



Fig. 2. Spiral fractures meeting in glass resin.

after preparing prepolymer according to the directions of the manufacturer. Figs. 1 and 2 (magnification, $50\times$) were obtained with polytriallylisocyanurate (Fig. 1) and glass resin (Fig. 2).

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¹ Gillham, J. K., Applied Polymer Symposia, 2, 45, in *Thermoanalysis of Fibers and Fiber Forming Polymers*, Schweiker, R. F. (ed.) (Interscience, New York, 1966).

Similarity between "Chukhrovite" and the Octahedral Crystals found in Gypsum in the Manufacture of Phosphoric Acid

THE presence of minute colourless octahedral crystals has long been noticed in gypsum made during the manufacture of phosphoric acid from phosphate rock and sulphuric acid. They normally occur at a concentration of 0.1 weight per cent or less of the gypsum and, therefore, separation for analysis is extremely difficult. The use of selective dissolution, density separation, and sedimentation to produce a sufficient quantity for chemical analysis yielded material contaminated with silica and calcium fluoride. In 1959, however, using X-ray powder and single-crystal diffraction techniques, we determined their unit cell to be cubic, of parameter $16.75 \pm 0.05 \text{ \AA}$, and probable space-group T_h^h-Fd3 .

In 1960, Yermilova, Moleva and Klevtsova¹ published details of a new mineral found in Central Kazakhstan, which they named "chukhrovite". Its formula was given as $\text{Ca}_3\text{Al}_2(\text{R.E.})\text{SO}_4\text{F}_{13}\cdot 10\text{H}_2\text{O}$, where "R.E." could be a mixture of rare earths and yttrium. X-ray diffraction studies showed it to have a face-centred cubic lattice of parameter $16.80 \pm 0.10 \text{ \AA}$, class T_h^h-m3 . The published powder-diffraction pattern showed the stronger lines of the pattern for our octahedral crystals; the crystal

habit was octahedral, with some development of the cube faces, and the various chemical reactions listed agreed with those found by us for our unknown material. It seemed, therefore, that our octahedral crystals were at least isomorphous with chukhrovite.

Lehr, Frazier and Smith² have recently published an article on the impurities precipitated from a wet process phosphoric acid preparation which includes a material $\text{Ca}_4\text{AlSiSO}_4\text{F}_{12}\text{OH}\cdot 12\text{H}_2\text{O}$ the X-ray powder-diffraction pattern of which is in close agreement with that from our octahedral crystals. They suggest that they are cubic, and of octahedral habit; an indexing of their powder pattern yields a cell parameter of $16.70 \pm 0.05 \text{ \AA}$. A material of this composition was first reported in a patent³ in 1937 and has recently been the subject of a further patent⁴ on the purification of phosphoric acid.

A relationship between chukhrovite and Lehr's material can be shown by slight isomorphous replacements in the two formulae. F^- and OH^- are commonly interchangeable, and therefore F_{12}OH is equivalent to F_{13} ; $(\text{Ca}^{2+}\text{Si}^{4+})$ can be replaced by $(\text{Al}^{3+}\text{X}^{3+})$. Thus, Lehr's material becomes $\text{Ca}_2\text{Al}(\text{AlX}^{3+})\text{SO}_4\text{F}_{13}\cdot 12\text{H}_2\text{O}$, or $\text{Ca}_3\text{Al}_2(\text{R.E.})\text{SO}_4\text{F}_{13}\cdot 12\text{H}_2\text{O}$ in the notation quoted for chukhrovite. The excess of $2\text{H}_2\text{O}$ over that present in the chukhrovite formula is a weight error of only 4.5 per cent, and in addition some variation of hydration level without destruction of the crystal structure may well be possible in such a material.

Recent changes in the source of phosphate rock used for the manufacture of phosphoric acid have led to increased production of octahedral crystals, and by good fortune these have been segregating from the gypsum. The only contamination present was amorphous organic material, which has made elemental analysis possible. These crystals have the formula $\text{Ca}_{4.03}\text{Ba}_{0.04}\text{X}_{0.07}\text{Al}_{1.21}\text{Si}_{0.75}(\text{SO}_4)_{1.00}\text{F}_{13.0}\cdot 10\text{H}_2\text{O}$. The trivalent metals, X, were yttrium and lanthanum. The crystals therefore have a chemical composition and unit cell size intermediate between chukhrovite and the crystals described by Lehr *et al.*, which confirms the similarity between those from a natural source and those precipitated in the phosphoric acid process. It would seem that all three materials are part of an isomorphous series in which Al^{3+} can be replaced by other trivalent ions or by Ca^{2+} and Si^{4+} jointly, and F^- by OH^- . The difference in water of hydration could be caused by experimental error, as fluorine was lost in addition to water on heating. If all the weight loss on heating were attributed to water, with no correction for fluorine loss, our results would have given $12\text{H}_2\text{O}$ rather than $10\text{H}_2\text{O}$.

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¹ Yermilova, L. P., Moleva, V. A., and Klevtsova, R. F., *Zap. Vsesoyuzn. Miner. Obshch.*, 89, 15 (1960).

² Lehr, J. R., Frazier, A. W., and Smith, J. P., *J. Agric. and Fd. Chem.*, 14, 27 (1966).

³ Kuntsdinger-Patent-Verwertungs-A-G, Brit. Patent 467,843 (1937).

⁴ Brit. Patent 1,024,924 (1966).

CHEMISTRY

Growth of Single Crystals of Lead Sulphide in Silica Gels near Ambient Temperatures

THE application of intermetallic compounds in electronic devices has been limited by the difficulties of preparing single crystal materials with desirable properties¹. Typical techniques used involve growth from the melt at high temperatures and, frequently, high pressures, or by chemical transport. We wish to report an alternative method—the growth of single crystals of lead sulphide in silica gels near ambient temperatures. This shares