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Characterization of Silver-Rich Ternary Oxides with Photoelectron Spectroscopy

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The silver-rich ternary oxides $Ag_6Si_2O_7$, $Ag_{10}Si_4O_{13}$, $Ag_6Ge_2O_7$, and $Ag_{10}Ge_4O_{13}$, as well as Ag_2SO_4, have been investigated with photoelectron spectroscopy. The Ag 3*d* core level binding energies in all four ternary oxides were found to be identical with that of Ag metal, compared to the small negative chemical shift observed in $AgSO_4$ and most other silver compounds. The Mg*K*α and HeI valence band spectra are both dominated by Ag 4*d* emission; at the lower photon energy O 2*p*-derived states are also observed. There is some evidence for a direct Ag 4*d*–O 2*p* interaction. © 1990 Academic Press, Inc.

Introduction

It is a general crystal chemical feature of the ternary silver-rich oxides that the cationic (Ag^+) and anionic parts tend to be separate (*1*). The structures typically show sequences of alternating anionic and cationic slabs. In spite of the formal positive charge the cations form cluster-like agglomerates which, quite independent of the type of chemical bond between oxygen and silver or of the anionic matrix present, display surprisingly uniform topological features. The Ag–Ag distances are very similar to those in the metal and the local silver groupings are suggestive of the fcc structure. These observations have led us to suggest the existence of weak attractive Ag^+–Ag^+ interactions (*2*). This notion is admittedly in contradiction to the generally accepted rule that closed-shell configurations such ad d^{10} do not undergo significant bonding interactions. In addition to the structural features, however, there is further evidence for a special type of Ag(I) bonding in these compounds. Thus in UV/VIS diffuse reflectance spectra the absorption edges are shifted drastically (by up to 2 eV) to lower photon energy on forming or increasing the size of the silver aggregates (*3*). These oxides also show mixed ionic and electronic conductivity, whereas Ag_2SO_4 and AgCl with structurally "normal" Ag(I) are purely ionic conductors (*4*).

Although qualitative models can be proposed in order to explain the observed phenomena, little is so far known about the electronic structure of these silver-rich ternary

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oxides. In particular, no band structure calculations are at present available. The most useful experimental probe of the electronic structure of solids is photoelectron spectroscopy, or photoemission. When single crystal samples showing the truncated bulk structure at the surface are available, photoelectron spectra can be used to derive quite detailed information on the bulk band structure (*5*). If only polycrystalline samples are available, as in the present case, useful information can still be obtained, particularly in comparative studies. This also applies to work done with conventional laboratory sources, although synchrotron radiation with its possibility of continuously varying the photon energy in the photoemission experiment has definite advantages (*6*). In the present study we have used photoelectron spectroscopy with Mg$K\alpha$ ($h\nu$ = 1253.6 eV) and HeI ($h\nu$ = 21.2 eV) to study the Ag 3*d* chemical shifts and the valance bands of some silver(I) silicates and germanates, and, for comparison, of silver(I) sulfate.

Experimental

The crystalline compounds $Ag_6Si_2O_7$, $Ag_{10}Si_4O_{13}$, $Ag_6Ge_2O_7$, and $Ag_{10}Ge_4O_{13}$ were synthesized by solid state reaction from the binary oxides Ag_2O (Degussa, Hanau), SiO_2, and GeO_2 (p.a., Merck, Darmstadt). Oxygen pressures of about 200 MPa were applied in order to prevent decomposition of Ag_2O. Detailed information on the preparation is given elsewhere (*7, 11, 12*). Commercially available Ag_2SO_4 (p.a., Merck) was used. The composition of all samples was checked with X-ray powder diffraction (Guinier technique). The compounds were milled and pressed into pellets of 1–3 mm thickness and 10 mm diameter, at a pressure of 50 MPa. The substances were handled under exclusion of light since some of them are photosensitive.

The photoelectron spectroscopy was performed in a commercial ESCA instrument (Vacuum Generators, England). The samples (up to three at a time) could be mounted on the manipulator in a preparation chamber. In order to eliminate the effect of chemical reactions and photoeffects, which might have occurred at the surface, the samples were scraped with a diamon-coated file before taking each series of spectra. After transferring the samples into the measuring chamber, which is kept under ultrahigh vacuum conditions, it was found that they could be kept for several days in this ambient without any signs of change in the spectra.

The photoelectron spectra of the ternary oxides showed no charging effects. Their Ag $3d_{5/2}$ binding energies were referenced to the $3d_{5/2}$level of metallic silver at 368.0 eV (*8*). Silver was evaporated directly onto the samples in the preparation chamber for this purpose. These values were then checked against the Au $4f_{7/2}$ level at 84.0 eV (*8*) by evaporating gold in the same way. The valence band spectra were referenced to the Fermi level, E_F, of gold. This proved straightforward for the HeI measurements where the Fermi level could be clearly identified in the Au valence band spectrum. For the Mg$K\alpha$ data the position of E_F was estimated from spectra in the literature for polycrystalline gold (*9*). The Ag_2SO_4 samples showed considerable charging, although referencing of the core levels to metallic gold and silver still proved possible.

Results and Discussion

Core level binding energies. The Mg$K\alpha$ data are summarized in Fig. 1 and Table I. All four ternary oxides have an identical Ag $3d_{5/2}$ binding energy of 368.0 eV which is the same value as for metallic silver. Ag_2SO_4 shows a negative chemical shift of 0.2 eV relative to metallic silver in good agreement with the 0.3 eV measured by Gaarenstrom and Winograd (*10*). The corrected linewidth (fwhm) increases from 0.45 eV in silver to 1.1 eV in the ternary oxides which, consid-

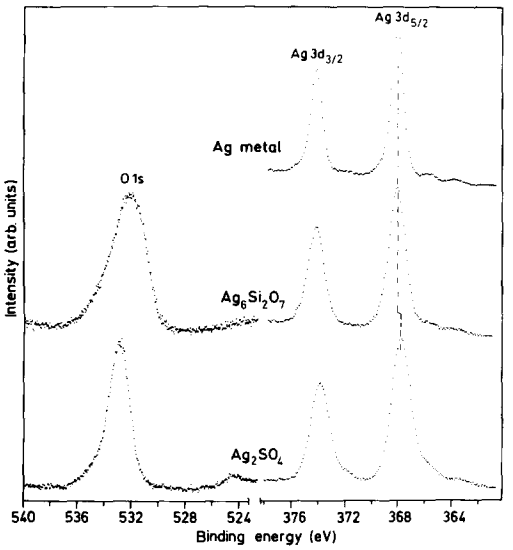

FIG. 1. Core level photoelectron spectra for Ag metal, $Ag_6Si_2O_7$, and Ag_2SO_4; Mg$K\alpha$ (see also Table I).

ering the nature of the samples, is probably due to inhomogeneous line broadening. The further increase to 1.4 eV in Ag_2SO_4 is certainly connected with sample charging effects. The O 1*s* halfwidth in Ag_2SO_4 (1.9 eV) is on the other hand lower than that in the ternary oxides (3.0–3.5 eV). This probably reflects the contribution of different types of oxygen atoms, as indicated by the asymmetric peak form. In the spectra of some samples there was evidence for structure on the high binding energy side of the O 1*s* peak, but it was not reproducible. The disilicate (digermanate) anion has two types of inequivalent oxygen atoms, namely, terminal and bridging (*11*). The tetrasilicate (tetragermanate) anion has three: terminal, "included" terminal, and bridging (*12*). The binding energy difference between the terminal and "included" terminal atoms is expected, however, to be very small (probably of the order of 0.1 eV). In general, the O 1*s* linewidth varied within the range given, without showing any systematic differences due to the different anions.

Ag 3*d* core level binding energies for silver compounds are almost always lower than in the metallic state. This appears at first to be a strange result, since according to the simple interpretation of chemical shifts in terms of initial state properties (*13, 14*) a silver cation might be expected to have a higher binding energy: The lower charge density on the cation gives rise to a decrease in the electrostatic potential at the core. More energy is then required to create a core hole, i.e., the binding energy should increase. This simple argument excludes, however, other initial state contribution effects such as the Madelung contribution, which is particularly important in an ionic solid. This generally decreases the size of the shift expected simply on the basis of the charge on one atom alone (*14*). A further important factor affecting the chemical shift derives from "final state" effects (*13*): The relaxation energy and the change in correlation which contribute to the binding energy are certainly different for the cation in an ionic solid than for an atom in the metal. In the overwhelming majority of transition metal compounds the cation actually does exhibit higher binding energies; the chemical shifts of the oxides

TABLE I

COMPARISON OF Ag 3*d* BINDING ENERGIES AND LINEWIDTHS FOR METALLIC SILVER, THE SILVER SILICATES, AND GERMANATES AS WELL AS Ag_2SO_4 (eV)

	BE $Ag3d_{5/2}$	Experimental linewidth (fwhm)	Corrected linewidth[a] (fwhm)
Ag metal	368.0	1.1	0.45
$Ag_6Si_2O_7$			
$Ag_6Ge_2O_7$	368.0	1.5	1.1
$Ag_{10}Ge_4O_{13}$			
$Ag_{10}Si_4O_{13}$			
Ag_2SO_4	367.8	1.7	1.4

[a] Corrected for an estimated instrumental resolution of 1.0 eV.

and halides are among the greatest. It is now generally accepted that the dominant contribution to these large positive chemical shifts is provided by the ionic charge on the atom in the initial state. Gaarenstrom and Winograd (*10*) show in their careful analysis of core level binding energies for silver compounds that the shift per unit cationic charge is small for Ag relative to the transition metals due to the fact that an *s*-electron rather than a *d*-electron is removed in the valence shell.

How is this discussion relevant for the silver ternary oxides investigated here? First, it tells us that the zero chemical shift (compared to -0.2 eV in Ag_2SO_4, -0.4 eV in Ag_2O (*10*), and -0.5 eV in AgF (*10*)) is significant and that its origin may well lie in an initial state effect. Although the differences are relatively small, it is striking that all four compounds exhibit the same Ag 3*d* binding energy. This is also higher than in all the simple Ag(I) salts and identical with that of the metal. Without being able to eliminate final state effects, we would not like to claim that this necessarily indicates a metallic-like nature for the silver aggregates. However, it does add to the evidence from diffuse reflectance and conductivity measurements that these compounds are different than simple Ag(I) salts in their crystal chemical behavior.

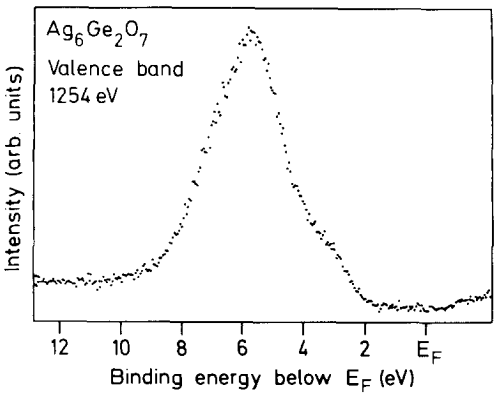

FIG. 2. Valence band photoelectron spectrum of $Ag_6Ge_2O_7$; Mg$K\alpha$.

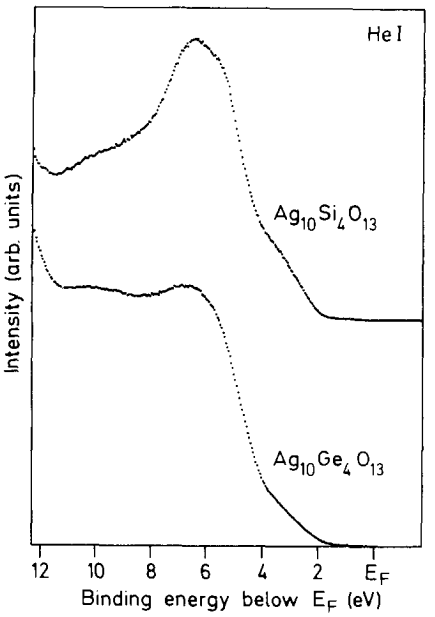

FIG. 3. Valence band photoelectron spectra of $Ag_{10}Si_4O_{13}$ and $Ag_{10}Ge_4O_{13}$; HeI.

Valence band spectra. The Mg$K\alpha$ valence band photoelectron spectra were essentially identical for all four ternary oxides. The spectrum for $Ag_6Ge_2O_7$ is shown in Fig. 2 as an example. The main feature is a broad peak (halfwidth ~3eV) centered at 5.7 eV below E_F with a shoulder at ~3.5 eV. There is no evidence for emission from states between the valence band edge at about 2 eV and E_F, although the relatively high electronic conductivity measure for these compounds suggests that this might be the case. In fact, the corresponding HeI spectra (Fig. 3) do show very weak emission in this region, probably due to impurity states. At the lower photon energy the two silicates and the two germanates each showed identical spectra, but differed slightly from each other. Figure 3 compares the spectra from $Ag_{10}Si_4O_{13}$ and $Ag_{10}Ge_4O_{13}$. It should be remembered that the peaks are superimposed

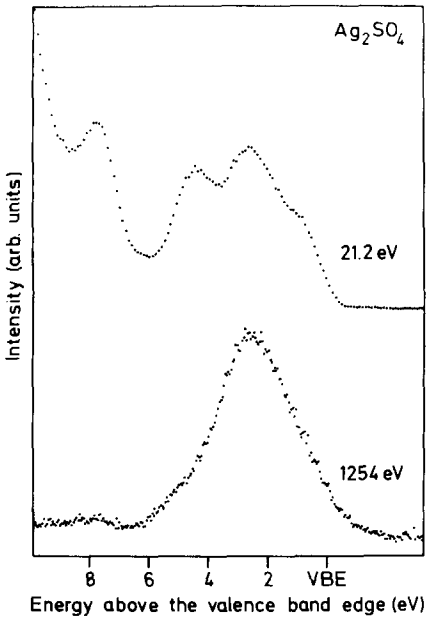

FIG. 4. Valence band photoelectron spectra of Ag_2SO_4; HeI (above) and Mg$K\alpha$ (below).

on a steeply sloping background due to the emission of secondary electrons. The broad feature at 6.2 eV in the germanate appears to consist of two components at ~5.6 and ~6.6 eV in the silicate. In addition, there is a low binding energy should at ~3.5 eV which is more pronounced in the case of the silicate. A further, broad feature is observed at ~10 eV. For the purposes of comparison, the valence bands of Ag_2SO_4 measured with Mg$K\alpha$ and HeI are shown in Fig. 4.

Comparing the valence bands of the ternary oxides measure at low and high photon energies it is immediately apparent that the dominant feature in both spectra is at roughly the same energy (5–6 eV) and that the shoulder at ~3.5 eV is present in both cases. However, the 10-eV feature in the HeI spectrum is absent in the Mg$K\alpha$ spectrum. The Ag_2SO_4 spectra at the two photon energies show little resemblance to each other, nor to the spectra from the ternary oxides. Since no band structure calculations are available for the silicates and germanates, we have to rely on cross-section arguments and on comparison with other systems, in order to be able to assign the spectral features and to perhaps learn more about the electronic structure.

The valence bands of these compounds are expected to contain contributions from O 2*p*, Si 3*s*, and 3*p* (Ge 4*s* and 4*p*) as well as Ag 4*d* and 5*s*. Calculated partial photoionization cross-sections (*15*) show that the Ag 4*d* emission is much stronger than the 5*s* emission at all photon energies, as is clear from photoelectron spectra of the clean metal surface. This does not mean of course that the role of Ag 5*s* can be neglected but, rather, that we have no effective probe for this particular subshell. If the silver aggregates are cationic, we would, however, expect the Ag 5*s*-derived bands to be largely unfilled, i.e., to lie above E_F. Whereas the Ag 4*d* cross section is only a factor of 2–4 higher than that of O 2*p* at 21 eV (*15*), this factor is 2 orders of magnitude at 1250 eV photon energy. The situation with respect to the Si levels is somewhat different, in that the Ag 4*d* cross section is greater by 1–2 orders of magnitude at all photon energies. In the interpretation of the present data we would therefore expect features with O 2*p* character and present in the HeI spectrum to be no longer visible in the MgK_α spectrum. State deriving from Si 3*s* and 3*p* would perhaps contribute only a low relative intensity at either energy.

Before returning to the spectra of Figs. 2 and 3 it is also useful to review what is known about the electronic structure of silicates based on molecular orbital calculation for the SiO_4^{4-} anion (*16*), the photoelectron spectrum of SiO_2 (*17*), and band structure calculation for lithium and sodium silicates (*18, 19*). The latter calculations are particularly useful here because these silicates consitst of chains or sheets

of linked SiO_4 tetrahedra. They thus contain both bridging and terminal oxygen atoms as in the di-and tetrasilicates considered here. The ca. 10-eV-wide valence band can be divided into two regions. At binding energies 6–10 eV below the valence band edge the states derive from σ bonding orbitals containing Si $3s$, Si $3p$, and O $2p$. The states in the range 0–5 eV are mainly nonbonding oxygen $2p$ orbitals but still contain some silicon character. In the lithium and sodium silicates the bridging and terminal oxygens produce two maxima in the density states, which in turn give rise to two peaks in the Al$K\alpha$ photoemission spectrum at ~4.5 and ~2 eV, respectively.

With this information in mind we can offer the following, tentative explanation of the valence band photoelectron spectra of the silver ternary oxides investigated here. The peak at 5–6 eV is due to the Ag $4d$ band; its width of ~3 eV at both photon energies is similar to that of metallic silver and indeed suggest that there is only a weak chemical interaction between the Ag d states and the Si and O levels (see below). The Ag–Ag separation in these compounds is ~2.95 Å as in the metal, and the silver skeletal structure is fcc-like. The individual d bands are thus expected to be relatively flat as in the metal and to give rise to a total d band of similar width. At the high photon energy the ~10-eV feature disappears since it is entirely derived from oxygen and silicon states. What remains is the shoulder at ~3.5 eV which we suggest is due to an interaction between Ag $4d$ and O $2p$. At the higher photon energy the silver states are still visible. Since the feature lies above the d band, it is assigned to states which are antibonding with respect to this interaction. The corresponding bonding orbitals must lie in the d band. The most obvious candidates for this interaction are the terminal oxygen atoms which lie on average several tenths of an angstrom nearer to the Ag chains or layers than the bridging species.

A comparison of the germanate and silicate spectra with those from Ag_2SO_4 (Fig. 4), which might perhaps be expected to lend support to this conclusion, is difficult: We have even fewer clues as to the assignment in sulfate spectra. The d band width is only marginally greater at the higher photon energy which may be due to charging. The 21.2-eV spectrum is quite different from that of the ternary oxides, but the feature at 8 eV is not reproducible and is probably connected with the effect of charging on the secondary electron yield. Finally, we should also note that the discussion above has been largely concerned with the silicates. Clearly, the substitution of Si by Ge produces no effect at $h\nu$ = 1253.6 eV, as expected. At $h\nu$ = 21.2 eV the main effect is to smear out the structure in the Ag $4d$ band.

Conclusions

Both the core level binding energies and the valence band photoelectron spectra of $Ag_6Si_2O_7$, $Ag_6Ge_2O_7$, $Ag_{10}Si_4O_{13}$, and $Ag_{10}Ge_4O_{13}$ are indicative of the particular crystal chemical properties of these compounds. The Ag $3d$ binding energy in each case is the same as in Ag metal. This zero chemical shift may be compared to the negative shift of up to 1 eV in virtually all other silver compounds. The Mg$K\alpha$ valence band spectra are also identical, indicating highly similar silver $4d$-derived electronic energy levels. The HeI valence band spectra for the silicates also differ only slightly from those of the germanates. The ~3.5-eV shoulder at $h\nu$ = 21.2 eV remains at the higher photon energy and is taken to indicate an interaction between Ag $4d$ and the (nonbonding) O $2p$ orbitals on the terminal oxygen atom of the silicate (germanate) anions. Further measurements over a wider range of photon energies are required to substantiate these as-

signments and to investigate the small differences between the silicates and germanates at low photon energies.

Acknowledgments

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