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# P-type conductivity in transparent oxides and sulfide fluorides

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## Abstract

Thin films of  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$  have been rendered conducting by intercalation of oxygen. Hole conductivities up to of order 10 S/cm can be achieved at the expense of visible transparency, especially in the blue region of the spectrum. Hole conductivities up to 100 S/cm have been achieved in pressed pellets of K-doped BaCuSF, and a band-gap of 3.2 eV has been measured on undoped films.

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## 1. Introduction

Transparent electronic and optoelectronic devices may be realized if sufficiently high conductivity can be achieved in transparent semiconductors [1]. Although high conductivity and visible transparency can be simultaneously achieved in a few materials such as  $\text{In}_2\text{O}_3:\text{Sn}$  (Sn-doped indium oxide or ITO),  $\text{SnO}_2:\text{F}$ , and  $\text{ZnO}:\text{Al}$ , the carriers are invariably n-type. Significant p-type conductivity in transparent materials is required for junction devices, but it is much more difficult to obtain because of the generally lower carrier mobilities and densities associated with narrow valence bands.

In 1997, Kawazoe and co-workers reported the synthesis of transparent p-type conducting films of  $\text{CuAlO}_2$  [2], and although the conductivity of 1 S/cm was about 3 orders of magnitude smaller than that found in n-type materials, the result was promising. Subsequently, improved p-type conductivity was found in a number of related delafossite structures, e.g.,  $\text{CuScO}_2:\text{Mg}$  [3] and  $\text{CuCrO}_2:\text{Mg}$  [4]. All-oxide diodes have been fabricated by using these materials [5], including the one using the only delafossite structure known to exhibit bipolar conductivity, i.e., n-type  $\text{CuInO}_2:\text{Sn}$  and p-type  $\text{CuInO}_2:\text{Mg}$  [6].

These  $\text{CuMO}_2$  p-type transparent conductors have small hole mobilities of order  $0.1 \text{ cm}^2/\text{V s}$  or less, much smaller than the values of order  $10\text{--}100 \text{ cm}^2/\text{V s}$  found for commercial n-type transparent conductors. Intermediate hole mobilities of order  $3 \text{ cm}^2/\text{V s}$  have been measured in thin films of  $\text{BaCu}_2\text{S}_2$ , along with p-type conductivity of 17 S/cm [7]. In contrast to the linear coordination of Cu in the delafossites (Fig. 1a), this compound contains Cu atoms in distorted tetrahedral coordination; these tetrahedra condense by sharing edges to form one-dimensional chains featuring a Cu...Cu distance, which at 0.271 nm is shorter than the corresponding distance in the delafossites (0.286 nm in  $\text{CuAlO}_2$  and 0.322 nm in  $\text{CuScO}_2$ ). Both the relatively high mobility and conductivity of  $\text{BaCu}_2\text{S}_2$  are encouraging, but the band-gap of 2.3 eV is too small to render the material completely transparent in the visible. To increase the band-gap, we turned to a layered sulfide-fluoride variant, BaCuSF [8] (Fig. 1b), in which the important feature of edge-shared  $\text{CuS}_4$  tetrahedra is retained, but the dimensionality of the compound is reduced to increase the gap beyond the 3.1 eV required for visible transparency.

In this paper, we report optical and transport measurements of both oxide and sulfide wide band-gap conductors. We describe variation of p-type conductivity and transparency by controlled oxygen doping of  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$  films [9], and we document the observation of p-type conductivity in powders and films

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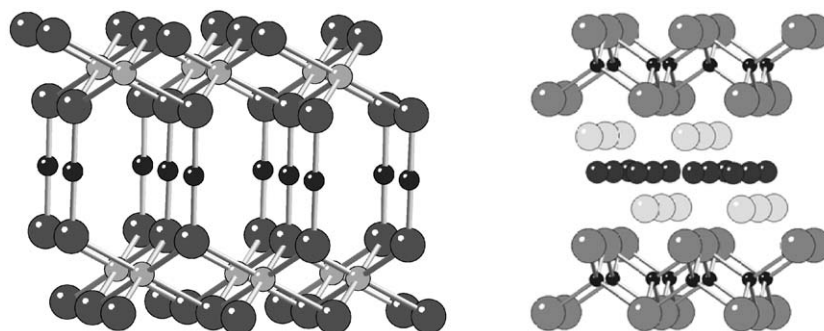


Fig. 1. Crystal structures of  $\text{CuScO}_2$  (left) and  $\text{BaCuSF}$  (right). For  $\text{CuScO}_2$ , Cu atoms are represented by smallest spheres and O atoms by largest spheres. For  $\text{BaCuSF}$ , Cu (small dark spheres) binding to S (large gray spheres) is emphasized. Lightly shaded spheres represent Ba, and the middle layer of dark spheres represents F atoms.

of  $\text{BaCuSF}$ . The band-gap of  $\text{BaCuSF}$  is established from measurements of the absorption coefficient in films.

## 2. Experimental

A series of films of  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_2$  were produced by rf magnetron sputtering from a Mg-doped  $\text{CuScO}_2$  sputter target produced by solid-state synthesis. The sputter gas was Ar with 1 at%  $\text{O}_2$  at 10 mTorr; the substrates (fused  $\text{SiO}_2$ ) were maintained at  $350^\circ\text{C}$  at a distance of 2.5 cm from the target in an on-axis configuration. As-deposited films were amorphous and insulating with a Cu:Sc ratio approximately 1.1:1 as measured by electron probe microanalysis. The concentration of Mg in the films was 1% for the series presented here. Following deposition, the films were subjected to rapid-thermal annealing in oxygen at  $750^\circ\text{C}$  for 3 min to produce  $\text{Cu}_2\text{Sc}_2\text{O}_5$ , and then reduced in Ar at  $900^\circ\text{C}$  for 2.5 min to produce transparent, insulating  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_2$ . Finally, the films were annealed in various pressures of oxygen at  $400^\circ\text{C}$  for 10 h, producing  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$ . It was important to keep the temperature below  $450^\circ\text{C}$ , since at this temperature decomposition of the 3R polytype is observed [10]. Typical films are shown in Fig. 2. They are of similar thickness, about 220–250 nm, with the exception of the most transparent film, A, which is 350 nm. Film A was not subjected to the 10-h,  $400^\circ\text{C}$  anneal, and films B–G were annealed under oxygen at pressures of 3, 2, 50, 120,  $10^4$  and  $10^5$  Torr, respectively.

$\text{BaCuSF}$  powders were produced by heating stoichiometric mixtures of  $\text{BaF}_2$  (Cerac 99.9%),  $\text{Cu}_2\text{S}$  (Cerac 99.5%), and BaS at  $450^\circ\text{C}$  for 15 h in a sealed silica tube. Alternatively, stoichiometric quantities of  $\text{BaCO}_3$  (Cerac 99.9%),  $\text{Cu}_2\text{S}$ , and  $\text{BaF}_2$  were heated at  $550^\circ\text{C}$  under flowing  $\text{H}_2\text{S}(\text{g})$  and cooled to room temperature under flowing Ar(g). To induce conductivity, K was introduced as a dopant by using KF in the reactions.

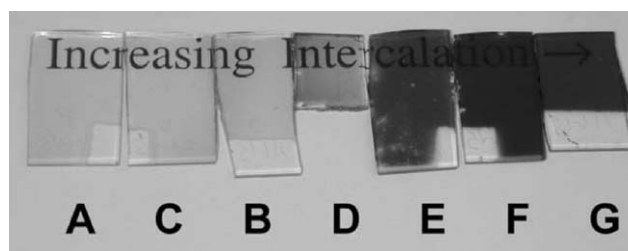


Fig. 2. A series of  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_2$  films intercalated with oxygen at various pressures.

The powder were pressed into 1.25-cm pellets of 4.5 tons and then annealed at  $650^\circ\text{C}$  for 30 min in an evacuated silica tube. The pellets are very stable in air under ambient laboratory conditions, and also withstand moderate heating in air. After 1 h at  $500^\circ\text{C}$  in air, they begin to decompose. In direct contact with water, the pellets darken and become more conductive. The X-ray diffraction pattern still shows  $\text{BaCuSF}$  as the major phase. To form films, Cu metal and  $\text{BaF}_2$  were coevaporated from refractory boats onto  $\text{SiO}_2$  or MgO substrates held at  $200^\circ\text{C}$ . The stoichiometry was controlled by the relative deposition rates, which were adjusted by varying the current through the boats. The films were subsequently treated under a flowing stream of  $\text{H}_2\text{S}(\text{g})$  at temperatures of  $350^\circ\text{C}$  for 3 h. As with pellets, we find that films are very stable under ambient conditions, but they also darken in contact with water.

X-ray measurements for both powders and films were performed with a Siemens D-5000 diffraction unit. Film thicknesses were determined with an Alpha-Step 500 surface profilometer. Conductivity measurements were obtained in a four-terminal, constant current configuration. The measurement temperature was slowly varied by allowing liquid nitrogen to evaporate from the cryostat housing. Seebeck coefficients were measured at room temperature by maintaining a small temperature gradient across the sample, and measuring the resulting thermal voltage. The thermal voltage varied

linearly with gradient up to at least 5 K, and the resulting coefficient was corrected for the Seebeck coefficient of the sample holder. Optical transmission and reflection were measured with a grating spectrometer based on an Oriel double monochromator illuminated by a 150-W Xe arc lamp. The entrance and exit slits yielded a resolution of 7 nm, and data were acquired between 250 and 900 nm.

### 3. Results and discussion

Annealed films of  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$  are polycrystalline, and the peaks in the X-ray diffraction patterns are consistent with a mixture of 2H and 3R polytypes. As the oxygen content of the films increases, the transparency decreases (Fig. 2). A systematic increase of the  $a$ -axis lattice parameter is also observed as oxygen enters the structure; a detailed discussion of the structures of these intercalated materials will be published elsewhere [9]. The temperature-dependent conductivity of the films shown in Fig. 2 is summarized in Fig. 3. As expected, the most transparent film is the least conducting, while the darkest film is the most conducting. In each case, the conductivity increases with temperature, although the temperature dependence becomes weaker for more conducting films. The conductivity data are plotted as a function of  $T^{-1/4}$  to show that a variable-range hopping model is reasonable over a relatively large temperature range, although the data are not perfectly linear. The highest conductivity measured in this particular series was 12 S/cm at room temperature, although values greater than 20 S/cm have been found in other films. The conductivity was established as p-type at all temperatures by measurement of the Seebeck coefficient; the dc Hall voltage was too small to measure, placing an upper limit on the mobility of about  $0.5 \text{ cm}^2/\text{Vs}$ .

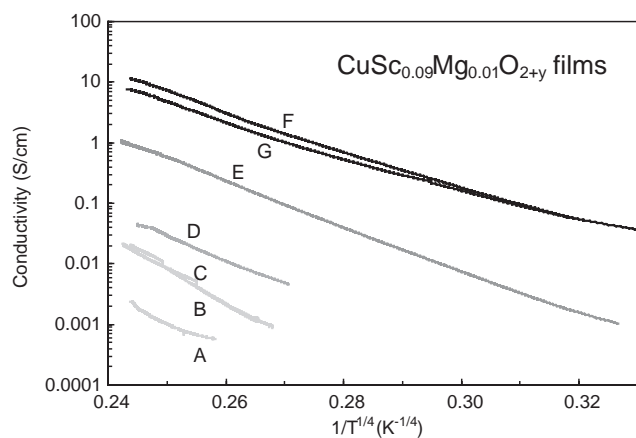


Fig. 3. Temperature-dependent conductivity of films of  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$  with increasing oxygen content. The labels on the curves correspond to the labels in the photograph in Fig. 2.

Transmission and reflection of the  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$  films were measured in the range 250–900 nm. Both quantities are strongly modulated by thin-film interference effects. In order to extract the absorption coefficient, the effect of the interference fringes was removed by plotting  $T/(1-R) \approx \exp(-\alpha d)$  [11], where  $\alpha$  is the energy-dependent absorption coefficient and  $d$  is the film thickness. Fig. 4 is a plot of  $T/(1-R) \approx \exp(-\alpha d)$  for some of the films in Fig. 2. The transmission of unintercalated or lightly intercalated  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_2$  is above 80% across the visible range. Oxygen intercalation, which increases the conductivity by introducing carriers, occurs at the expense of the transparency. The films take on a brownish hue resulting from increased absorption at all wavelengths, predominantly in the blue, but extending into the red. If the band-gap is assumed to be direct, it can be determined from the intercept on the energy axis of a plot of  $(\alpha E)^2$  against  $E$  [12], where  $\alpha$  is the absorption coefficient at energy  $E$ . This analysis yields values between 3.57 and 3.6 eV for all the films in Fig. 2.

Following preparation at temperatures as low as  $450^\circ\text{C}$ , powders of  $\text{BaCuSF}$  were largely single phase at the level established by X-ray diffraction (Fig. 5a). A small amount of residual  $\text{BaF}_2$  is commonly observed in the sealed-tube reactions, while no  $\text{BaF}_2$  is detected following treatment with  $\text{H}_2\text{S}(\text{g})$ . Refined parameters for a tetragonal cell are  $a = 0.4123(1)$  and  $c = 0.9021(1)$  nm. Undoped powders are light tan, and they become progressively darker as K-dopant concentration increases. The conductivity of  $\text{BaCuSF}$  pellets was measured at room temperatures for concentrations of K ranging from 0 to 10% (Fig. 6). The conductivity increases with K concentration, reaching a maximum value of 100 S/cm at 10% K. Again, the Seebeck coefficient establishes the conductivity as p-type (Fig. 6). Further, the pellet conductivity was measured

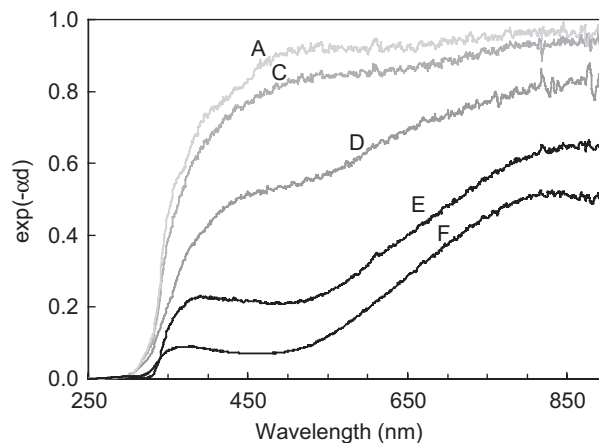


Fig. 4. UV-visible plot of  $T/(1-R) \approx \exp(-\alpha d)$ , where  $\alpha$  is the absorption coefficient, for some of the  $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_{2+y}$  films shown in Fig. 2.

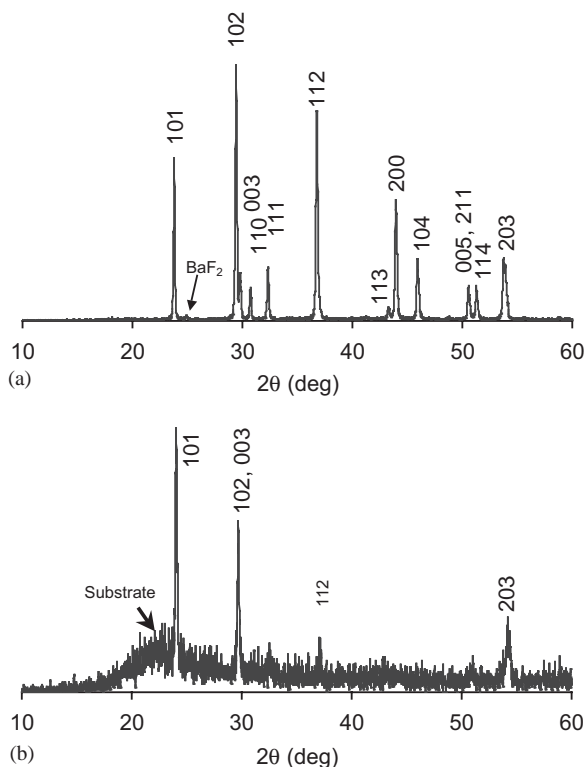


Fig. 5. X-ray diffraction patterns of BaCuSF. (a) Powder, (b) polycrystalline film on fused SiO<sub>2</sub>.

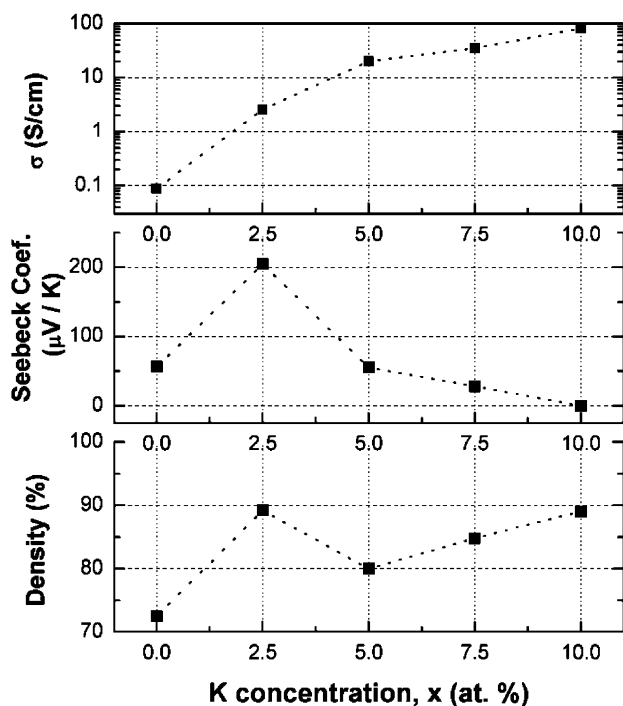


Fig. 6. Room temperature conductivity, Seebeck coefficient, and density of BaCuSF pellets.

as a function of temperature and K concentration, and the results are displayed in Fig. 7. The semiconducting nature of the undoped and lightly doped materials

changes to metallic at heavier doping levels with a crossover at about 5 at% K.

Film conductivity does not yet match that of the pressed powders (see inset to Fig. 7). The best film conductivity was obtained from a film prepared by co-evaporation of BaF<sub>2</sub> and Cu onto a glass substrate at 200°C, with subsequent annealing in H<sub>2</sub>S for 3 h at 350°C. Films made by evaporation of BaCuSF pellets with similar post-processing yielded lower conductivities. The Seebeck coefficient of BaCuSF and BaCuSF:K films was positive, again confirming p-type conductivity, and the exact value depends on the K dopant concentration.

The transmission and reflection of thin films of BaCuSF on SiO<sub>2</sub> were also measured, and Fig. 8 shows the results for an undoped, 250-nm film on a 1-mm substrate. Again, there is strong modulation from thin-

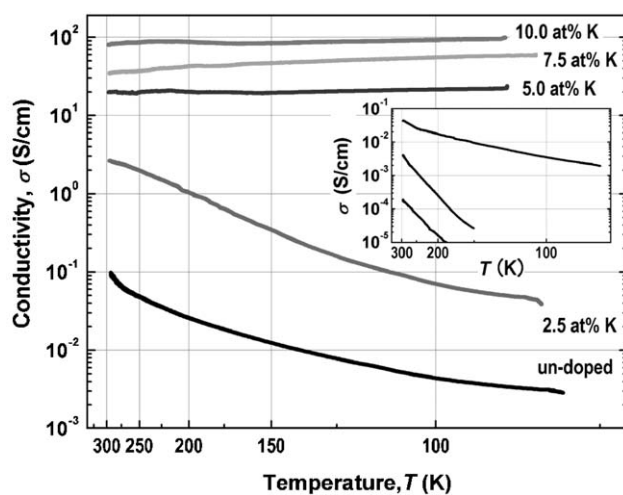


Fig. 7. Temperature dependence of the conductivity of BaCuSF powders doped with different amounts of K. The inset shows the conductivity of three BaCuSF films prepared under different conditions (see text).

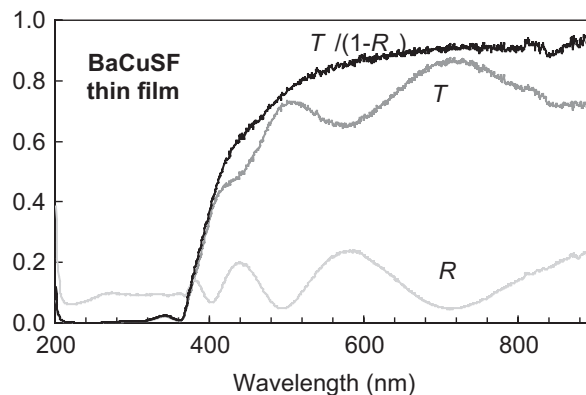


Fig. 8. Transmittance ( $T$ ) and reflectance ( $R$ ) of a BaCuSF film on SiO<sub>2</sub>. The effect of the interference fringes is removed in the plot of  $T/(1-R) \approx \exp(-\alpha d)$ , where  $\alpha$  is the absorption coefficient of BaCuSF. Crystal structures of CuScO<sub>2</sub> (left) and BaCuSF (right).

film interference effects, which is removed by plotting  $T/(1-R) \approx \exp(-\alpha d)$ , as described above. Analysis of the onset of absorption yields a band-gap for BaCuSF of 3.2 eV, assuming that the gap is direct and that the optical transition is allowed at the band minimum. As expected from a material with this gap, undoped films are rather transparent, achieving a transparency of 80% above 550 nm. With increasing K dopant, the films darken somewhat, though the band-gap does not change, there being instead increased absorption at all wavelengths, particularly in the blue.

The 100 S/cm conductivity measured in BaCuSF:10% K pellets is higher than that reported for transparent conductors  $\text{CuMO}_2$  ( $M$ =trivalent cation), and this represents a promising avenue for further study. Powder conductivity is generally limited by grain boundaries, so that phase-pure, epitaxial films should achieve even higher conductivity. The maximum conductivity of polycrystalline films produced to date is of order 1 S/cm, much smaller than the BaCuSF:K pellets of similar concentration. Although the X-ray diffraction patterns of the films are consistent with polycrystalline BaCuSF, we cannot rule out accumulation of small amounts of  $\text{BaF}_2$  in grain boundaries, which would limit conductivity.

#### 4. Summary

In the p-type transparent conductor  $\text{CuScO}_2$ :Mg, systematic variation of the conductivity and transparency with oxygen doping has been demonstrated. The band-gap of 3.6 eV makes the undoped films very transparent. Relatively high conductivities of 10–20 S/cm can be achieved in films at room temperature, although with loss of transparency. Bulk BaCuSF is readily doped with K to produce p-type conductivity. High conductivities of 100 S/cm have been obtained in sintered BaCuSF pellets with 10 at% K doping. Thin

films of BaCuSF are transparent, and a band-gap of 3.2 eV has been obtained from variable-wavelength transmission and reflection measurements. Transmission is above 85% for undoped films, and it decreases as carriers are introduced via K doping.

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