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Ion-beam damage in hollandite

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The phenomenon of ion-beam damage in hollandite, first reported by Headley [1], has been investigated in the hollandite phase in Synroc, and a related electron-beam damage phenomenon has been investigated in a synthetic barium aluminium hollandite. An explanation of the beam damage phenomena is proposed in terms of twinning in the monoclinic form of hollandite.

1. Introduction

Compounds possessing structures similar to that of hollandite, $BaMn_8O_{16}$, have recently been the subject of intensive study [1], because one such compound (of ideal formula $BaAl_2Ti_6O_{16}$) occurs as one of the main phases in "Synroc", a synthetic rock developed for the purpose of nuclear waste storage [2].

The hollandite structure consists of a framework of octahedra of stoichiometry MO_2 linked so as to form square tunnels [3] which can accommodate a wide variety of large cations in varying ratios. According to a detailed structure analysis of synthetic hollandites, $Ba_xTi_{8-x}Mg_xO_{16}$ ($0.6 < x < 1.14$), the structure is tetragonal with space group $I4/m$ [4]. However, monoclinic variations with β very close to 90°, space group $I2/m$ have also been recognized [5].

In a recent high-resolution investigation of two hollandites – a Ba,Cs,K-titanate (as a simulated waste-containing form) and a synthetic $BaAl_2Ti_6O_{16}$ containing 4.7 wt% Cs_2O – Headley [1] reported that specimens prepared by Ar^+ ion-beam thinning showed a complex, modulated structure, which was not present in crushed specimens. These observations are highly relevant to the proposal to retain cations such as Cs^+ in the hollandite phase of Synroc.

In this paper we present some ultrahigh-resolution electron microscope observations of hollandites – both synthetic and incorporated in Synroc – on the basis of which we propose an explanation for the Ar^+ ion-induced modulations as first reported by Headley.

2. Experimental techniques

Synroc, prepared by ball milling and hot pressing of the constituent oxides TiO_2, Al_2O_3, ZrO_2, $BaCO_3$ and $CaCO_3$ [6] was made available by the Australian Atomic Energy Commission Research Establishment. Without added waste this material is known as "Synroc B" and consists mainly of a three-phase assemblage of hollandite, perovskite and zirconolite. Using a scanning transmission electron microscope fitted with an energy dispersive X-ray detector it was shown that the hollandite in this assemblage is variable in composition and has revealed the presence of calcium and zirconium.

Synthetic $BaAl_2Ti_6O_{16}$ prepared by the same method was also provided by the same source.

After sawing and mechanical polishing, specimens of Synroc B were thinned to electron transparency by Ar^+ ion bombardment. The synthetic hollandite specimen was prepared by crushing in an agate mortar and pestle, and deposited on a perforated carbon film. The specimens were examined at 200 kV in a JEOL 200CX electron microscope equipped with a high brightness LaB_6 cathode, a high resolution objective lens (C_s = 1.2 mm) and a ± 10° double tilt goniometer. Crystals were identified by electron diffraction and oriented with [0 0 1] of the pseudo-tetragonal cell parallel to the incident electron beam.

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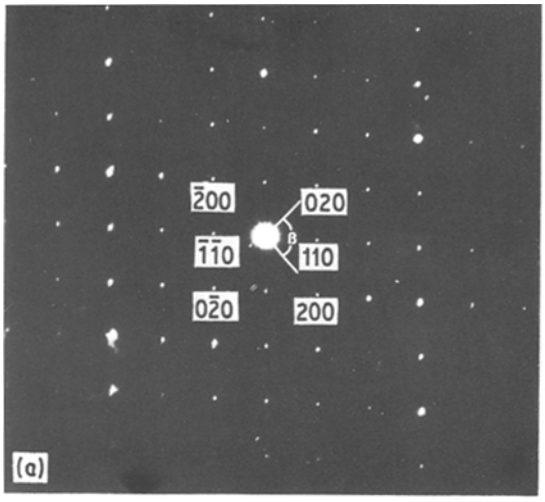

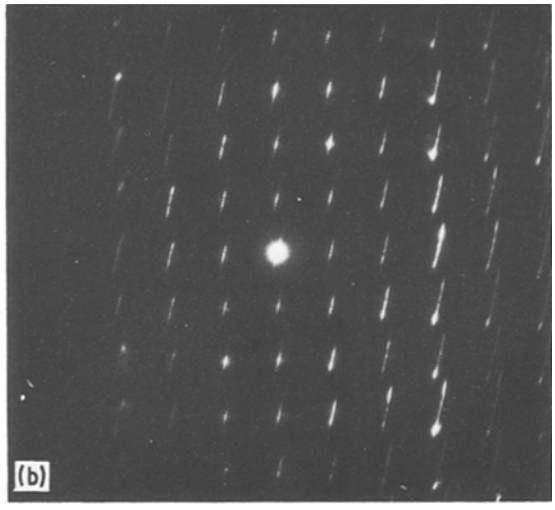

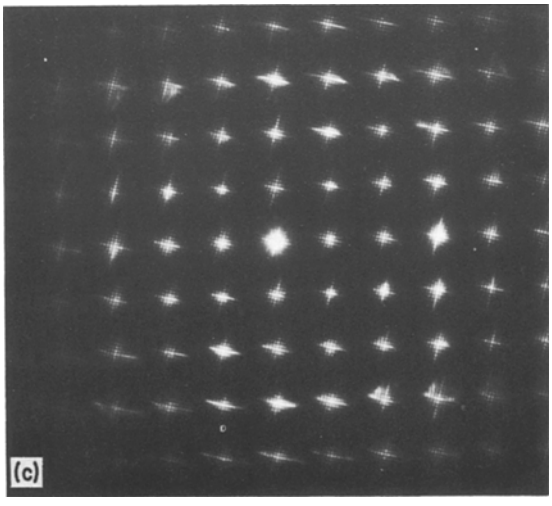

Figure 1 (a) An hollandite electron diffraction pattern viewed along the pseudo-tetragonal [0 0 1] direction. The measured value of β is 94°. (b) A diffraction pattern from a different region of the hollandite crystal mentioned in (a) which manifests a one-dimensional modulation. $\beta =$ 96° (i.e. β varies slightly from region to region in the same crystal). The satellite spots arising from the one-dimensional modulation are inclined at about 12° to the sublattice spots. (c) The two-dimensional modulation is reflected in the diffraction pattern as a roughly square grid of satellite spots surrounding, and inclined at about 12° to each sub-lattice spot.

3. Results

3.1. Ion-thinned sample

In the ion-thinned material we observed three separate but closely related phenomena: (i) monoclinic unmodulated hollandite, (ii) one-dimensional modulations, and (iii) two-dimensional modulations. The latter two phenomena were previously reported by Headley [1, 7].

3.1.1. Monoclinic hollandite

Fig. 1a shows a hollandite electron diffraction pattern viewed along the pseudo-tetragonal [0 0 1] direction in which the two main axes are clearly non-orthogonal. Here the measured angle is 94°. A high-resolution image reveals the tunnel structure of hollandite similar to that shown by Headley [1] and by Bursill and Wilson [8].

We note here that other deviations from $\beta = 90°$ have been recorded in hollandites. Monoclinic hollandites were found in the early X-ray studies already mentioned [5], and in a recent critical X-ray investigation by Post *et al.* [9] in which a diversity of synthetic and natural hollandites were shown to have $a \simeq c$ and β within 1° of 90°. In an electron microscope study, Turner and Buseck [10] reported variations of β within individual crystals, but gave few details. The images of $BaMgTi_7O_{16}$ published by Bursill and Wilson [8] show an angle of 95°, although this was not mentioned by the authors.

The distortion of the ideal hollandite structure to form a range of monoclinic variants gives rise immediately to the possibility of twinning; we will consider this further below.

3.1.2. One-dimensional modulation

Fig. 1b is an electron diffraction pattern from a one-dimensional modulated region of the same crystal as in Fig. 1a; the orientations are identical. Rows of closely spaced satellite spots surround the main spots, and are inclined to them.

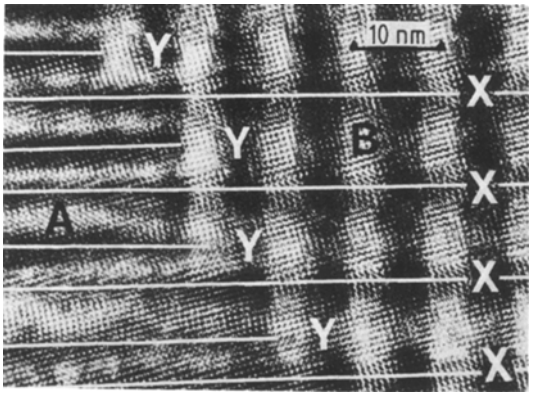

Figure 2 An image of both the one-dimensional and the two-dimensional modulation. Two interleaving sets of bands, labelled X and Y, are apparent in the image. The set X continue uninterruptedly into the two-dimensional region, but the set Y stop abruptly at the interface between the one-dimensional and the two-dimensional regions.

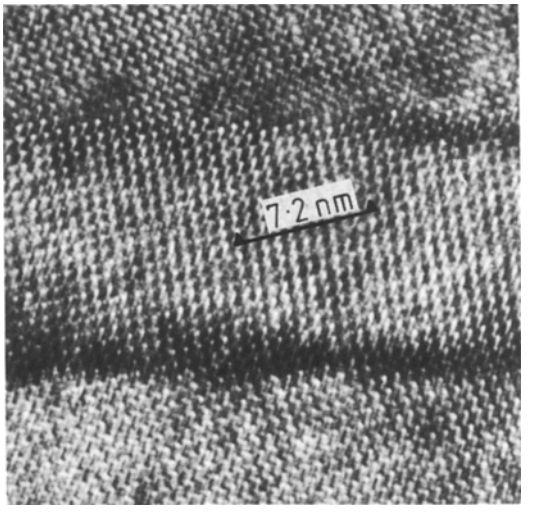

Figure 3 An enlarged area of the twin boundary confirms that the basic hollandite framework remains intact. The inclination of the twin boundaries to the twinning plane of 12° corresponds to the inclination of the rows of satellite spots to the main reciprocal lattice rows in the diffraction pattern (cf. Fig. 1b).

Region A of Fig. 2 shows clearly this modulation in the structure, in which two interleaving sets of bands (labelled X and Y) are apparent. Close to the thin edge of the crystal it is evident that the complex structure is due to multiple twinning, the width of the twin lamellae (~ 10 nm) being reflected in the satellite spot spacing (Fig. 1b). The angle β measured from the high-resolution images of the one-dimensionally modulated region (Figs. 2 and 3) is 96°. β may vary from region to region in the same crystal (the unmodulated region had an angle β of 94°). The inclination of the twin boundaries to the twinning plane of 12° corresponds to the inclination of the rows of satellite spots to the main reciprocal lattice rows in the diffraction pattern. A highly enlarged area of a twin boundary (Fig. 3) confirms that the basic hollandite framework remains intact.

3.1.3. Two-dimensional modulation

The two-dimensional modulation is seen in electron diffraction as a roughly square grid of satellite spots surrounding each main spot, again inclined at about 12° to them, as shown in Fig. 1c. Fig. 2, region B shows the appearance of this two-dimensional modulation which also has a periodicity of about 10 nm, corresponding to about fourteen inter-tunnel spacings. The key to understanding this structure lies in the junction between one- and two-dimensional modulations; the transition between regions A and B in Fig. 2 is smooth: however, we note that only half of the modulation bands in region A, set X, continue into region B. We will return to this observation later.

3.2. Crushed $BaAl_2Ti_6O_{16}$

Examination of crystal flakes of crushed hollandite confirmed the absence of any obvious structural modulation [1]. However, under prolonged electron irradiation, small changes occurred on a local scale, in the angle β. This was manifested in the appearance of minor irregularities in the lattice images as shown in Fig. 4. This crystal was sub-

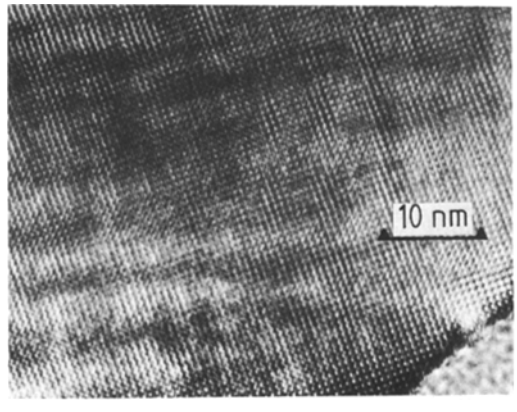

Figure 4 An image of a crystal flake from crushed $BaAl_2Ti_6O_{16}$ after prolonged electron irradiation. Minor irregularities in the images correspond to small changes on the local scale of the angle β.

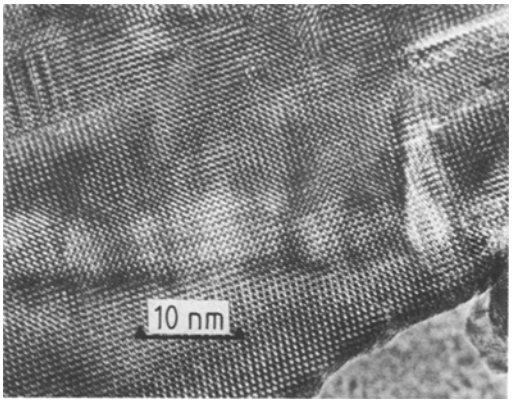

Figure 5 The same crystal flake as shown in Fig. 4 after it was subjected simultaneously to elevated temperature and high electron dose (by the removal of the condenser aperture). This treatment resulted in a large change of the angle β. Nevertheless, the structure seems to remain hollandite-like.

sequently subjected to a very intense electron beam (by removal of the condenser II aperture). The combination of elevated temperature and high electron dose brought about major alterations in the structure, although it did seem to remain hollandite-like (Fig. 5). These latter changes, particularly in the angle β, appeared to be related to the growth of crystalline globules on nearby carbon film.

4. Discussion

A considerable variation in the angle β occurs in hollandite. Its value depends in part upon the ratio of the radii of octahedral cations to the tunnel cations [9]. The effect of a change in β is to alter the size of the tunnels. It is likely that the Ar^+ ion bombardment displaces ions in the tunnels, and may in addition deposit argon ions in them. The process of ion displacement damage commonly causes randomization of complex structures so that they become simpler [11].

To understand the two types of modulation it is necessary to consider the ion-beam thinning process further; as each side of the bulk specimen is bombarded it becomes monoclinic (or the angle β departs further from 90° if the structure was already monoclinic) and twinning is generated in the damaged layers to relieve the misfit between the monoclinic surface structure and the tetragonal (or nearly so) bulk crystal. Ultimately the thickness of the specimen is reduced to that of a single grain, about 500 nm and the two twinned and ion-damaged regions from either side approach one another. The composition planes in the two twinned layers appear to lie in one of two approximately perpendicular directions; apart from the more-or-less uniform spacing of about 10 nm to optimize the relief of long-range stresses, the position of these composition planes is somewhat arbitrary. Thus, in the two ion-beam damaged surfaces of the specimen they may be either nearly parallel or nearly perpendicular. In region A of Fig. 2 the composition planes in the top and bottom regions of the specimen are parallel, but not coincident. In projection, therefore, we have the appearance of two interleaved sets of twin bands, as shown schematically in Fig. 6a. In region B of Fig. 2 the composition planes of *one* surface of the specimen adopt the alternative orientation with respect to region A, whereas those in the other surface are continuous across both regions. It is seen that half the parallel bands of region A terminate abruptly at its border with B (set Y) whilst the other half continue smoothly into region B (set X).

On the basis of the previous argument a greater *apparent* regularity may be expected in the two-dimensional modulations as compared with the one-dimensional bands – see Fig. 6b. This is observed in the micrographs, and is also reflected in the clarity of the satellite spots in the corresponding diffraction patterns.

The observations on the crushed sample reveal that hollandite may suffer ion displacement damage when irradiated by 200 kV electrons. This is of relevance to high-resolution imaging of hollandites since the structure may alter during prolonged observation.

In considering the significance of these results to the possible retention of radioactive waste elements in Synroc, it is worth noting that Ar^+

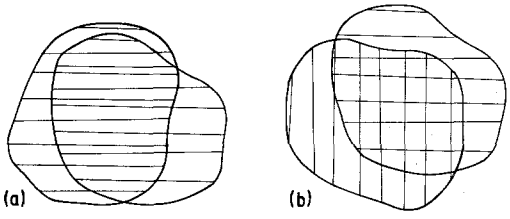

Figure 6 (a) A schematic diagram showing two interleaved sets of twin bands (cf. region A of Fig. 2). (b) The same as (a) except that one set of twin bands is rotated through 90°. The intersecting sets of twin bands have a greater *apparent* regularity as compared to the interleaved sets shown in (a).

ion-beam thinning is a particularly severe form of radiation damage; moreover, the hollandite component of Synroc would not be expected to contain any actinides (alpha emitters) and would therefore accumulate displacement damage due to incorporated waste more slowly than the other phases.

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