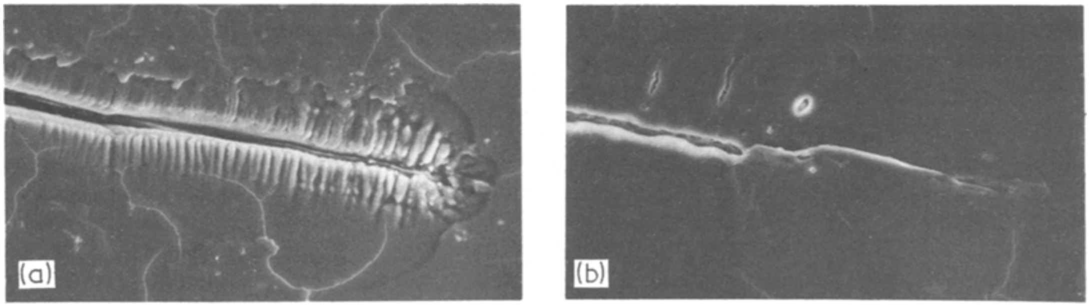

Figure 2 Scanning electron micrographs of etched surfaces of NaCl single crystals showing the effect of annealing on the deformed region near the crack. (a) An etch pattern showing the severity of the damage along the crack path (as cracked), (b) an etch pattern from a specimen annealed for 5 h at 200° C, × 230.

ation during heat-treatment. Fig. 2 shows the severity of structural damage near the crack plane at room temperature, and the progressive annihilation of dislocations and the resulting structural relaxation after annealing for 5 h at 200° C. The structural damage adjacent to the plane of the cleavage crack is greater near the crack tip. Since the severity of the structural damage is proportional to the amount of stored energy, the probability of crack pinching is highest near the tip of the crack. As the etch pattern in Fig. 2 demonstrates, the reduction in structural damage through a dislocation annihilation process is the main cause for the decrease in crack width in NaCl at 200° C. This evidence indicates that, although the exact healing mechanism depends on the annealing temperature, low temperature crack healing in NaCl single crystals is a continuous process aided by the relaxation of local strain in the deformed microvolume adjacent to the crack plane. At temperatures above 500° C diffusional processes play the dominant role in crack healing.

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SANG M. PARK
DENNIS R. O'BOYLE
*Departments of Ceramic Engineering and
Nuclear Engineering,
University of Illinois at Urbana-Champaign,
Urbana,
Illinois, USA*

Deterioration in air of silicon arsenide and silicon phosphide

Preparative and structural studies have for several years been conducted at this Institute on binary compounds of elements of the IV and V groups of the Periodic Table [1]. In this connection it has been observed that deterioration of SiP and SiAs crystals, when exposed to laboratory air for some time, takes place to such an extent to render X-ray investigations or studies of their physical properties difficult or impossible. The considerable interest in these materials shown by many research workers seemed to warrant an analysis of the character of the deterioration process.

The samples of SiP and SiAs used in this investigation were prepared from silicon, red phosphorus and arsenic in sealed evacuated silica tubes by direct combination of the elements or by transport reaction techniques. The products were characterized by their X-ray powder patterns, which have been reported previously [1]. It was observed that specimens which had been exposed to the laboratory atmosphere for about 1 year showed substantial increases in weight. A fresh

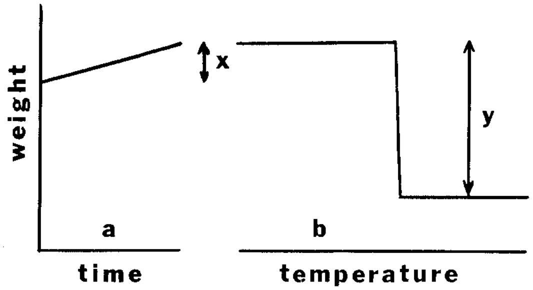

Figure 1 Oxidation effect on SiAs.

sample of SiAs was used for a series of weighings over a period of several months, the specimen being kept in a container with free communication to the laboratory atmosphere. A continuous increase in weight was observed as shown in Fig. 1a. When studied by thermogravimetric analysis, the specimen showed a sudden decrease in weight at about 190° C, as indicated in Fig. 1b. Part of the material evolved at this sublimation process was collected and identified by its X-ray powder pattern as the cubic modification of arsenic trioxide (arsenolite). The observed sublimation temperature was found to be in agreement with that of a standard arsenolite sample. The ratio of the weight changes in the two experiments indicated in Fig. 1 (y:x) were in agreement with a simple mechanism comprising formation of arsenic trioxide by room temperature oxidation and subsequent sublimation at the thermal analysis experiment. X-ray powder patterns of the residue showed only the reflections of SiAs.

In a study of the thermal decomposition of SiAs in vacuum [3] the formation of an intermediary product of the composition Si_6As has been observed. This substance forms at around 925° C and is stable in vacuum at least up to 1100° C. It does not give X-ray powder reflections and may thus be described as amorphous in that respect. In the electron microscope, however, it gives a characteristic diffraction pattern.

When in the thermal decomposition experiment the starting material was SiAs which had undergone surface oxidation, the electron diffractogram of the residual sample in addition to the Si_6As ring pattern was found to contain spots which could be interpreted as due to elemental silicon. The presence of the latter was confirmed by the appearance in an amply exposed X-ray powder photograph of weak broad silicon pattern lines.

The experimental evidence thus shows that the deterioration of silicon monoarsenide in air is an oxidation of the surface according to the formula

$$2SiAs + \tfrac{3}{2}O_2 = As_2O_3 + 2Si.$$

Analogous studies on the deterioration of SiP have given less conclusive results. It shows a slow weight increase when exposed to air but the decrease by thermal decomposition is not a distinct one and the reactions cannot be interpreted in simple terms. The early observation that this material gives a "disagreeable smell" [2] suggests that this is not exclusively an oxidation process but complex by the formation of volatile compounds (e.g. hydrid) in the presence of moisture.

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TOMMY WADSTEN
Department of Inorganic Chemistry,
Arrhenius Laboratory,
University of Stockholm,
S-104 05 Stockholm,
Sweden