of phillipsite, clinoptilolite, mordenite, erionite, and chabazite (*2*); furthermore he infers from studies of Quaternary saline-lake deposits that analcime in the Green River Formation formed by the reaction of alkali-rich zeolites. Only in this way can analcimic tuffs in the Green River Formation be reconciled with zeolitic tuffs of modern desert lakes, in which silicic glass alters directly to phillipsite, clinoptilolite, and erionite.

Petrographic study (*5*) of analcimic tuffs in the Miocene Barstow Formation of California has shown that analcime formed from clinoptilolite and phillipsite precursors instead of directly from silicic glass. Relict glass occurs in some tuffs of the Barstow Formation, but nowhere is analcime associated with the glass. Moreover, analcime probably has replaced phillipsite and clinoptilolite in the Miocene tuffs at Kramer, California (*2*). Thus it appears that analcime in saline-lake deposits characteristically forms from an alkali-rich zeolite precursor rather than by the direct reaction of saline-lake water with silicic volcanic glass.

In modern, saline, alkaline lakes a relation exists between salinity and zeolite reaction rates (*6*): in general, high salinity correlates with increased reaction rates. In addition, high salinity decreases the activity of water, possibly favoring a less hydrous phase such as analcime over more hydrous phases such as clinoptilolite or mordenite (*2*). The same relations hold true in the Green River Formation, where clinoptilolite and mordenite are preserved *only* in tuffs deposited in water that is relatively fresh.

Lake Gosiute, in which the Eocene Green River Formation was deposited, underwent several phases of expansion and contraction, possibly because of both climatic and tectonic changes (*7*). The Tipton shale member was deposited when the lake had great extent, whereas the overlying Wilkins Peak member was deposited when the lake was at its minimal extent. Extensive deposits of trona and other saline minerals in the Wilkins Peak member in Wyoming are well documented (*8*), but saline minerals are absent from the Tipton shale member. The high yields of oil by shales in the Tipton, higher than yields by the shales of Wilkins Peak, indicate relatively deep waters of moderate salinity. Organisms that thrived near the surface of the lake were preserved in the strongly reducing environment of a monimolimnion in the bottom layers of the lake water (see *9*).

Thus it is suggested that, in the relatively saline environment where the Wilkins Peak member was deposited, reaction rates were higher and the activity of water was lower, and tuffs containing clinoptilolite and mordenite reacted to form analcime; in the most saline environments, the analcime reacted to form albite or K-feldspar (*2*). In the less saline environment where the Tipton shale member was deposited, some of the tuffs containing clinoptilolite and mordenite have been preserved.

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10. Supported by the graduate division of the University of Wyoming. We thank G. U. Dinneen (research director), G. F. Dana, J. W. Smith, L. Trudell, and W. Robb, of the Laramie Petroleum Research Center, U.S. Bureau of Mines, for cooperation; and R. L. Hay and R. A. Sheppard for comments on the manuscript.

30 April 1967

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High-Conductivity Solid Electrolytes: MAg_4I_5

Abstract. *The solid electrolytes MAg_4I_5, where M may be potassium, rubidium, or ammonium, have an ionic conductivity of 0.2 (ohm cm)$^{-1}$ at 20°C. Although pure $CsAg_4I_5$ does not form, partial substitution of cesium into the M position was obtained. The high-conducting phases of KAg_4I_5 and $RbAg_4I_5$ may be quenched to low temperatures, where they transform to resistive phases at $-136°$ and $-155°C$, respectively.*

Solid electrolytes at ambient temperatures generally have extremely low ionic conductivities, less than 10^{-6} (ohm cm)$^{-1}$ whereas aqueous electrolytes have specific conductivities of nominally 0.5 (ohm cm)$^{-1}$. We were quite interested in the reports (*1*) that the compound Ag_3SI has a conductivity of 10^{-2} (ohm cm)$^{-1}$, and subsequently we have investigated a number of other double salts of AgI. We now report our electrical conductivity results for the compounds of the group MAg_4I_5 (M = K, Rb, NH_4, or, to a limited extent, Cs) in which we have observed conductivities of 0.21 (ohm cm)$^{-1}$ at 20°C.

An investigation of the alkali metal iodide–silver iodide systems has recently been carried out by Bradley and Greene (*2*). They also observed high ionic conductivity in MAg_4I_5, although the values of 0.05 and 0.12 (ohm cm)$^{-1}$ which they report for KAg_4I_5 and $RbAg_4I_5$, respectively, are somewhat lower than our result of 0.21 (ohm cm)$^{-1}$.

Bradley and Greene report conductivities for the temperature interval from room temperature to the incongruent melting points of KAg_4I_5 (253°C) and $RbAg_4I_5$ (228°C). Furthermore, these authors reported that conductivity was due entirely to silver ion. We investigated the conductivity of these compounds over the interval from $-165°$ to 150°C and found a reversible transition to a nonconductive phase occurring at low temperatures.

We prepared the MAg_4I_5 compounds by combining stoichiometric amounts of AgI and the alkali iodide, melting the mixture, and then quenching it. This intermediate product was ground,

Table 1. Low-temperature transition in solid electrolytes MAg_4I_5.

Compound	Transition temp. *T* (°C)	Specific conductivity (ohm cm)$^{-1}$ at *T*	
		α-Phase	β-Phase
KAg_4I_5	−136	5×10^{-4}	2×10^{-6}
$(K_3Rb)_{\frac{1}{4}}Ag_4I_5$	−139	2×10^{-4}	1×10^{-6}
$RbAg_4I_5$	−155	5×10^{-5}	6×10^{-7}

Table 2. Lattice constants (*a*), x-ray densities, and bulk densities of MAg_4I_5.

Formula	*a* (Å)	X-ray density (g/cm^3)	Bulk density (g/cm^3)
KAg_4I_5	11.13	5.32	
$K_{0.5}Rb_{0.5}Ag_4I_5$	11.19	5.35	
$NH_4Ag_4I_5$	11.19	5.14	
$RbAg_4I_5$	11.24	5.38	5.30
$K_{0.5}Cs_{0.5}Ag_4I_5$	11.25	5.37	

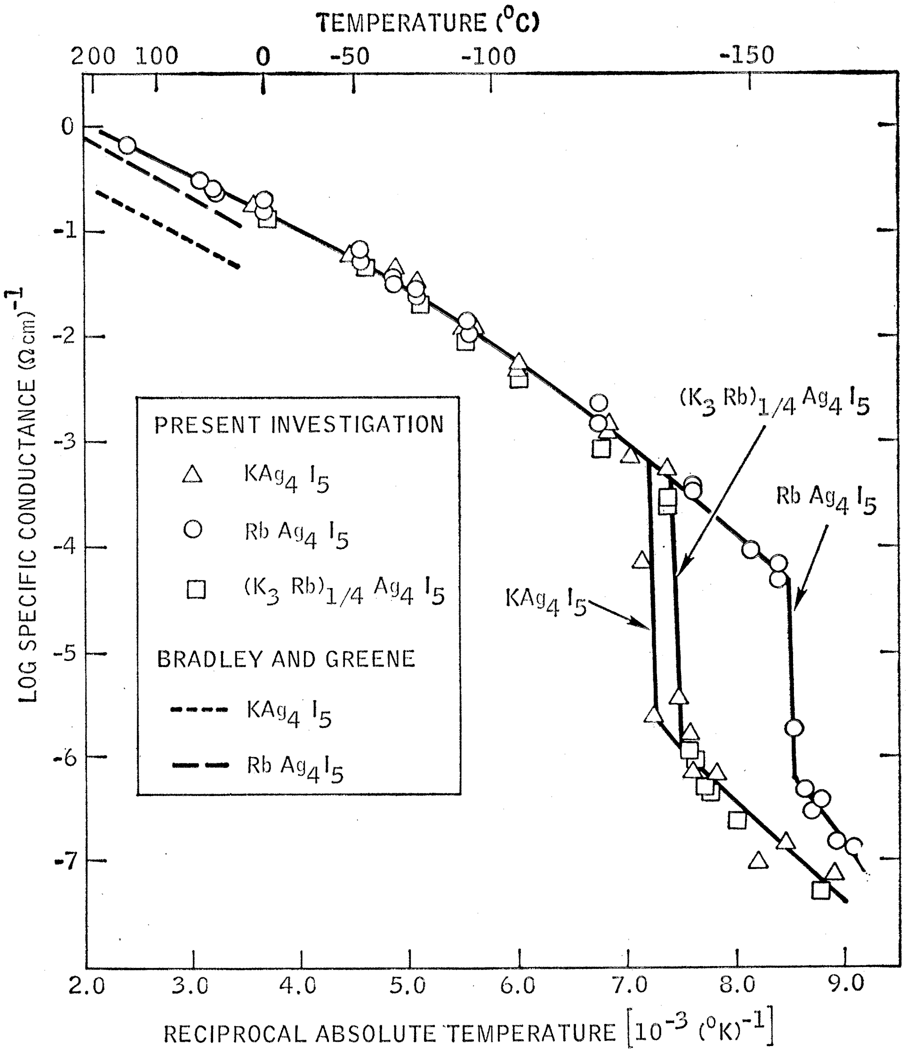

Fig. 1. Ionic conductivity of KAg_4I_5, $RbAg_4I_5$, and $(K_3Rb)_{1/4}$ Ag_4I_5. The temperature range is from 150° to −160°C. Bradley and Greene's conductivity curves for the high-temperature region are included (2).

made into pellets, and then annealed at 165°C for 16 hours. The products obtained in this manner were shown to be single phase by x-ray powder analysis. We observed that KAg_4I_5 is hygroscopic and deteriorates during prolonged exposure to the atmosphere whereas the $RbAg_4I_5$ is relatively inert. Consequently, subsequent operations were carried out in a dry box.

The conductivities were determined by making the polycrystalline product into pellets and measuring its resistance with a 1000 cycle/second conductivity bridge (ESI, Model 250 DA). Contact resistance was appreciable when we used flat silver electrodes to contact the sample. Little improvement was observed when evaporated silver contacts or amalgamated silver electrodes were used on the pellet sample. We found, however, that electrodes made of mixtures of electrolyte and powdered silver permitted low contact resistance measurements to be carried out on the samples.

The conductivities were measured over the range from −165° to 150°C. Samples for low temperature measurement were prepared by encapsulating the conductivity pellet and then cooling it in a Dewar. The temperature could thus be regulated down to liquid N_2 temperature. The high temperature samples were heated in an environmental oven to temperatures of up to 150°C. No corrections were applied for the expansivity of the sample since the reproducibility of the measurements was ± 10 percent.

Figure 1 shows our conductivity results for KAg_4I_5, $RbAg_4I_5$, and the solid solution $(K_3Rb)_{1/4}$ Ag_4I_5 (this can be written $K_{3/4}$ $Rb_{1/4}$ Ag_4I_5) and also those of Bradley and Green (*2*). These authors reported that the solid electrolyte KAg_4I_5 is thermodynamically unstable below 38°C with respect to a disproportionation reaction to form K_2AgI_3 and AgI. However, the disproportionation reaction is quite sluggish; no difficulty was encountered in the low-temperature measurements.

Our results represent several cooling and heating cycles, and the low temperature transformation from the conductive (α) phase to the resistive (β) phase occurred reversibly. The transition temperatures and the conductivities of the α- and β-phases are given in Table 1. The transition temperatures were reproducible to within ± 2°C, and the conductivities were reproducible to within a factor of 2 or 3 at low temperatures and to 10 percent at superambient temperatures. Within the accuracy of the data, the conductivities of the α-phases of KAg_4I_5, $RbAg_4I_5$, and their solid solutions are identical over the entire temperature range investigated, in contrast to the results of Bradley and Greene; they reported that the conductivity of $RbAg_4I_5$ is greater than that of KAg_4I_5. The discrepancies between their results and ours may be due to contact-resistance problems in their work because we did observe such problems with silver-foil contacts, and the essential difference in the two experimental procedures appears to be in the method of contacting the samples.

The transition to the nonconductive β-phase occurs at a temperature that is a function of the alkali metal cation M in MAg_4I_5; the expanded unit cell (see Table 2) associated with the larger alkali metal cation permits the high mobility of the silver ion to persist to the lower temperatures.

The x-ray powder patterns of the MAg_4I_5 compositions listed in Table 2 showed that the compounds were isostructural. Geller (*3*) has shown that the unit cell is cubic; the lattice constants and corresponding densities are reported in Table 2. (The bulk density obtained from a pressed pellet of $RbAg_4I_5$ was in fair agreement with the x-ray density.) We found that although Cs was too large to form the compound $CsAg_4I_5$, it did form solid solutions with K, Rb, or NH_4 in the MAg_4I_5 structure.

The crystal structure of $RbAg_4I_5$, determined by Geller (*3*), indicates the unusual nature of the arrangement of anions and M^+ ions. It is this arrangement which accounts for the high mobility of the silver ion in these materials.

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4 May 1967 ■

Crystal Structure of the Solid Electrolyte, RbAg$_4$I$_5$

Abstract. *The crystal structure of the solid electrolyte* RbAg$_4$I$_5$ *has been determined from single-crystal x-ray diffraction counter data. There are four* RbAg$_4$I$_5$ *in a cubic unit cell with* $a = 11.24$ Å. *The structure refinement, by least squares, is based on space group* P4$_1$3 (O^7). *The arrangement of the iodide ions is similar to that of the manganese atoms in* β*-manganese, and provides 56 iodide tetrahedra per unit cell, which share faces in such manner as to provide diffusion paths for the silver ions. The occurrence of the two low-temperature phases of* RbAg$_4$I$_5$ *has been established by x-ray diffraction and optical examination.*

The unusual family of isostructural solid electrolytes with formula MAg$_4$I$_5$ in which M is K$^+$, Rb$^+$, or NH$_4^+$ was discovered at the Atomics International laboratories by B. B. Owens (*1*). Inasmuch as it appeared that the material would have considerable application, publication was delayed. However, two papers have now been published by Bradley and Greene (*2*) on their independent discovery of the compounds.

No clue to the structure of the compounds has as yet been given. I have determined it, however, and my purpose here is to describe it and show how it accounts for the conductivity.

The compound which appeared to be the best suited for this work is that in which M is Rb, because it is the most stable against moisture (*1*). The x-ray data, on which the structure reported here was based, were obtained from a single crystal ground to a sphere of 0.22-mm diameter with a Bond (*3*) sphere grinder. The single crystal was grown by Hiller and Owens (*4*), under conditions based on a phase diagram worked out by Topol (*5*).

Crystals of RbAg$_4$I$_5$ are optically isotropic, therefore cubic, with a equal to 11.24 ± 0.02 Å and cell content of four RbAg$_4$I$_5$. The x-ray density is 5.384 g/cm^3, in good agreement with the density, 5.30 g/cm^3, measured by Owens (*1*). The crystals have diffraction symmetry $m3m$; the only systematic absences are those for $h00$ with $h \neq 4n$. On the assumption that intensities of such reflections are identically zero, the crystal belongs to one of the enantiomorphous space groups $P4_33(O^6)$ or $P4_13(O^7)$. No attempt has been made to determine the absolute configuration; the imaginary contributions of the anomalous dispersion for MoKα radiation are small, and no deviation from $m3m$ symmetry was observed on a set of Buerger precession camera photographs. (When larger single crystals are available, polarimetric examination will be made.) The determination and refinement of the structure was based on space group $P4_13$.

With the knowledge of the properties of the crystal (*1*), it was apparent that the Ag$^+$ ions would not be ordered. Disorder of the I$^-$ and Rb$^+$ ions appeared to be precluded by their sizes. Thus the iodide ions were probably in sets 8(*c*) and 12(*d*) of the space group. The combination of these two sets allows only moderate variation on one logical arrangement of these ions in the unit cell: the arrangement is that of the Mn atoms in β-Mn (*6*). (β-Manganese and some isostructural intermetallic compounds are the only other crystals known to belong to the space group.) The Rb$^+$ ions are in the 4(*a*) sites, which are surrounded by distorted octahedra of iodide ions. It remained to determine the parameters of the iodide ions and to find the sites for the Ag$^+$ ions and their occupation numbers.

The intensity data were collected manually with a Buerger-Supper goniometer and North American Philips cir-

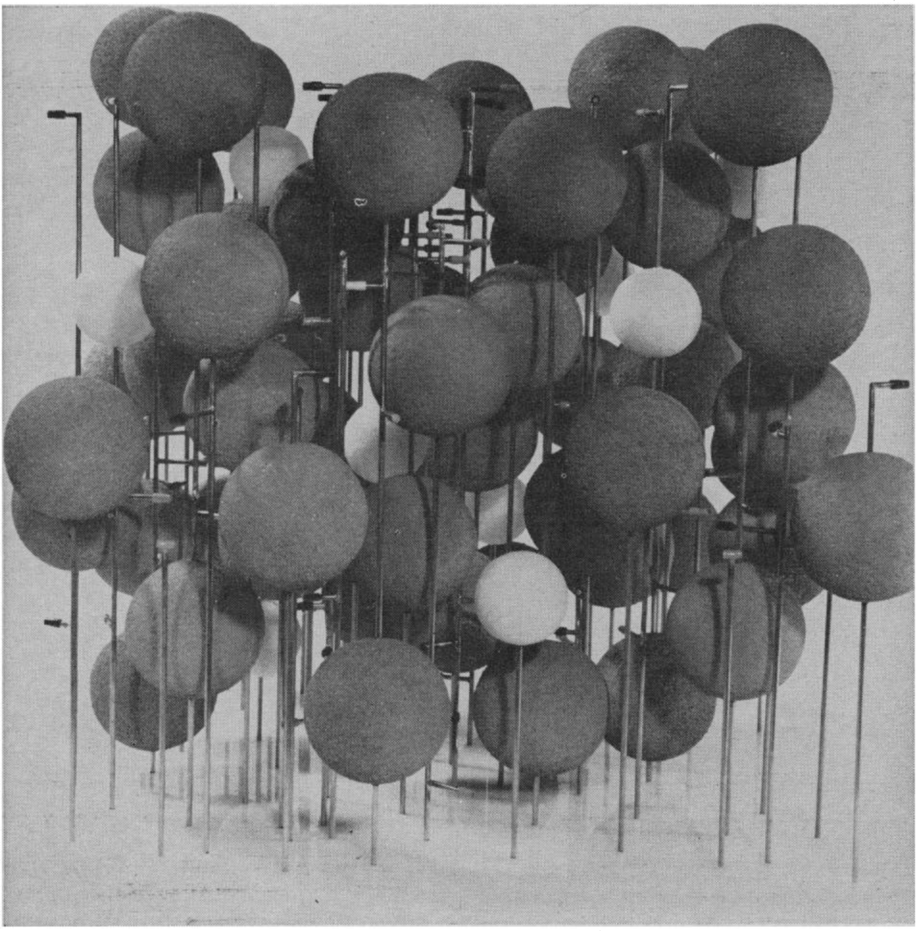

Fig. 1. Model of the structure of RbAg$_4$I$_5$. Large spheres represent iodide ions, small white spheres, Rb$^+$ ions. Centers of sleeves on short horizontal arms designate possible positions of Ag$^+$ ion. The three shades represent the three crystallographically nonequivalent sites. Note the channels in the upper middle and lower left parts of the model.