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X-ray topography study on imperfections in synthetic mica (fluorophlogopite) crystal

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The X-ray diffraction topography study of imperfections in synthetic mica (fluorophlogopite) crystal is reported. The main defects in synthetic fluorophlogopite crystal are one-dimensional disorder, sub-grain boundaries and dislocations. The orientations of the sub-grain boundaries and dislocations are normal to the growth front. Many defects in synthetic micas originate from the seed crystal. By controlling the orientation of the seed crystal, large-sized fluorophlogopite crystals with almost no central defects have been synthesized. In view of its excellent chemical and electrical properties, flat surface and strong X-ray diffraction intensity, large-sized fluorophlogopite crystal will find many important applications in various fields.

1. Introduction

Mica is a typical sheet structured crystal. Owing to its excellent electrical insulating property, high resistence to irradiation and high temperatures, as well as other valuable properties, single crystal fluorophlogopite has been regarded as an important material. Due to the complexity of crystal structure as well as technical experimental difficulties, only little progress has so far been made in the study of imperfections in mica [1–5]. No X-ray studies on imperfections in synthetic mica have yet been reported.

Large-sized (150 mm × 100 mm × 100 mm) single crystals of fluorophlogopite have been successfully grown using the Stockbaraer method with a seed crystal [6]. This paper reports the X-ray diffraction topography study on imperfections in fluorophlogopite.

2. Crystal structure of fluorophlogopite

Fluorophlogopite ($KMg_3AlSi_3O_{10}F_2$) has the same structural characteristics as other sheet silicate minerals. The silicon–oxygen tetrahedra $(SiO_4)^{4-}$ are linked together forming a hexagonal network (Fig. 1a) in which a quarter of the silicon is replaced by aluminium to give a tetrahedral single layer $(AlSi_3O_{10})_n^{5n-}$. The fluorine atoms are in the centre of the hexagonal ring formed by oxygen at the apices of each tetrahedron in the tetrahedral single layer, forming a fluorine–oxygen close-packed atomic layer. Mg^{2+} ions fill the centre of the octahedral interstices formed by two of these close-packed atomic layers (Fig. 1b). They are bonded to the surrounding oxygen and fluorine ions and have a co-ordination number of 6. Mg–(O, F) bonds connect the two layers resulting in a stable double layer of tetrahedra (Fig. 1b). The opposing hexagonal rings of oxygen atoms of the two double layers constitute oxygen cubo-octahedra with K^+ ions located in the centre. However, this bond is rather weak because the K^+ ions are of low electro-valence and comparatively large radius. As a consequence, the crystal of mica exhibits a distinct sheet structure and is easily subject to cleavage along the potassium layer. The cleavage plane is a *c*-plane, i.e. (001) plane, and is also the main slip plane.

Due to the fact that the atoms of the oxygen layers below or above the potassium layer are arranged in exact superposition in fluorophlogopite crystal, imperfections such as the stacking fault four-fold ribbon found in talc [7] or the perfect dislocations by slipping along the [100] direction are difficult to form. The slip process from A to B shown in Fig. 1c would dissociate into the two steps, $\overrightarrow{AC}$ and $\overrightarrow{CB}$, and the possible dislocation reactions can be denoted as follows:

$$\tfrac{1}{6}[310] + \tfrac{1}{6}[3\bar{1}0] \rightarrow [100]; \quad (1)$$

$$\tfrac{1}{3}[010] + \tfrac{1}{6}[310] \rightarrow \tfrac{1}{2}[110]; \quad (2)$$

$$\tfrac{1}{3}[0\bar{1}0] + \tfrac{1}{6}[3\bar{1}0] \rightarrow \tfrac{1}{2}[1\bar{1}0]. \quad (3)$$

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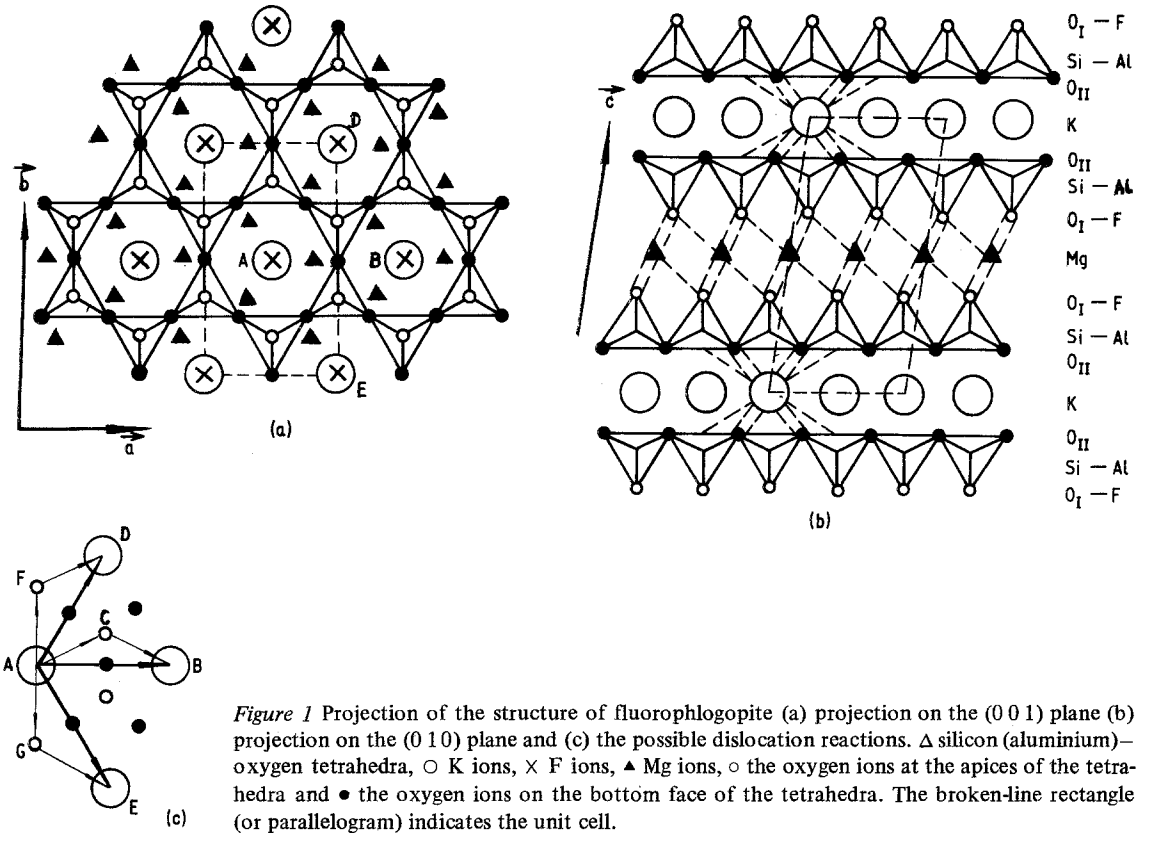

Figure 1 Projection of the structure of fluorophlogopite (a) projection on the (0 0 1) plane (b) projection on the (0 1 0) plane and (c) the possible dislocation reactions. Δ silicon (aluminium)–oxygen tetrahedra, ○ K ions, × F ions, ▲ Mg ions, ○ the oxygen ions at the apices of the tetrahedra and • the oxygen ions on the bottom face of the tetrahedra. The broken-line rectangle (or parallelogram) indicates the unit cell.

Because the radius of the potassium ion is large while the interstice in the C position is small, the potassium atoms slipping to such intermediate positions are unstable. It can be seen that in fluorophlogopite there is a tendency to form perfect dislocations during crystal growth or slip at high temperature.

Double layers with interlayer stacking vectors are stacked periodically into various polytype structures of mica. Polytype 1M belongs to the monoclinic system (space group $C2/m$, with unit cell parameters $a = 5.308$ Å, $b = 9.183$ Å, $c = 10.139$ Å, $\beta = 100.07°$ and $Z = 2$) and is common to fluorophlogopite [8].

3. Experimental methods

According to the theoretical formula of fluorophlogopite the mass absorptions, μ, for Kα radiation of Ag, Mo, Cu, Fe and Cr are 2.40, 4.73, 41.9, 79.8 and 128 $cm^2 g^{-1}$, respectively. The density of fluorophlogopite is 2.82 g cm^{-3}. The critical thicknesses, t, satisfying the conditions of $\mu t = 1$ in X-ray traverse topography at the wavelength mentioned above are 1480, 750, 85, 44 and 28 μm, respectively. Mica crystal can be easily cleaved into thin sheets of the order of ten micrometers in thickness, and therefore any wavelength may be used. However, very thin mica sheet will easily bend elastically and the diffraction topograph of the whole crystal sheet is difficult to obtain. Therefore, specimens with a thickness of 0.2 to 1 mm and Mo radiation were generally adopted in topography studies. For the thin mica sheet used in the manufacture of condensers, Cu radiation was employed.

In traverse X-ray topographic experiments, (060) diffraction was chosen. For CuKα, $2\theta = 60.46°$ and for MoKα, $2\theta = 26.84°$. The topographic photographs of small mica sheets were taken with a microfocus X-ray generator and a commonly used topographic camera. The focus size was 0.2 mm × 0.6 mm, the distance between focus and crystal was 350 mm and the distance between crystal and film was about 10 mm. For large crystal sheets (100 mm × 75 mm), direct observation was conducted and photographs were taken using a 60 kW rotating anode high-intensity X-ray generator and the associated X-ray topographic television system.

An investigation was made on numerous synthetic mica and some natural mica specimens,

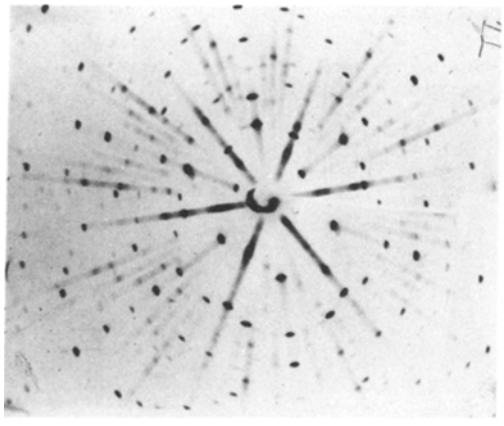

Figure 2 Transmission Laue photograph of synthetic fluorophlogopite crystal using unfiltered Cu radiation. (The film is at a distance of 3 cm from the crystal).

using X-ray transmission and back reflection Laue methods. When the incident X-ray beam scanned through the sub-grain boundary of a crystal specimen the changes of Laue pattern were directly observed using the orthicon tube X-ray television system attached to a 30 kW rotating anode high-intensity X-ray generator.

4. Experimental results

Besides the macroscopic defects, including random intercrystal growth, bubbles, inclusions, microcracks and so on, various microscopic defects such as sub-grain boundaries, one-dimensional structural disorder, dislocations etc. may also exist in fluorophlogopite crystals.

4.1. One-dimensional structural disorder

The results of investigation by the X-ray Laue method show that in contrast to the sharp Laue diffraction spots in the majority of natural mica the Laue spots which appeared in most of the synthetic mica are diffuse and have prolonged streaks in the radial direction showing rather serious one-dimensional disorder (Fig. 2). It can be seen from the structure of fluorophlogopite that the energy of stacking faults is very low. Therefore, during the short period of growth, even a slight change of the growth condition can cause a misarrangement in the stacking order of layers. Nevertheless, the crystal generally grows in a statistical way similar to 1 M-type stacking, but has a large number of stacking faults. However, the one-dimensional disorder could hardly be seen in natural mica grown gradually over very long geological periods.

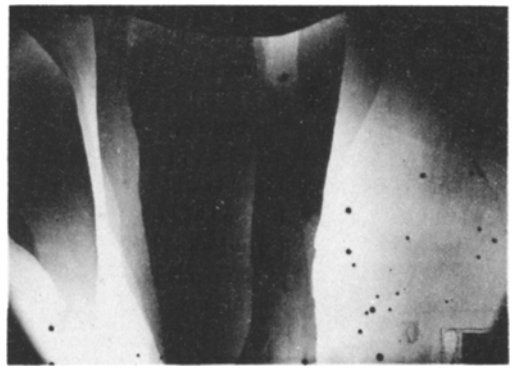

Figure 3 Photomicrograph of synthetic fluorophlogopite crystal viewed with crossed Nicols. The contrast shows the regions of stacking misarrangement.

4.2. Sub-boundary due to random stacking

Different layer arrangements in various areas within a single crystal lead to the formation of boundaries between these areas. In mica crystal of sheet structure, the "misarranged boundary", connecting two neighbouring regions with different stacking orders, is a kind of submicroscopic imperfection and it is called sub-boundary in this paper.

A number of fluorophlogopite sheets with distinct areas of different brightness (Fig. 3) were selected under a polarization microscope and a scanning X-ray transmission Laue examination was made. In most circumstances no change occurred in the Laue patterns when X-ray beams scanned across the sub-grain boundary, but in a few cases the Laue patterns of both sides of the sub-grain boundaries showed a 60° rotation relationship. This indicates that the lattice arrangements on both sides of the sub-grain boundary are a pair of twins. Sometimes the Laue pattern of the same area in the crystal showed two sets of spots with a rotation of 60°. It is clear that both the upper and lower parts of the crystal sheet are a pair of twins and the twinning plane in this case is the (001) plane.

The most prominent pattern in the X-ray traverse topographic photography of fluorophlogopite is the widespread strong contrast of the sub-grain boundaries (Fig. 4). Some of the sub-grain boundaries in the topograph correspond to those seen by the naked eye under reflecting light. The other sub-grain boundaries should be those which did not yet extend to the surface of the crystal sheet. Some of the sub-grain boundaries observed under the polarization microscope do not appear in

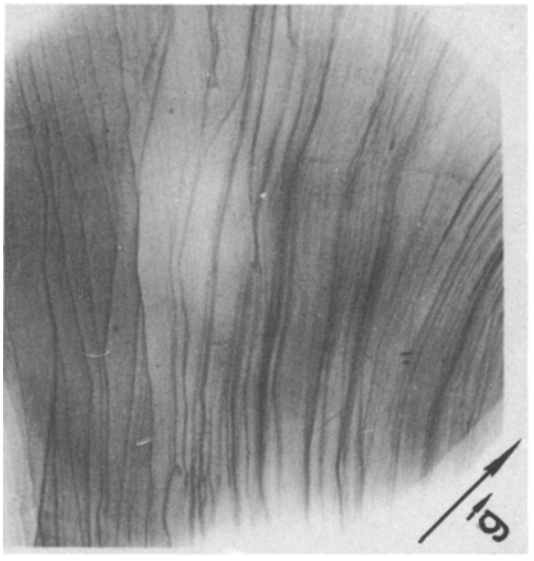

Figure 4 X-ray traverse topograph of synthetic fluorophlogopite. Mo radiation (060) reflection. The seed crystal being already cut away would otherwise occur at the lower side of the figure. (This is also valid for Figs 5 and 6). The contrast images are those of typical sub-grain boundaries. The orientation of the sub-boundary is normal to the growth front.

the topograph and this is probably due to the fact that the layer is too thin to have a noticable diffraction contrast.

A sub-boundary is a kind of sub-microscopic "plane" imperfection. The width of this imperfection is of the order of several atomic diameters. If it extended into a comparatively thick crystal, the fringes of the projection on the topograph would be wide whereas if it is involved only in a thin crystal, the fringes would be quite fine.

4.3. Dislocations

It can be seen from the crystal structure of fluorophlogopite that the dislocations in mica usually lie on the main glide plane (001). As shown in Fig. 5, the fringe image of the dislocation of synthetic mica is rather fine. However, the images of the sub-boundaries in a thin crystal are also quite fine, and it is difficult to distinguish them from the image of dislocations. If different diffraction vectors were used to form topographs a regular extinction appeared in the diffraction contrast image of dislocations according to the extinction condition of the dislocation fringe but no extinction occurred in the case of a sub-boundary.

Figure 5 X-ray traverse topograph of the surface layer of synthetic fluorophlogopite crystal using Mo radiation and (060) reflection. There are many sub-grain boundaries and dislocations along the growth direction.

4.4. Orientation of sub-grain boundaries and dislocations

Judging from the orientation of sub-grain boundaries and dislocations in Figs 4 and 5, it is evident that these defects in synthetic mica originate from the seed, possibly extended from the original defects in the seed crystal. During growth of the mica crystal, there is a tendency to maintain the stacking orders in each region due to the effect of long-range order force. Accordingly, if there are sub-boundaries in the seed crystal, the stacking orders and the sub-boundaries in each region would be maintained in further growth. It is clear that if a seed crystal is cut from an as-grown mica block and placed with its growth direction perpendicular to that of the original seed crystal, only very few crystal boundaries and dislocations are found at the boundary plane of growth and this greatly decreases the defects of extending growth. This method has been successfully employed by us to obtain crystals with fewer crystal boundaries.

The various layers of a crystal sometime exhibit different sub-boundary orientation. As a result of the projection of different layers to obtain a topograph, the images of sub-boundaries are frequently intersected.

Due to the change of growth conditions propagation defects in fluorophlogopite also exist. The macroscopic defects, such as random inter-crystal growth, bubbles, inclusions and microcracks can easily lead to the propagation of defects. The fluctuation of temperature during the growth of fluorologopite usually facilitates the segregation of

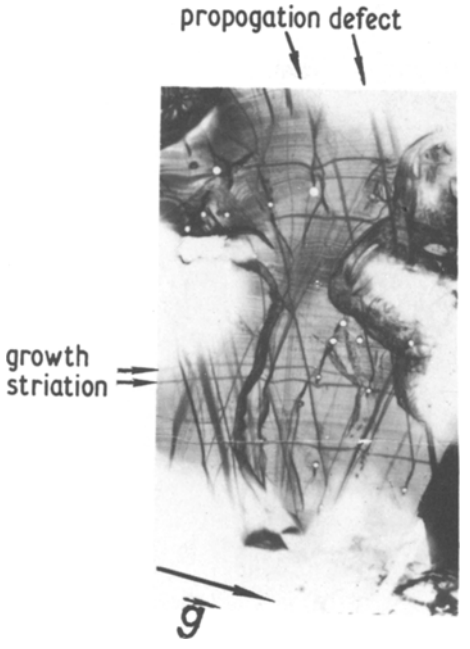

Figure 6 X-ray traverse topograph of synthetic fluorophlogopite. There are some contrast images of bubbles, growth striations and propagation defects using Mo radiation and (060) reflection.

impurities. Therefore, growth striations which are the markings of instantaneous growth fronts could be found in the topograph (Fig. 6). This is most probably caused by the lattice distortion which was formed by a concentration of impurity atoms.

In order to ascertain the distribution of defects in synthetic mica bulk, several pieces of bulk were sectioned and analysed. Each bulk was cut to a size of 70 to 100 mm × 100 mm × 10 mm. Then they were sectioned into 10 plates each 1 mm thick and the traverse topographic experiment carried out. The result revealed that the density of grain boundaries decreased quickly from the surface to the interior of the bulk. A typical topograph of a surface plate is shown in Fig. 5. Some of the central plates have almost no defects at all.

4.5. Comparison of defects in synthetic and natural mica

The X-ray diffraction topographs of natural mica show very inhomogeneous distortions. The crystal surface is uneven and there is an extremely high density of dislocations but very few sub-grain boundaries (Fig. 7). Generally speaking, under natural growth conditions, crystals can be formed in a nearly equilibrium state with little one-dimensional disorder and with sharp X-ray Laue

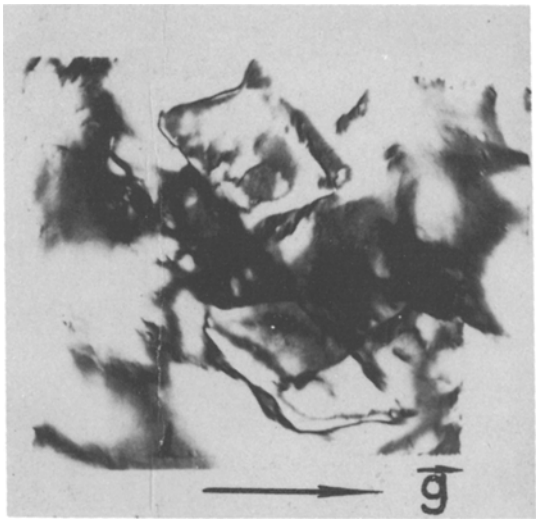

Figure 7 X-ray traverse topograph of natural mica (phlogopite) showing inhomogeneous deformations and numerous dislocations with a random distribution using Mo radiation and (060) reflection.

spots. However, the crystals are subjected to the influence of the surrounding rocks and a very inhomogeneous stress state may occur. Moreover, slip may occur at high temperatures and dislocations and other defects are thus produced.

On the other hand, the synthetic fluorophlogopite crystal has a flat surface, without much inhomogeneous distortion, but sub-grain boundary defects become predominant. Ordinarily sub-boundaries and dislocations do not have any detectable deleterious effects on diffraction intensity and resolution. Therefore synthetic mica crystals have been successfully used as the analysing crystal in X-ray spectroscopy. In general, sub-grain boundaries and inhomogeneous deformation induced by growth in fluorophlogopite crystals have no serious influence on their voltage puncture property.

As mentioned above, fluorophlogopite sheets, unlike natural mica, do not have inhomogeneous deformation. However, the degree of inhomogeneous deformation in synthetic mica produced in the course of condenser fabrication, is becoming a serious problem, especially through the processes of core setting, punching and forming. Such deformation introduced by the manufacturing processes of a condenser may be considered as one of the factors which induce voltage puncture.

5. Conclusion

The main defects in fluorophlogopite crystal are

one-dimensional disorder, sub-boundaries and dislocation. These defects have no drastic influence on the properties of voltage puncture and X-ray diffraction intensity. The locally concentrated and intersected sub-grain boundaries may affect the mechanical properties, such as separation ability and brittleness. By controlling the orientation of the seed crystal, large-size fluorophlogopite crystals with almost no defects in the centre part have been synthesized. In view of its chemical stability, excellent electrical insulating property, high resistance to irradiation and high temperature, good separation ability, flat surface and strong X-ray diffraction intensity, the large-sized fluorophlogopite crystal will find many important applications in various fields of the electronics industry including instrument-making.

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