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First Observation of Electronic Conductivity in Mixed-Valence Tellurium Oxides

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High electronic conductivity is readily obtained on n-type doping of CdO, In_2O_3, and SnO_2; however, such behavior has apparently not been observed on moving further along this row to Sb and Te. The conduction band for CdO, In_2O_3, and SnO_2 is dominated by cation 5s states; thus, these n-type doped compounds can be viewed as s^0/s^1 mixed valent compounds of type III according to the classification of Robin and Day.[1] Mixed valent oxides of Te are known. For example, Te_2O_5 ($Te^{4+}Te^{6+}O_5$), $Ag_2Te_2O_6$ ($Ag_2Te^{4+}Te^{6+}O_6$), and $SrTe_3O_8$ ($SrTe_2^{4+}Te^{6+}O_8$) are all type I mixed valent compounds with distinctly different sites for Te^{4+} and Te^{6+}.[2−4] The compound $CsTe^{4+}_{1/2}Te^{6+}_{3/2}O_6$ can be viewed as a type II mixed-valence compound because it is highly colored with both Te^{4+} and Te^{6+} on octahedral sites.[5] However, $CsTe^{4+}_{1/2}Te^{6+}_{3/2}O_6$ has no measurable electronic conductivity at room temperature. The only oxide of Te reported to be electronically conducting is $BaTl_{1/2}Te_{1/2}O_3$, where the conductivity is likely related to Tl/Te valence degeneracy caused by an overlap of the Tl 6s and Te 5s bands.[6] We have now prepared a new series of Te oxides that are electronically conductive with conductivities as high as 2 S/cm at room temperature.

Compounds of the general formula AM_2X_6 with a pyrochlore related structure are well-known where MX_6 octahedra share corners to form a cubic network (Figure 1).[7,8] The anion X is O or a mixture of O and F. Large A^{1+} cations, such as K, Rb, Cs, or Tl, occupy interstitial sites in the network. The three hexavalent cations found in this structure are Mo^{6+}, W^{6+}, and Te^{6+}, leading to compounds such as $RbTaWO_6$, $CsSbTeO_6$, $CsNbMoO_6$, $RbTi_{1/2}Te_{3/2}O_6$, and $KAl_{1/3}W_{5/3}O_6$. These are large band gap materials consistent with their white or light yellow colors. High ionic conductivity of the A^{1+} cation is generally observed.[7,8] Formation of $CsTi_{1/2}Te_{3/2}O_6$ has been reported but properties were not measured.[9] The compound $CsTe_2O_6$ has been reported with a rhombohedral distortion of the cubic pyrochlore structure.[5] Structure analysis shows cation ordering of Te^{4+} and Te^{6+} yielding a $CsTe^{4+}_{1/2}Te^{6+}_{3/2}O_6$ formula. A remarkable feature of $CsTe_2O_6$ is the very high symmetry of the Te^{4+} octahedron. This Te^{4+} is at a center of symmetry fixing all six Te−O distances to be equal. The O−Te−O angles deviate from 90° by less than 1°. Such high symmetry is unknown for any other oxide of Te^{4+} and unknown in oxides for any other $5s^2$ cation such as Sn^{2+} or Sb^{3+}. It was this highly unusual symmetry for Te^{4+} that suggested to us that it might be possible to prepare mixed-valence Te pyrochlores that were electronically conducting.

$Cs(M,Te)_2O_6$ oxides were prepared from appropriate quantities of $CsNO_3$, TeO_2/H_6TeO_6, and an oxide of M by heating in air at 450 to 650 °C. They were characterized by X-ray powder diffraction, dc electrical conductivity, and Seebeck coefficients at 25 °C. Neutron diffraction data were collected on three compounds at NIST.

The nominal compositions of the new $Cs(M,Te)_2O_6$ pyrochlores prepared in this study are given in Table 1 with their cubic cell edges at 25 °C. These include compounds of the types $CsM^{4+}_{1/2}Te^{6+}_{3/2}O_6$, $CsM^{3+}_{1/3}Te_{5/3}O_6$ and $CsM^{2+}_{1/4}Te_{7/4}O_6$. A plot of unit-cell parameters versus average ionic radius of octahedral cations for all the compounds shows a linear behavior (Figure 2). All of these compounds are black. Electronic conductivity cannot be detected in some of these compounds, indicating that the conductivity is less than 1×10^{-6} S/cm. However, others show electronic conductivity at room temperature that can be as high as high as 2 S/cm (Table 1). For those that conduct, the temperature dependence of the conductivity generally indicates semiconducting behavior (Figure 3). However, the lack of significant temperature dependence for some suggests degenerate semiconducting behavior. The Seebeck coefficients (Table 1) indicate that the conductivity is due to electrons rather holes. Low Seebeck coefficients are observed for the better conductors, as would be expected. The higher Seebeck coefficients for the insulating samples suggests that grain boundaries are not the cause of the high resistance. Plots

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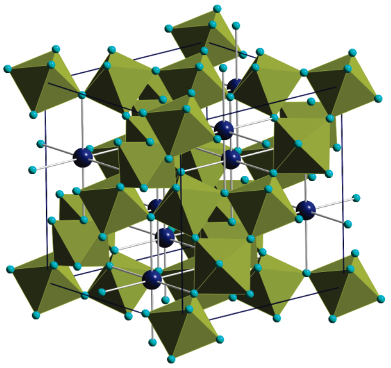

Figure 1. Structure of cubic CsM_2X_6 pyrochlores as a network of corner-shared MO_6 octahedra with Cs (blue atoms) in an interstitial site.

Table 1. Room-Temperature Values of the Cubic Cell Edge, Electrical Resistivity, And Seebeck Coefficient for $Cs(M,Te)_2O_6$ Pyrochlores

compd	a (Å)(±0.005)	ρ (Ωcm)	S (μV/K)
	$CsM^{3+}{}_{1/3}Te_{5/3}O_6$		
$Cs(Al_{1/3}Te_{5/3})O_6$	10.085	10	−87
$Cs(Cr_{1/3}Te_{5/3})O_6$	10.159	$> 1 \times 10^6$	
$Cs(Mn_{1/3}Te_{5/3})O_6$	10.186	3×10^3	−390
$Cs(Fe_{1/3}Te_{5/3})O_6$	10.183	42	−130
$Cs(Co_{1/3}Te_{5/3})O_6$	10.175	118	−206
$Cs(Ga_{1/3}Te_{5/3})O_6$	10.158	3	−50
$Cs(Sc_{1/3}Te_{5/3})O_6$	10.256	1×10^5	
$Cs(In_{1/3}Te_{5/3})O_6$	10.281	33	−150
$Cs(Tl_{1/3}Te_{5/3})O_6$	10.345	3	−70
$Cs(Lu_{1/3}Te_{5/3}O_6$	10.348	$> 1 \times 10^6$	
$Cs(Yb_{1/3}Te_{5/3})O_6$	10.357	$> 1 \times 10^6$	
$Cs(Tm_{1/3}Te_{5/3})O_6$	10.364	$> 1 \times 10^6$	
$Cs(Er_{1/3}Te_{5/3})O_6$	10.375	$> 1 \times 10^6$	
$Cs(Ho_{1/3}Te_{5/3})O_6$	10.394	$> 1 \times 10^6$	
	$CsM^{4+}{}_{1/2}Te_{3/2}O_6$		
$Cs(Ge_{1/2}Te_{3/2})O_6$	10.044	0.5	−51
$Cs(Ti_{1/2}Te_{3/2})O_6$[a]	10.150	$> 1 \times 10^6$	
$Cs(Rh_{1/2}Te_{3/2})O_6$	10.181	1×10^3	−90
$Cs(Ru_{1/2}Te_{3/2})O_6$[a]	10.158		
	$CsM^{2+}{}_{1/4}Te_{7/4}O_6$		
$Cs(Mg_{1/4}Te_{7/4})O_6$	10.220	482	−180
$Cs(Zn_{1/4}Te_{7/4})O_6$	10.233	$> 10^6$	
$Cs(Ni_{1/4}Te_{7/4})O_6$	10.219	$> 10^6$	

[a] MO_2 impurities.

of log ρ vs 1/T do not show a linear dependence (Figure S1 in the Supporting Information), but a nearly linear dependence is found by plotting log ρ vs $1/T^{1/4}$ (Figure S2 in the Supporting Information), behavior that has been attributed to a variable range hopping of carriers. The color and the conductivity of $CsTl_{1/3}Te_{5/3}O_6$ can be attributed to Tl/Te valence degeneracy as in the case of $BaTl_{1/2}Te_{1/2}O_3$. However, the color and electrical properties of the other compounds are inconsistent with their ideal formulas. Apparently, there is some mixed valency of Te and therefore some deviations from the ideal stoichiometries, which may be very small. Possible deviations from ideal stoichiometry include concentration of Cs^{1+} interstitial cations, the precise M/Te ratio, and oxygen deficiency. Synthesis under pure oxygen still gives black phases. Our experimental variations of the M/Te ratios suggest some range of stoichiometry, but all compositions are black. Normally, significant oxygen vacancies do not exist on the octahedral network of the pyrochlore structure.

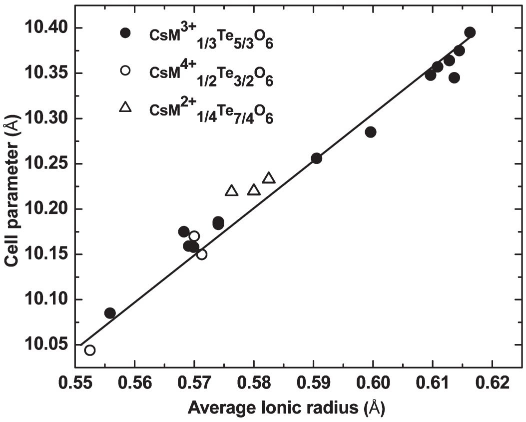

Figure 2. Average ionic radius of octahedral cations vs a lattice parameter for $Cs(M,Te)O_6$ phases.

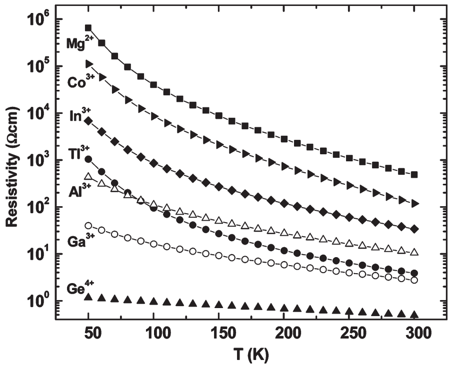

Figure 3. Resistivity for $Cs(M,Te)_2O_6$ phases plotted vs. temperature.

An apparent exception is $TaWO_{5.5}$, but this compound was prepared by an unusual multistep synthesis and oxygen vacancies were not fully confirmed by a neutron diffraction study.[10] Titration could potentially determine the amount of Te^{6+} reduction, but our attempts at titration have been thwarted by our inability to dissolve these pyrochlores.

The structure of TeO_3 consists of a network of Te^{6+} octahedra sharing corners with a Te−O−Te angle of 138°, essentially the same Te−O−Te angle as in the $Cs(M,Te)_2O_6$ pyrochlores.[11] Although TeO_3 is nearly white, its color is actually a very light gray. This indicates a high band gap material with a low level of optical absorption throughout the visible region because of defects. The color centers in TeO_3 leading to the gray color may well be the same color centers causing the black color in our Te pyrochlores, and this center would be associated with a slight reduction of Te^{6+}.

Neutron diffraction studies were conducted on our $CsGe_{1/2}Te_{3/2}O_6$ and $CsAl_{1/3}Te_{5/3}O_6$ samples in an effort to determine if their relatively high conductivities might be due to detectable deviations from ideal stoichiometry or ideal structure. A neutron diffraction study of $CsMn_{1/3}Te_{5/3}O_6$ was included because the relative

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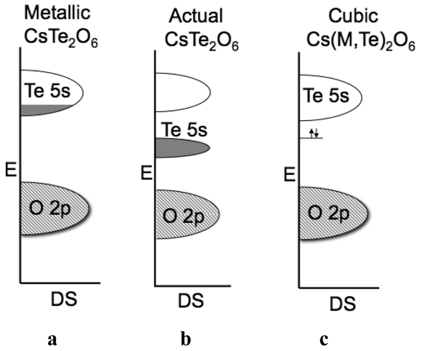

Figure 4. Schematic energy diagrams for (a) hypothetical cubic $CsTe_2O_6$ that is metallic due to a 5s band that is 1/4 filled, (b) actual rhombohedral $CsTe_2O_6$, and (c) cubic $Cs(M,Te)_2O_6$ phases. If $CsTe_2O_6$ had the ideal cubic pyrochlore structure with all Te atoms on equivalent sites, (a) would pertain. Charge ordering results in distinctly different Te sites in rhombohedral $CsTe_2O_6$ (b), with Te^{4+} having longer Te−O distances than Te^{6+}, leading to a splitting of the 5s band with filled 5s states associated with Te^{4+} and empty 5s states associated with Te^{6+}. For the $Cs(M,Te)_2O_6$ pyrochlores, the number of filled 5s states is much fewer than in $CsTe_2O_6$, but the energy of these states can be higher in the more contracted lattices leading to electronic conductivity.

scattering powers of Mn and Te are very different, thus giving a very accurate determination of the Mn/Te ratio on the octahedral sites. Refinements included variations of the relative scattering on the 3 sites: Cs, (M,Te), and O. For all three compounds, no improvement in fit to the observed data was obtained by consideration of any possible deviation from the ideal stoichiometry. Details are provided in the Supporting Information. Although these refinements provide no evidence for a deviation from the ideal formulas, the accuracy of this determination cannot exclude the possibility of as much as 10% Te^{4+} in the Al and Ge compounds. The scattering power of Mn provides a much more accurate determination of the M/Te ratio. Refinement gives $CsMn_{0.31}Te_{1.69}O_6$, suggesting slight reduction of Te^{6+} assuming that Mn is Mn^{3+}. However, this deviation from ideal is only two times the standard deviation; thus, it does not reliably indicate any deviation from ideal stoichiometry. Deviations from ideal stoichiometry that may occur for this sample of $Cs(Mn,Te)_2O_6$ would give a maximum of 2% Te^{4+}. The average Te^{6+}−O distance in the rhombohedral pyrochlore $CsTe_2O_6$ is 1.922(5) Å. In $CsAl_{1/3}Te_{5/3}O_6$ and $CsGe_{1/2}Te_{3/2}O_6$, we find (M,Te)-O distances of 1.917(1) and 1.914(1) Å, respectively. These slightly smaller distances for the Al and Ge compounds are expected based on the smaller radii of Al and Ge relative to Te^{6+}: 0.535 Å for Al, 0.53 Å for Ge, and 0.56 Å for Te^{6+}.[12]

We conclude that the black color of all of our cubic $Cs(M,Te)_2O_6$ pyrochlores indicates some reduction of Te^{6+}. The number of associated filled 5s states is significant enough to produce color and sometimes electronic conductivity but may be very small, especially relative to $CsTe_2O_6$. Explaining the conductivity variations is a challenge because there would appear to be at least three important variables: the number of occupied 5s states, the energies of these occupied 5s states relative to the conduction band, and the mobility of the conduction electrons. Only the $CsM^{3+}_{1/3}Te_{5/3}O_6$ series is large enough to expect the emergence of reliable trends. Two trends seem apparent in this series. Conductivity is enhanced by a smaller lattice and by M cations having states of the appropriate energy to mix into the Te 5s band. The higher conductivity we observe for some of our cubic $Cs(M,Te)_2O_6$ pyrochlores must be due to occupied 5s states that are closer to the conduction band than in rhombohedral $CsTe_2O_6$ (Figure 4), which has a conductivity less than 1×10^{-6} S/cm at room temperature. This is not surprising because in our cubic $Cs(M,Te)_2O_6$ pyrochlores there is no cooperative lattice distortion stabilizing Te^{4+} with longer Te−O distances as occurs in rhombohedral $CsTe_2O_6$. Because none of the cubic $Cs(M,Te)_2O_6$ pyrochlores are metallic, it appears that 5s electrons are always trapped in pairs forming Te^{4+} through a local lattice distortion with longer Te−O distances. The higher energy of these filled 5s states relative to rhombohedral $CsTe_2O_6$ for at least some of our cubic $Cs(M,Te)_2O_6$ pyrochlores indicates that the Te^{4+}−O distances are not as long as in rhombohedral $CsTe_2O_6$. Smaller cell edges for the $CsM^{3+}_{1/3}Te_{5/3}O_6$ pyrochlores tend to be associated with higher conductivities (Table 1), suggesting that the more compact lattices weaken the stabilization of the of the trapped 5s electrons. The $CsM^{3+}_{1/3}Te_{1/3}O_6$ pyrochlores with the larger cell edges promote a deeper trap, resulting generally in no observable conductivity at room temperature. The trend with size alone, however, does not explain the conductivity in all cases. For example, a higher conductivity would be expected for M = Al and a lower conductivity for M = In. A possibility is that M cations having states of the appropriate energy to mix into the Te 5s band will enhance conductivity. The band gap of Al_2O_3 is greater than 6 eV and thus Al does not have states of suitable energy to mix into the Te 5s band. The band gap of In_2O_3 is about 3 eV, which means that In will contribute 5s states that will mix into the Te 5s band and possibly enhance conductivity. The impact of this mixing is so great for M = Tl that good conductivity occurs despite the relatively large cell edge. Trends within the $CsM^{4+}_{1/2}Te_{3/2}O_6$ and $CsM^{2+}_{1/4}Te_{7/4}O_6$ series are less clear because of the small number of examples in each series. However, we do note the highest conductivity we have thus far observed is for $CsGe^{4+}_{1/2}Te_{3/2}O_6$, which also has the smallest cell edge we have observed.

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Supporting Information Available: Synthesis and characterization details and information on some new $Rb(M,Te)_2O_6$ pyrochlores (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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