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$CsFe_xAg_{2-x}Te_2$ ($x = 0.72$): The First Quaternary Iron Telluride Synthesized from Molten Salt

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Chemical reactions in molten salts have been investigated extensively during the last several decades.[1,2] The molten salts in these reactions are utilized as solvent or reacting species, or sometimes both. In other cases they are also used as catalysts. Since the discovery of the first ternary transition-metal polysulfide by the flux growth method in 1987,[3] a considerable amount of research has been carried out in the synthesis of solid-state polychalcogenides from molten alkali-metal polychalcogenide salts (A_xQ_y, A = alkali metal, Q = S, Se, Te).[4,5]

Our recent work in the quaternary metal chalcogenides has shown that the flux growth techniques can be used efficiently to grow single crystals of a number of mixed-metal tellurides.[6] A variety of combinations have been found, including phases of mixed main-group metal (M), transition metal (T), and alkaline-earth metal (A), or M–T, T–T, A–M, and A–T compounds. Many of them exhibit unique structural features and properties. In this communication, we describe the synthesis and structure characterization of the first quaternary T–T type mixed-metal iron telluride, $CsFe_{0.72}Ag_{1.28}Te_2$.

Table 1. Selected Crystal Data for $CsFe_{0.72}Ag_{1.28}Te_2$

empirical formula	$CsFe_{0.72}Ag_{1.28}Te_2$	formula weight	566.21
space group	*I4/mmm* (No. 139)	T (°C)	20
a (Å)	4.5058(4)	λ (Å)	0.71073
		ϱ_{calcd} (g/cm^3)	5.992
c (Å)	15.4587(8)	μ (mm^{-1})	20.3
V (Å^3)	313.85(4)	$R(F)^a$ ($I > 2\sigma$, all I)	0.035, 0.038
Z	2	$wR(F^2)^b$ ($I > 2\sigma$, all I)	0.086, 0.088

[a] $R(F) = \sum||F_o| - |F_c||/\sum(|F_o|)$. [b] $wR(F^2) = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum w(F_o{}^2)^2\}^{0.5}$, where $w = 1/[(\sigma^2(F_o{}^2) + 0.0368P^2 + 0.8182P]$, $P = [0.33333\ \mathrm{MAX}(0,F_o{}^2) + 0.66667F_c{}^2]$.

Black, platelike crystals of $CsFe_{0.72}Ag_{1.28}Te_2$ were grown from a Cs_2Te/Te flux. A sample containing 0.1967 g (0.5 mmol) of Cs_2Te (Cs, 99.5%, Aldrich Chemical Co.), 0.0279 g (0.5 mmol) of Fe (99.9%, Strem Chemicals, Inc.), 0.0539 g (0.5 mmol) of Ag (99.9%, Aldrich Chemical Co.), and 0.1914 g (1.5 mmol) of Te (99.8%, Strem Chemicals, Inc.) was sealed in a Pyrex ampule under vacuum. The mixture was slowly heated to 450 °C and kept at this temperature for 4 days. The container was then cooled slowly to 120 °C (4 °C/h). Dimethylformamide (DMF) was used to isolate the final product from the excess flux. Microprobe analysis (JEOL JXA-8600 Superprobe) on the selected crystals indicated the presence of all four elements. The approximate atomic ratio was found to be Cs:Fe:Ag:Te = 1:0.5:1.5:2.25.

A powder X-ray diffraction measurement was performed on the sample after the isolation process. The resulting XRD pattern indicated the existence of $CsFe_{0.72}Ag_{1.28}Te_2$ as the major phase along with several small impurity peaks. The estimated percentage of the impurity phases was about 4–5%. The accurate structure of $CsFe_{0.72}Ag_{1.28}Te_2$ was determined by single-crystal X-ray diffraction.[7,8] Three standard reflections were examined every 2 h and showed no significant variation in intensity during the data collection. A numerical grid method was employed for the absorption correction.[9] An approximate isotropic extinction correction was applied (SHELXL93). Selected crystal data and lattice parameters are given in Table 1. Atomic coordinates and equivalent isotropic displacement parameters are in Table 2. The sum of the occupancies of the Ag and Fe atoms was restrained to be 0.125, yielding 0.080(1) for the Ag atom and 0.045(2) for the Fe atom. Thus, a value of $x = 0.72(2)$ was obtained for $CsFe_xAg_{2-x}Te_2$. At all times, the positions and displacement parameters of the Ag and Fe atoms were varied but constrained to be equal.

[†] Henry Dreyfus Teacher-Scholar 1994–1998.

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(8) Crystal size 0.16 × 0.12 × 0.06 mm; diffractometer used CAD4; number of data collected 1076; number of independent reflections 328 [$R(\mathrm{int}) = 0.044$]; observed reflections 300 [$I > 2\sigma(I)$], θ range 3–40 °C; number of variables 10; scan type ω, range 1.5–1.8; scan speed 2–8° min^{-1}; index range $0 \le h \le 8$, $-8 \le k \le 8$, $0 \le l \le 27$; goodness-of-fit 1.25; extinction coefficient 0.0097(12); largest ΔF peak and hole 1.3 and -1.7 e Å^{-3}.

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Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (U(eq)[a], Å^2 × 10^4) for $CsFe_{0.72}Ag_{1.28}Te_2$

atom	position	x	y	z	U(eq)
Cs	2a	0	0	0	343(2)
Fe/Ag	4d	0.5	0.0	0.25	303(3)
Te	4e	0.5	0.5	0.14405(4)	340(2)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

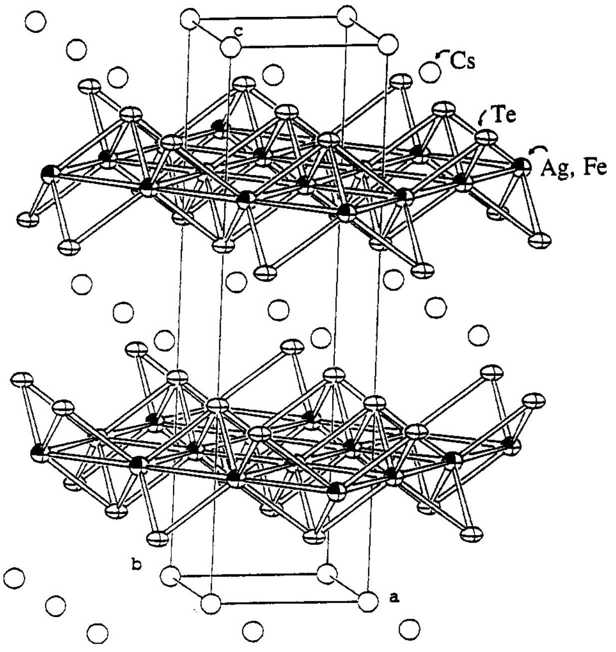

Figure 1. ORTEP representation of the $CsFe_{0.72}Ag_{1.28}Te_2$ structure along the a axis. The partially filled circles are Fe/Ag, cross-hatched circles are Te, and open circles are Cs. Two M_2Te_2 layers (M = Fe, Ag) are shown in the figure.

$CsFe_{0.72}Ag_{1.28}Te_2$ has a $ThCr_2Si_2$ type structure or, more generally, an AB_2X_2 (B = transition metal or main-group metal, X = group 15, 14, and sometimes 13 element) type structure.[10] It can be classified as a metal-rich telluride having a transition metal-to-tellurium ratio of 1:1. As shown in Figure 1, the structure consists of $[(Fe_xAg_{1-x})_2Te_2]^-$ layers and Cs^+ located between the layers. The Fe and Ag atoms share the same crystallographic site (4d) resulting in a (mixed) metal square lattice. The nearest-neighbor metal−metal distance is 3.1861(3) Å. The Te atoms are capped on both sides of the metal square lattice. The metal to tellurium coordination is a distorted tetrahedron with a bond length of 2.7853(4) Å. No Te−Te bond is observed in this structure as the shortest Te−Te distance between the two neighboring layers is 4.4554 Å and the shortest Te−Te distance within each layer is 4.5058 Å. Thus, $CsFe_{0.72}Ag_{1.28}Te_2$ is a monotelluride. The M_2Te_2 layer (M = Fe, Ag in $CsFe_{0.72}Ag_{1.28}Te_2$) is a common structural motif in all $ThCr_2Si_2$ (or AB_2X_2) type structures. What is interesting about $CsFe_{0.72}Ag_{1.28}Te_2$ is that Fe and Ag coexist in the same crystallographic site and that Fe may have mixed valencies.

The structure of $CsFe_{0.72}Ag_{1.28}Te_2$ is closely related to $K_{0.33}Ba_{0.67}AgTe_2$.[11a] Both have puckered metal−tellurium (M_2Te_2) layers that are separated by cations. The M−Te and M−M bonds are slightly longer in $K_{0.33}Ba_{0.67}AgTe_2$, 2.905(2) and 3.269(2) Å, respectively. The $K_{0.33}Ba_{0.67}AgTe_2$ structure also contains a second type of tellurium atoms [Te(2)] which form an isolated planar lattice. Such a Te lattice is absent in $CsFe_{0.72}Ag_{1.28}Te_2$. Another structural difference is found in the (M_2Te_2) layer: in $K_{0.33}Ba_{0.67}AgTe_2$, the metal atoms (M) are exclusively Ag, whereas 36% of the Ag atoms are replaced by Fe in the $CsFe_{0.72}Ag_{1.28}Te_2$ structure. Clearly, the layers in the two structures do not carry the same amount of charge. In the $K_{0.33}Ba_{0.67}AgTe_2$ structure, a −2 charge on the $Ag_2Te(1)_2$ layer leads to a reasonable oxidation state assignment to the elements: Ag(+I) and Te (−II). The total $+^{10}/_3$ charge (+1 × $^2/_3$ from K, and +2 × $^4/_3$ from Ba) leaves $^4/_3$ electrons to be accommodated by the second tellurium, Te(2), which enters as a planar lattice $(Te_2)^{4/3-}$. Band calculations have confirmed such an electron distribution.[11b] A −0.99 charge was computed for each AgTe(1) unit in the $Ag_2Te(1)_2$ layer, and a −0.68 charge for each Te(2) in the $Te(2)_2$ lattice. In the $CsFe_{0.725}Ag_{1.275}Te_2$ structure, however, such a "pure" Ag_2Te_2 layer would have resulted in an electron-deficient case with a single Cs^+ cation. To overcome this difficulty some Ag may be replaced by an element that provides more electrons to the layer, in this case, the Fe atom. The structure refinement yields 0.362 occupancy for Fe, and 0.638 occupancy for Ag in the 4d site. Assuming an oxidation state of +I for Ag and −II for Te, we are most likely to have mixed-valent Fe, Fe^{2+}, and Fe^{3+}, which gives rise to a total −1 charge for the layer. A partially filled Fe 3d band is therefore anticipated, and the compound is expected to be metallic. Accurate temperature-dependent electrical conductivity measurements and Mössbauer experiments are necessary for more reliable data.

It is likely that weak metal−metal interactions present in this structure. Electronic band calculations[12] on a model system[13] indicated weak bonding interactions between the metals in the square lattice. A subsequent crystal orbital overlap analysis (COOP)[14] generated a COOP value of 0.02 for the M−M bond.

The discovery of $CsFe_{0.72}Ag_{1.28}Te_2$ has provided an example of a mixed-metal telluride synthesized from the alkali-metal polytelluride flux. Using the same technique, it is possible to prepare other quaternary tellurides containing a variety of metals. Metal-rich tellurides often contain an interesting metal network. Many of these compounds have been synthesized at higher temperatures. $CsFe_{0.72}Ag_{1.28}Te_2$ is a monotelluride having rather high metal content. Its formation in the polytelluride flux at a relatively low temperature

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(11) (a) Li, J.; Guo, H.-Y.; Zhang, X.; Kanatzidis, M. G., manuscript in preparation. (b) A square-lattice geometry was used for Te(2) in the band calculations. However, some experiments have shown evidence for a superstructure in this compound. Further studies confirming and understanding such a superstructure are currently in progress.

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(13) The model used in the calculations contains equal number of Fe and Ag atoms in the square lattice. Alternate positions were assigned for these atoms. A 108K point set was taken in the average property analysis.

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has shown an alternative synthetic route for new materials of this type.

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Supplementary Material Available: Summary of the crystallographic data and tables of interatomic distances and angles and anisotropic displacement parameters (5 pages); listing of observed and calculated structure factors (1 page). Ordering information is given on any current masthead page.

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