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Final Report on AFOSR ~~XXXXXXXXXXXXXXXXXXXX~~

During the period 1975-1981 we endeavored to characterize two classes of silver-ion solid-state electrolytes for potential use in batteries of structure $\text{Ag}/\text{X}/\text{AgI}$ and other similar anode/cathode chemistry; here X is the electrolyte. Most of our attention was focused upon the stoichiometric compounds arising from mixtures of AgI and Ag_2WO_4 . The phase diagram for this system was initially studied by Takahashi and his colleagues in the Applied Chemistry Department at Nagoya University, Japan; further detailed analyses of some of the phases resulting from $\text{AgI} + \text{Ag}_2\text{WO}_4$ mixtures was also carried out by Geller and his co-workers at The University of Colorado. In our work specimens were received from Geller and from Takahashi and were found to be equivalent for the purposes of our measurements.

In 1980 the principal investigator of this grant, Prof. J. F. Scott, traveled to Japan as guest of the Physical Society of Japan to present lectures on the work supported by this grant. At this time several days were spent in Nagoya to permit detailed exchanges of scientific information, particularly with Prof. Takahashi, who had become a collaborator in the work on $\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$.

The initial work by Takahashi et al.¹ on the $\text{AgI} + \text{Ag}_2\text{WO}_4$ family revealed at least four stable stoichiometric phases of general formula $\text{Ag}_x\text{I}_y(\text{WO}_4)_z$. X-ray crystallographic measurements by Chan and Geller² permitted unambiguous determination of percentages x, y, and z for the compound which had displayed the best ionic conductivity. This material, originally labeled $\text{Ag}_6\text{I}_4\text{WO}_4$ by Takahashi et al., was found to be $\text{Ag}_{13}\text{I}_9\text{W}_2\text{O}_8$, and is usually written as $\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$ in order to display explicitly the unusual $\text{W}_4\text{O}_{16}^{8-}$ ion. It is noteworthy⁴ that this ion is octahedrally coordinated, in contrast to the more usual tetrahedral coordination of WO_4 in tungstates (such as the scheelite family, etc.).

$\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$ had its potential use as a solid state battery electrolyte recognized immediately during the work by Takahashi et al., and in fact it was used to produce a "super-ionic" cell shortly after its discovery. For that reason it was emphasized in all our spectroscopic and electrical measurements.

As a first step in our understanding of the microscopic dynamics characterizing lattice properties and ionic conduction in this class of materials, we began with an analysis of the starting material, Ag_2WO_4 , since it has none of the complications associated explicitly with silver ion mobility and general behavior. In addition, the original electrical work had revealed a break in slope in its electrical conductivity at about 300°C, suggestive of ionic conduction. It was therefore essential to understand whether some ionic conduction was present in this family of crystal even in the absence of silver ions; such conductivity could in principle arise from defects or vacancies, particularly oxygen vacancies. Our combined spectroscopic and electrical results on Ag_2WO_4 were published in Materials Research Bulletin.³ They showed spectroscopic² and electrical anomalies near the temperature at which Takahashi's group originally found a change in slope in conductivity versus temperature; however, our results showed that this phenomenon was not a simple phase transition: The kinetics were irreversible and interpreted as simple chemical degradation. The laser Raman spectroscopy was especially revealing in this respect; the spectral changes noted were not in the low-frequency silver-ion vibrations, but in the tungsten-oxygen stretching modes near 800 cm^{-1} . This leads us to hypothesize that oxygen was being lost from the crystal at slightly elevated temperatures.

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Such a hypothesis of oxygen loss at elevated temperatures was in total disagreement with the weight measurements on Ag_2WO_4 reported earlier in the Ph.D. thesis of Bottelberghs at Utrecht,⁴ but was confirmed in subsequent measurements by our group. Most important, this conclusion permitted the growth of very large single crystals of $\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$ subsequently at our university, for we concluded that if oxygen were lost from Ag_2WO_4 at such modest temperatures (300°C), that a similar process must be going on in the growth of $\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$, resulting in a deviation from stoichiometry and difficulty in producing large single crystals. Working under this hypothesis, Prof. Geller and his assistants attempted to grow $\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$ under much higher overpressures of oxygen (7 atm) than had ever been used before. The results were immediately successful, with single crystals of order 1 cc resulting.

Thus armed with both an understanding of Ag_2WO_4 and large specimens of $\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$, we proceeded to obtain and analyze the laser Raman spectra of the latter material. In the initial study⁵ we found evidence for two structural phase transitions: a superionic one near 280°K was continuous; and a ferroelectric one at 199°K was nearly continuous (slightly first order). In addition a small anomaly was also observable at 247°K but was too ambiguous in the early measurements to be identified clearly as a third phase transition. A second study⁶ of these phase transitions characterized the ferroelectric properties near 199°K in more detail, yielding the Curie constants, demonstrating the expected mean-field behavior, and measuring the hysteresis. It also produced the frequency dependence of the a.c. conductivity, which was found not to agree with the predictions of Lines,^{7,8} but with a more general theory of Habbal, from our own group, as well as with experimental results on related superionic materials.^{10,11} The important qualitative point is that the a.c. conductivity in the superionic phase varies linearly with frequency at low frequencies, and not quadratically (the quadratic prediction is that of Lines^{7,8}).

Our final study of the three phase transitions in $\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$ was made via specific heat techniques employing scanning calorimetry. These studies confirmed our earlier hypotheses: that the transition near 280°K was second-order and to a superionic state; and that the transition at 199°K was slightly first-order. In addition, the third tentatively observed transition at 247°K was also found to be first order. Thermal hysteresis widths for both first-order transitions were measured. Characteristics for all three transitions were found¹² to be in accord with predictions of the phenomenological theories generally in use for ferro-electrics; parameters characterizing the free energy of $\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$ were evaluated or at least estimated. The shape of the $C_p(T)$ curve near the second-order transition at about 280°K was fitted and found to be in accord with theoretical predictions. Finally, the electrical conductivity temperature dependence reported by Geller et al.¹³ above 200°K was reconciled: Because of Geller's failure to recognize the second-order transition at 280°K , he had fitted his conductivity data above 247°K to a bizarre, nonlinear temperature dependence; this was simply wrong, and incidentally resulted in the equally erroneous conclusion that $\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$ is an ionic conductor, fully disordered, above 247°K .

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Two other systems were analyzed during the course of work sponsored by this grant. The first of these was strontium tetraiododisargentate octahydrate ($\text{SrAg}_2\text{I}_4 \cdot 8\text{H}_2\text{O}$). The primary motivation for the study of this material is that it had been observed previously that anhydrous compounds of silver halides with strontium or barium halides were unobtainable under normal growth conditions. It had been speculated¹⁴ that this is due to the particular coordination requirements of the alkaline earth ions, and that the addition of waters of hydration would allow that coordination to be satisfied. Thus, $\text{SrAg}_2\text{I}_4 \cdot 8\text{H}_2\text{O}$ was selected for study, even though it is not itself an ionic conductor, because its understanding should lead to the ability to comprehend subtleties involving anhydrous double salts of silver which are of more practical utility.

Two results of interest were obtained for $\text{SrAg}_2\text{I}_4 \cdot 8\text{H}_2\text{O}$. Firstly, it was determined that the energies of the silver ion vibrations were higher than in silver electrolytes, in general, with the two lowest lying modes at 65 and 25 cm^{-1} (compared, for example, with 23 and 32 cm^{-1} in RbAg_4I_5 or 20 and 35 cm^{-1} in $\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$); this is compatible with tighter silver ion bonding in the nonconducting compounds. Second, the very low frequency mode at 25 cm^{-1} remains underdamped in saturated aqueous solution, confirming the hypothesis of Geller and Dudley that "it is probable that the saturated solution itself contains... AgI_4 chain entities."¹⁴ The spectral verification of intact AgI_4 chains in an aqueous solution of ionic compound is itself highly unusual,¹⁵⁻²⁰ although similar evidence has been reported for NiCl_2 .

The second system we studied during the last year of AFOSR grant NP77-3105A was pyridinium silver iodide, $(\text{C}_5\text{H}_5\text{NH})\text{Ag}_5\text{I}_{16}$.²¹ This material has a sufficiently high ionic electrical conductivity to qualify as a practical material for silver ion batteries (30 inverse ohm-cm at 100°C).²² Its crystal structure²³ in the ordered phase below 50°C is P6/mcc with two formula groups in the primitive hexagonal unit cell. The phase transition at 50°C is thought to be order-disorder, involving silver ion hopping with an activation enthalpy of 0.21 eV .²⁴ Our spectroscopic study²¹ confirmed the order-disorder character of this phase transition, and further showed that the silver ion vibration which changes from vibrational (and underdamped) to diffusive at 50°C lies at 32 cm^{-1} at ambient temperatures (295K). This mode is considerably broader in width (full width at half maximum is 24 cm^{-1} at 295K) than all other vibrations in the crystal, but it remains a propagating excitation up until 50°C . Its temperature dependence of linewidth and cross-section contains the dynamic information of interest regarding the kinetics of silver ion behavior in the region of interest above room temperature.

In summary, the studies performed under AFOSR grant NP77-3105/A have permitted an understanding of the microscopic dynamics of three families of silver salts of importance for solid state batteries: the $\text{Ag}_x\text{I}_y(\text{WO}_4)_z$ family, which already has seen device application in Japan;²⁵ the pyridinium silver iodide family, which has ionic conductivity near that of RbAg_4I_5 ; and the hydrates of silver-barium and silver-strontium, which cannot yet be grown at ambient pressure in the amorphous (and presumably conducting) forms.

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Publications resulting from AFOSR grant NP77-3105/A:

- 1) "High Temperature Raman Spectroscopy of Silver Tetraiodate, $\text{Ag}_8\text{W}_4\text{O}_{16}$," Materials Research Bulletin 12, pp.189-196 (1977), by A. Turkovic, D. L. Fox, J. F. Scott, S. Geller, and G. F. Ruse.
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- 3) "Raman Spectroscopy of Structural Phase Transitions in $\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$," Journal of Chemical Physics 69, 4984-4989, by F. Habbal, J. A. Zvirgzds, and J. F. Scott (1978).
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