achieved by reacting the binary constituents applying an elevated pressure of oxygen in a steel autoclave at a temperature of 350 °C. The experimental X-ray powder diffraction pattern (Table 1), which has been indexed based on the monoclinic crystal system with the refined lattice parameters $a = 9.247(1)$, $b = 7.152(1)$, $c = 17.674(2)$ Å, and $\beta = 91.492(2)°$, has proven the sample to be single phase; also, the measured pattern agrees perfectly with the calculated one. The crystal structure of $Ag_{13}I_4(AsO_4)_3$ has been solved from single-crystal data, collected at r. t. It consists of Ag^+ and I^- ions and isolated, fairly regular $AsO_4{}^{3-}$ tetrahedra (Fig. 1). As expected, arsenic is oxidized to a maximal oxidation state of +5, under the reaction conditions applied. The arsenate tetrahedra show only slight devia-

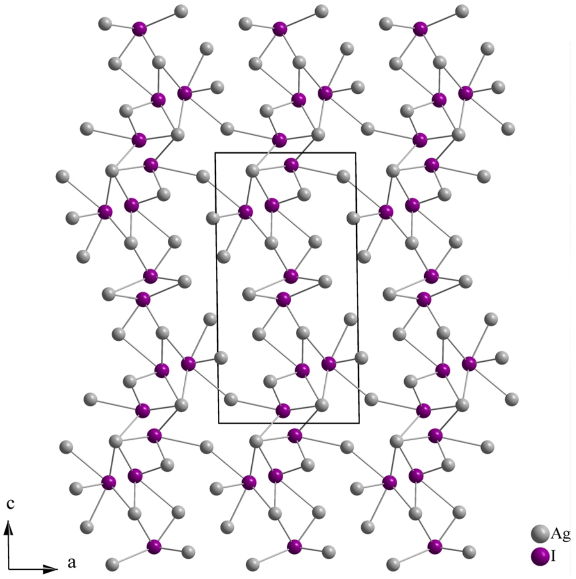

Fig. 2. View of the silver iodide partial structure of $Ag_{13}I_4(AsO_4)_3$ along [010].

tions from ideal T_d symmetry with respect to the angles (Table 4). The structure can be described as a complex layered polycationic framework of the general formula $[Ag_{13}I_4]^{9+}$, with the layers stacked perpendicular to the crystallographic *ac* plane, and tetrahedral anions AsO_4^{3-} embedded in between as guest anions (Fig. 1). Neither the $[Ag_{13}I_4]^{9+}$ layers nor the arrangement of the AsO_4^{3-} units within the silver iodide matrix can be attributed to a known structure type. Within the silver iodide partial structure the Ag–I bond lengths can be subdivided into two groups, representing the first coordination sphere with short distances between 2.701 and 3.321 Å, and a second sphere including distances ranging from 3.499 to 3.709 Å. The short bonds are located inside the Ag/I slabs, whereas the long Ag–I distances are bridging bonds to the neighboring silver iodide layers (Fig. 2). The linkage between the AsO_4^{3-} units and the Ag–I framework is established through Ag–O contacts. The Ag–O distances lie in the range of 2.281 – 2.559 Å, corresponding to silver oxygen bonds also found in silver iodide phosphates [5, 6]. The Ag^+ cations are in an environment of iodine and oxygen atoms showing strongly different coordination polyhedra. Four Ag^+ are in a trigonal-bipyramidal environment, and each two silver atoms are arranged in a distorted octahedral or tetrahedral coordination. Such a widely adaptable crystal–chemical behavior of silver has frequently been observed before in various mixed silver iodide-silver oxyacid compounds [6 – 10]. Iodide is exclusively coordinated by silver with the aforementioned Ag–I distances.

Table 5. Ionic conductivities (σ) and activation energies (E_a) for $Ag_{13}I_4(AsO_4)_3$.

	σ (Ω^{-1} cm^{-1})	E_a (eV)
heating	30 °C: 6.4×10^{-6} 130 °C: 2.3×10^{-4}	30 – 130 °C: 0.41
cooling	30 °C: 6.7×10^{-6} 130 °C: 2.2×10^{-4}	30 – 130 °C: 0.40

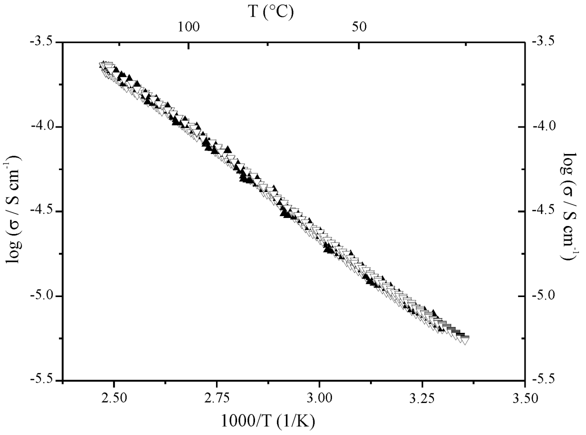

Fig. 3. Temperature dependence of the bulk ionic conductivity for $Ag_{13}I_4(AsO_4)_3$. Filled symbols represent heating, open symbols cooling mode.

Ionic conductivity

Ionic conductivities of $Ag_{13}I_4(AsO_4)_3$ were determined by employing AC impedance measurements (from 25 to 130 °C). A specimen for the conductivity measurements was prepared from the powder sample by pressing it into a pellet (see Experimental Section). On both sides of the pellet surface, gold was mounted in the form of thin foils as blocking electrodes. The Nyquist plots showed a typical behavior of an ionically conducting material. A semicircle at high frequencies is followed by a linear spike at low frequencies. DC [direct current] measurements were also performed with ion-blocking gold electrodes, and electronic transference numbers were calculated. There was negligible electronic contribution to conductivity, because electronic transference numbers were almost close to zero. The Arrhenius plot of the temperature-dependent bulk ionic conductivity for $Ag_{13}I_4(AsO_4)_3$ is displayed in Fig. 3.

Our investigations show that $Ag_{13}I_4(AsO_4)_3$ displays a comparatively low ionic conductivity with a r. t. value of 6.4×10^{-6} Ω^{-1} cm^{-1}. Between 30 and 130 °C, the conductivity increases by two orders of magnitude reaching a value of 2.3×10^{-4} Ω^{-1} cm^{-1}. These values compare well to the conductivity of Ag_4IPO_4 [6]. The calculated activation energies (E_a) obtained by applying the Arrhenius equation yield similar values of 0.41 and 0.40 eV for heating and cooling cycles, respectively (Table 5). In DSC measurements, no phase change or reaction could be observed in this temperature range. The conductivity is completely reversible in repeated heating and cooling cycles. After finishing the impedance measurements the samples were confirmed to be unaltered $Ag_{13}I_4(AsO_4)_3$ by X-ray powder diffraction experiments.

Conclusion

Single crystals of $Ag_{13}I_4(AsO_4)_3$ were prepared by an autoclave technique at elevated oxygen pressure and temperature. $Ag_{13}I_4(AsO_4)_3$ represents the first crystalline compound formed by combining a silver oxoarsenate and silver iodide. The crystal structure is built up from a layered silver iodide framework with composition $[Ag_{13}I_4]^{9+}$ and isolated AsO_4^{3-} anions in the interlayer space. In comparison with our earlier synthesized composite-type compounds, $Ag_{13}I_4(AsO_4)_3$ shows a low ionic conductivity of 6.4×10^{-6} Ω^{-1} cm^{-1} at 30 °C.

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