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Relationships between the Structures of the Rare Earth Fluorides and High Chalcocite Cu_2S. Implications for Solid Electrolyte Behavior

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Similarities between the high chalcocite (Cu_2S), tysonite (LaF_3) and YF_3 structures are noted. These prove useful in interpreting solid electrolyte behavior.

Despite the widespread interest in solid electrolytes, there has been remarkably little detailed investigation of the structures of high-temperature ion-disordered phases. The experimental difficulties are great; in addition to the usual problems of high-temperature X-ray diffraction, there are phase transitions which make it difficult to obtain single crystals suitable for study.

A notable exception is provided by chalcocite, Cu_2S. The low → high transition is essentially a disordering of the copper ions and is accompanied by a large increase in entropy (9.9 JK^{-1} $mole^{-1}$) (*1*). There is, however, only a small volume change and sulfur remains in approximately hexagonal close packing (*hcp*) in both phases. Both structures are now known (*2*, *3*), although each presented an unusually difficult problem. We have found that examination of the high chalcocite structure provides a valuable insight into the structure and properties another class of solid electrolytes; the rare earth fluorides such as LaF_3 and LuF_3 (*4*, *5*), previously considered somewhat enigmatic.

In retrospect it is not surprising to find similarities in structure and properties between copper and silver salts on the one hand, and oxides and fluorides on the other, as both types of ion display a penchant for low coordination number ($\leqslant 4$) in most of their compounds. Thus,[1] Cu_3N has the "anti" structure of ReO_3 and Cu_3P and LaF_3 are similarly related.[2] The occurrence of solid electrolyte behavior equally in compounds with the fluorite and antifluorite structures is now well documented (*7*). The relationship between high chalcocite and the rare earth fluorides is less obvious and is one we explore in this paper.

Comparisons of unit cell contents of different structures are rarely rewarding. In this instance the essential structural relationships are best identified by idealizing the structures slightly so that the immobile ions are in an ideal *hcp* array. For Cu_2S and LaF_3 this is just a change in the axial ratio (c/a). The fluorides of the heavier rare earths YF_3 and are orthorhombic, but again the structure can be idealized to *hcp* yttrium ions by a small distortion. Figure 1 shows the real and idealized LaF_3 (*8*) and YF_3 (*9*) structures in projection.

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[1] Structures for which no specific reference is given may be found in Ref. (*6*).

[2] The latter correspondence is not perfect, but the difference between the two structure types involves only minor changes in atomic coordinates.

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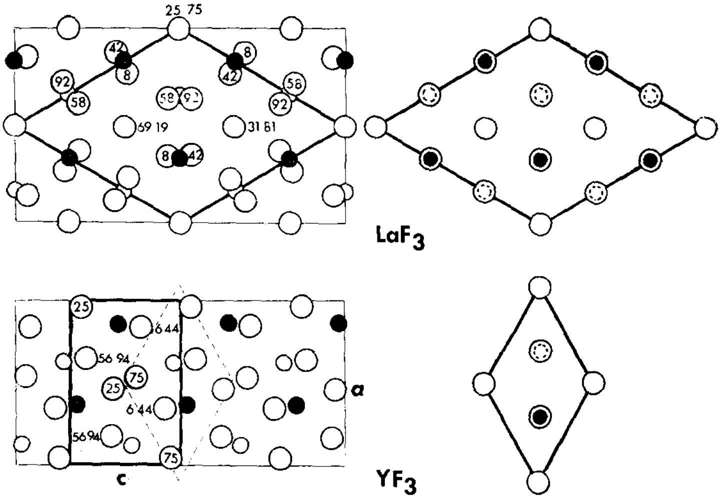

FIG. 1. The real and idealized structures of LaF_3 and YF_3. On the left are shown the contents of two unit cells of LaF_3 projected on (0001) and three unit cells of YF_3 projected on (010). Heavy lines outline the unit cell. Large circles represent F and the numbers are elevations in multiples of $c/100$ or $b/100$. Small open and filled circles are cations at elevations of $c/4$ or $b/4$ and $3c/4$ or $3b/4$, respectively. The idealized structures on the right are derived by displacements in the horizontal plane only. The asymmetric units of these idealized structures are represented in Fig. 3.

Their similarities are apparent. It should be noted that the conducting, high-temperature phase of YF_3 is hexagonal.

To compare the structures more clearly we employ the device used effectively by Gorter (*10*), of dividing the space of the close-packed ions into Voronoi polyhedra. Each of these space-filling polyhedra (Wigner–Seitz cells in the jargon of solid state physics) is the smallest volume containing a given site enclosed by all planes perpendicularly bisecting lines formed by joining that site to all other atom sites in the crystal. In the case of *hcp* the polyhedron is a trapezorhombic dodecahedron.

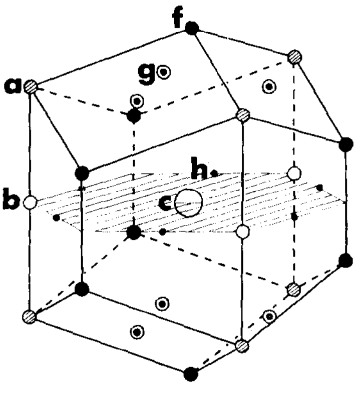

FIG. 2. The space-filling polyhedron for *hcp*. The hatched plane is a plane of close-packed ions. Letters refer to the special positions of $P6_3/mmc$.

This polyhedron is shown in Fig. 2. When packed to fill space, with the polyhedra of alternate layers perpendicular to the threefold axis rotated by $\pm 2\pi/3$, the centers form an ideal *hcp* array. The vertices and many other special points also form high-symmetry arrays with space group $P6_3/mmc$ so that they may conveniently be labeled by the Wyckoff notation for the equipoints of this group (*11*). The origin is at the center of symmetry ($\bar{3}m1$), and the polyhedron centers are placed at 2*c*. The vertices correspond to the regular octahedral and tetrahedral interstices of closest packing. The octahedral sites are then at 2*a* and tetrahedral sites at 4*f* ($z = 5/8$). Other important points are the 2*b* sites of threefold coordination in the middle of the long edges and sites of two fold coordination in face centers. The centers of the vertical faces are in 6*h* ($x = 5/6$) and of the other faces in 6*g*. The asymmetric units of all the structures to be discussed here can be represented with the *hcp* ion at the center of the polyhedron and its coordinating ions at some of these special positions on the surface.

Turning first to the structure of high chalcocite, Buerger and Wuensch (*2*) showed that the space group is $P6_3/mmc$ with S atoms at $2c$. The Cu distribution is continuous along channels through the structure with peaks at the $2b$, $4f$, and $6g$ positions. This structure is illustrated schematically in Fig. 3. The idealized YF_3 structure (which is essentially that of Na_3As) is also shown in Fig. 3. The correspondence between the two structures may be seen as follows. If the copper atom distribution were considered centered on equipoints, there would be approximately (*2*) 0.19 atoms at each of $6g$, 0.41 atoms at each of $4f$ and 0.62 atoms at each of $2b$. If, on the other hand, one had 2/3 Cu at each of the F positions of YF_3, there would be 0.67 atoms at each of $4f$ and $2b$. The difference is then mainly a small displacement along $(1/24)\langle 443\rangle$ of some of the Cu from the tetrahedral sites, $4f$, to two-coordinated sites $6g$.

The LaF_3 structure is still controversial (*12*). The probable structure as determined by X-ray diffraction (*8*) is shown in Figs. 1 and 3. The idealized structure differs from the idealized YF_3 structure only by displacement of 2/3 of the $2b$ atoms along [001] towards the octahedral sites, $2a$. The thermal motion of these atoms is apparently large and highly anisotropic with maximum amplitude along this direction. It is possible that this represents a static disorder, as NMR experiments (*13*) suggest that it is the tetrahedrally coordinated fluorine ions that are mobile in LaF_3 below 300°C. The anisotropic temperature factors for these latter ions determined by Mansmann (*8*) are also large and not incompatible with displacements as described above in the direction of $6g$. Above 300°C the NMR results suggest interchange of fluorines between the tetrahedral and threefold sites completing the analogy with Cu_2S.

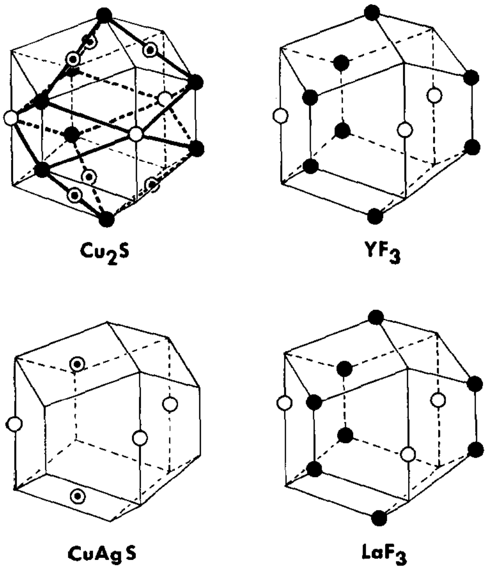

FIG. 3. Units of various structures according to the representation of Fig. 2. In Cu_2S (high chalcocite) the electron density is continuous along channels represented by the heavy lines.

These close similarities suggest strongly that conduction paths in the hexagonal fluoride solid electrolytes (*4*, *5*) are similar to those in high chalcocite. It is noteworthy that in the latter there is no Cu density either at octahedral sites or between nearest-neighbor tetrahedral sites.

The similarity between the structure types discussed here extends beyond the topological aspects so far discussed. In all the compounds the presence of tetrahedral ions causes an increase in the hexagonal c/a ratio from the ideal value of 1.633. For compounds with the Na_3As structure, $c/a = 1.76$–1.78; for Cu_2S, $c/a = 1.77$; and for LaF_3 and Cu_3P (*14*), $\sqrt{3}\, c/a = 1.75$. This increase in axial ratio results in a change in the z parameter for the tetrahedral sites ($4f$ of $P6_3/mmc$). Writing $c/a = \gamma(8/3)^{1/2}$, it is elementary to show that for the tetrahedral site to be equidistant from its four nearest neighbors, $z = 1/2 + 1/(8\gamma^2)$. Thus, for $c/a = 1.77$, the "ideal" value of z now becomes 0.606 rather than 0.625 for $c/a = (8/3)^{1/2}$. In fact, because of repulsion between pairs of tetrahedral ions they are displaced from the tetrahedron centers and in all these compounds $z \simeq 0.58$. The vector connecting the tetrahedral and adjacent twofold sites now becomes $\simeq 1/12\ \langle 221\rangle$.

The low-chalcocite structure (*3*) is complex, with 36 atoms in the asymmetric unit, however, the structure of stromeyerite, CuAgS (*15*), is simpler and is interesting in this connection. Again, one has approximately *hcp* S with the pseudohexagonal c axis parallel to the orthorhombic c axis. In the idealized structure the

$2b$ sites are occupied by Cu and 1/3 of the $6g$ sites filled by Ag in an ordered way (Fig. 3). This may be considered the completion of the transition $4f \rightarrow 6g$ that we have discussed.

Finally, it might be noted that above 435°C Cu_2S becomes cubic with cubic close packed sulfur atoms. The analogy with fluoride solid electrolytes with the fluorite structure (*5*, *16*) is obvious.

Acknowledgments

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