# *p*-type conductivity in wide-band-gap BaCuQF (Q=S,Se)

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BaCuQF (Q=S,Se) materials, candidate transparent *p*-type conductors, were prepared by solid-state reaction, and their bulk electrical and optical properties were evaluated. The room-temperature Seebeck coefficient and electrical conductivity of undoped BaCuQF pellets were $+56\ \mu$V/K and 0.088 S/cm, respectively, for the sulfide fluoride, and $+32\ \mu$V/K and 0.061 S/cm, respectively, for the selenide fluoride. The conductivity was greatly enhanced by the substitution of several percent of K for Ba; the highest conductivities were 82 S/cm for $Ba_{0.9}K_{0.1}CuSF$ and 43 S/cm for $Ba_{0.9}K_{0.1}SeF$. The band gaps for Q=S and Q=Se were measured to be 3.2 and 3.0 eV, respectively. Undoped BaCuSF exhibits strong red luminescence near 630 nm under ultraviolet excitation. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1571224]

Transparent *p*-type conducting oxides such as $CuMO_2$ (M=Al,Ga,In,Sc)[1–4] and $SrCu_2O_2$ (Ref. 5) have recently attracted attention as possible components of transparent electronic and optoelectronic devices. However, so far it appears that optimizing electrical conductivity in such Cu-based *p*-type oxides compromises the optical transparency to a greater extent than is the case for *n*-type conducting oxides, so that it seems sensible to search for alternate materials. A band gap greater than about 3.18 eV is necessary for optical transparency, and within this constraint, an improvement in hole mobility is desirable to improve conductivity. The more strongly covalent nature of the Cu—S bond compared to the Cu—O bond should improve hole mobility, and suggests examination of sulfides or other chalcogenide-based materials. $BaCu_2S_2$ has a hole mobility of 3.5 $cm^2/V\,s$, which is indeed much higher than the mobilities of order 0.1 $cm^2/V\,s$ reported for most Cu-based *p*-type transparent oxides, but the band-gap energy is 2.3 eV.[6] LaCuOS is also a *p*-type transparent conducting material,[7] but the mobility of 0.5 $cm^2/V\,s$ is still rather low.[8]

In 1994, Zhu *et al.*[9] reported the synthesis and crystal structure of two copper chalcogenide fluorides of BaCuQF (Q=S,Se). Figure 1 shows the BaCuQF crystal structure, which belongs to the space group P4/nmm. This is a layered structure with tetragonal symmetry, in which $(Ba_2F_2)^{2+}$ and $(Cu_2Q_2)^{2-}$ layers are alternately stacked along the *c* axis. The $(Cu_2Q_2)^{2-}$ layers, which can also be thought of as layers of edge-sharing $CuS_4$ tetrahedra, have an obvious correspondence to the $BaCu_2S_2$ structure, so that this is expected to be the plane for hole conduction. The BaCuQF layered structure is the same as that of LaCuOS, which has stacked $(La_2O_2)^{2+}$ and $(Cu_2S_2)^{2-}$ layers.[10] The similarity is interesting, because LaCuOS is not only a transparent *p*-type conductor, but also an ultraviolet light emitter that exhibits excitonic absorption and emission even at room temperature.[11] Experimental and theoretical analyses indicate that the $(Cu_2S_2)^{2-}$ layers contribute to both the top of the valence band and the bottom of the conduction band of LaCuOS.[12] Zhu and co-workers[9] reported semiconducting behavior of BaCuQF, but details were lacking, and other data available are from a preliminary study by Yanagi and co-workers.[13] Here, we report promising *p*-type electrical conductivity of bulk BaCuQF, a band gap of 3.0 eV or greater and strong photoluminescence of BaCuSF.

Powder samples of undoped and K-doped BaCuQF were prepared by heating stoichiometric mixtures of BaQ (Cerac, 99.5%), $Cu_2Q$ (Cerac, 99.5%), $BaF_2$ (Cerac, 99.9%), and KF (Alfa Aesar, 99%) at 450–550 °C for 12 h in an evacuated silica tube. The powders are generally stable in air, but reaction is evident upon exposure to water. All of the samples were characterized by powder x-ray diffraction on a Siemens D5000 diffractometer; they were predominantly single phase with only trace amounts of unreacted $BaF_2$ observed. For conductivity measurements, each powder sample was pressed into a pellet and annealed at 650 °C for 1 h in an evacuated silica tube. The pellets averaged 70%–80% of theoretical density; as detailed in Table I.

The electrical conductivities of the sintered pellets were measured from 300 to 77 K by a four-probe technique. Silver paste was used for electrodes and ohmic contact was confirmed before detailed measurements were made. The Seebeck coefficient was measured at room temperature with a temperature gradient of ~5 K across the pellet. The diffuse

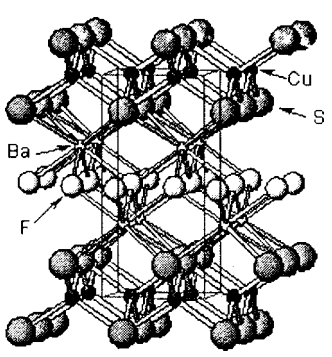


FIG. 1. Crystal structure of BaCuQF (Q=S,Se).

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TABLE I. Electrical properties (conductivity and Seebeck coefficient) and densities of $Ba_{1-x}K_xCuQF$ ($x=0$, 0.025, 0.05, 0.1, and Q=S,Se) pellets at room temperature.

| | $Ba_{1-x}K_xCuSF$ | | | | $Ba_{1-x}K_xCuSeF$ | | | |
|---|---|---|---|---|---|---|---|---|
| K (at. %) | 0 | 0.025 | 0.50 | 0.10 | 0 | 0.025 | 0.50 | 0.10 |
| $\sigma$ (S/cm) | 0.088 | 2.6 | 20 | 82 | 0.061 | 17 | 27 | 43 |
| $S$ ($\mu$V/K) | +56 | +205 | +55 | $<+5$ | +32 | +34 | +25 | +41 |
| Density (%) | 73 | 89 | 80 | 89 | 76 | 69 | 62 | 76 |

reflectance at room temperature of powdered BaCuQF was measured against MgO powder in the UV-visible region (300 to 900 nm) by using an integrating sphere and a double monochromator. Photoluminescence measurements were made with an Oriel 300 Watt Xe lamp and Cary model-15 prism monochromator for excitation, and an Oriel 22500 1/8 m monochromator and Hamamatsu R935 photomultiplier tube for detection. Each spectrum was corrected for the response of the system by using rhodamine B and a standardized tungsten lamp.

The temperature dependence of the electrical conductivity of $Ba_{1-x}K_xCuSF$ and $Ba_{1-x}K_xCuSeF$ pellets is illustrated in Fig. 2. Undoped pellets of BaCuSF and BaCuSeF have electrical conductivities in the range of $10^{-2}$ S/cm, and the conductivity increases with increasing K concentration. The room-temperature conductivity of the pellets is 82 S/cm for $Ba_{0.9}K_{0.1}CuSF$ and 43 S/cm for $Ba_{0.9}K_{0.1}SeF$. This compares favorably with the values of order 1–20 S/cm reported for other Cu-based $p$-type transparent conductors, including the structurally similar $LaCuOS_{1-y}Se_y$ system ($10^{-1}$–$10^{0}$ S/cm).[14] The temperature dependence of the electrical conductivity of $Ba_{1-x}K_xCuSF$ is semiconducting for $x<0.025$, with an activation energy around 60 meV near

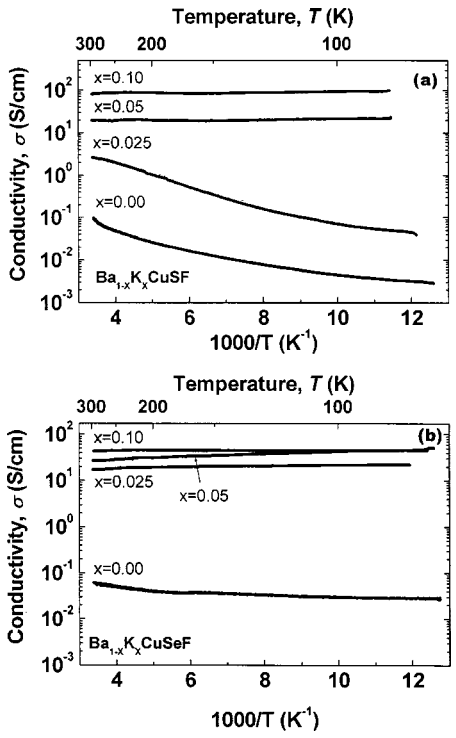


FIG. 2. Electrical conductivity of $Ba_{1-x}K_xCuQF$ pellets as a function of reciprocal temperature for (a) Q=S, and (b) Q=Se. In each case, $x=0$, 0.025, 0.05, 0.1.

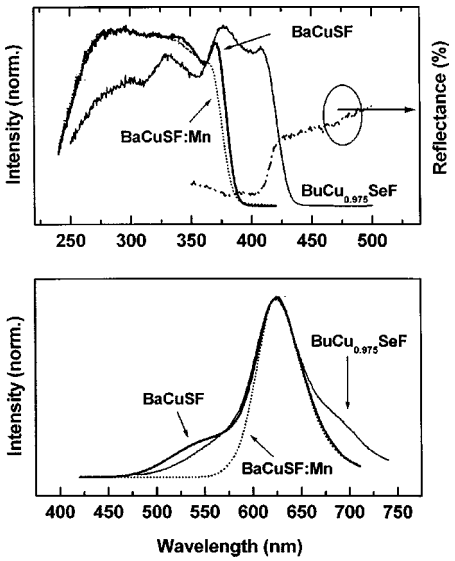


FIG. 3. (Top) reflectance spectrum for BaCuSeF and excitation spectra for BaCuQF and (bottom) emission spectra for BaCuQF.

room temperature, and there is a crossover to metallic behavior for $x>0.05$. The electrical conductivity of the undoped selenide fluoride has a very weak temperature dependence, and all of the doped pellets exhibit essentially metallic behavior. Seebeck measurements on all samples, except $Ba_{0.9}K_{0.1}CuSF$, gave a positive sign indicating that these materials are $p$ type conductors at all doping levels. In the case of $Ba_{0.9}K_{0.1}CuSF$, the voltage was too small to measure the Seebeck coefficient. The transport measurements are summarized in Table I. BaCuSF thin films were deposited on $SiO_2$ by thermal coevaporation. Undoped films are transparent, polycrystalline, and insulating. K-doped films do not yet exhibit conductivities higher than the pellets.

The diffuse reflectance of BaCuSeF (Fig. 3) is low at short wavelengths and increases sharply at ~400 nm. The energy band gap of 3.0 eV was estimated from a plot of $\{(k/s)\cdot h\nu\}^2$ versus $h\nu$, where $k$ and $s$ denote absorption and scattering coefficients, and $h\nu$ is the photon energy. The ratio $k/s$ was calculated from the reflectance via the Kubelka–Munk equation.[15,16] This gap value should be sufficient to transmit all but the deepest blue light. The band edge in diffuse reflectance spectra of BaCuSF is obscured by strong emission excited by ultraviolet light, but transmission measurements on an undoped transparent thin film of BaCuSF yielded a value of 3.25 eV.[13] As expected for a quasi two-dimensional layered structure like BaCuQF, the band-gap values are larger than for $BaCu_2S_2$, which has a three-dimensional arrangement of the $CuS_4$ tetrahedra.

Excitation and emission spectra for undoped and doped BaCuQF compositions are summarized in Fig. 3. Emission from each sample occurs in the orange-red to red portions of the spectrum. The onset of excitation near 425 nm for $BaCu_{0.975}SeF$ agrees well with the reflectance data, indicating excitation and emission occurs through band-gap absorption of the compound rather than an impurity. Similarly, the excitation spectrum of BaCuSF is consistent with the 3.2 eV band gap observed from thin-film transmission data.

The emission from BaCuSF is characterized by two broad peaks centered near 560 and 630 nm, giving rise to an

emission that appears orange to the eye. The peak near 560 nm can be quenched by altering the synthesis conditions or by selective doping. In the case of Mn doping, the 560 nm band is completely quenched, giving an emission with color coordinates $x=0.66$ and $y=0.34$, similar to those ($x=0.65$ and $y=0.34$) observed for the commercial red phosphor $Y_2O_3$:Eu. A more detailed accounting of the optical properties of these materials will be given elsewhere.

In summary, we have prepared undoped and K-doped BaCuQF, which is a promising transparent *p*-type conductor. The electrical conductivity was controlled by K doping and the bulk conductivity is 82 S/cm for sintered pellets of BaCuSF:K and 43 S/cm for BaCuSeF:K at a doping level of K of 10 at. %. The Seebeck coefficients were positive, indicating that undoped and K-doped BaCuQF are *p*-type conductors. The optical band gap of BaCuQF is larger than 3 eV, and strong luminescence is observed near 630 nm.

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