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TRANSFORMATION TWINNING IN SYNTHETIC NEIGHBORITE

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ABSTRACT

Synthetic neighborite, $NaMgF_3$, has been synthesised via a eutectic transformation in the NaF-MgF_2 system. Crystal plates extracted from the two-phase structure exhibit extensive micro-twinning. An analysis of the crystallography of twinning by electron microscopy and diffraction indicates their formation as a result of the asymmetric distortion accompanying the transformation from the tetragonal (pseudocubic) form at the growth temperature to an orthorhombic form on cooling.

INTRODUCTION

Neighborite, $NaMgF_3$, has been identified in the dolomitic oil shale of the Eocene River formation of South Ouray, Uintah County, Utah, by Chao *et al.*, (1961). These authors demonstrated, using Debye-Scherrer X-ray methods, that the naturally occurring mineral, as well as that prepared by reaction of NaF and MgF_2, is isostructural with 'perovskite,' $CaTiO_3$, and tentatively assigned it to space group *Pcmn*. This corresponds to the crystal structure at ambient temperatures, the dimensions of the orthorhombic unit cell being $a = 5.363$ Å, $b = 7.676$ Å, $c = 5.503$ Å. Chao *et al.* further demonstrated the similarity with $CaTiO_3$ (and other members of this perovskite group) by following structural changes to 950°C using a heating stage with their diffractometer. The orthorhombic a and c axes expanded at different rates with temperature increase, and became identical at 760°C. This structure, having a tetragonal unit cell, with $a = 3.942$ and $c = 3.933$, and therefore differing little from cubic symmetry, undergoes a final small anisotropic expansion up to $900° \pm 25°$C to adopt a cubic unit cell with $a = 3.955$. The relation between the low temperature orthorhombic unit cell and that for the cubic structure is illustrated in Figure 1. The relationship between the lattice vectors for the two structures is contained in the description:

$$\begin{pmatrix} a' \\ b' \\ c' \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{1}{2} & 0 \\ 0 & 0 & \frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$

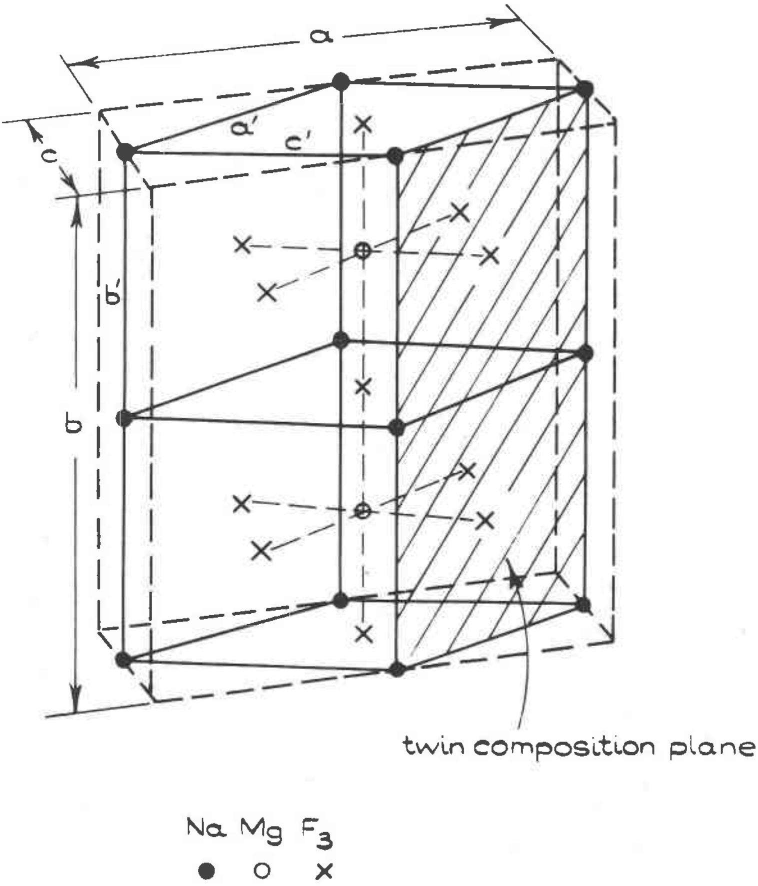

FIG. 1. Crystallographic relation between the cubic perovskite structure (two unit cells shown with ion positions indicated) and the unit cell for the orthorhombic modification with axes *a*, *b*, *c*.

Of particular interest in this paper is the transformation from the pseudocubic (tetragonal) form to the structure with orthorhombic symmetry. In the work described here neighborite is synthesised from NaF and MgF_2 via a eutectic solidification process in which the product is a two-phase mixture of NaF and $NaMgF_3$. The latter phase occurs microstructurally as plates of 1–2 μm in thickness which may be examined by electron microscopy and diffraction after extraction from the eutectic structure.

EXPERIMENTAL

Specimens were obtained by fragmentation of the interconnected plate structure of $NaMgF_3$ after chemical dissolution of the NaF second phase of the eutectic structure.

Identification of the phase as neighborite was accomplished by comparing Debye-Scherrer X-ray photographs with diffraction line positions computed from the orthorhombic unit cell parameters of Chao *et al.*, (1961) and their experimental table of allowed reflections. Large numbers of thin plate shaped fragments were attached to adhesive electron microscope grids, placed in a goniometer specimen holder and examined in a JEM 200 electron microscope operating at 200 kV. It is notable that ionic compounds such as $NaMgF_3$ undergo degradation by electron irradiation via an indirect displacement process. The degradation rate is markedly reduced at 200 kV relative to that at 100 kV.

ELECTRON DIFFRACTION

Two prominent selected area electron diffraction patterns from small fragments of $NaMgF_3$ are reproduced in Figure 2a. These patterns have

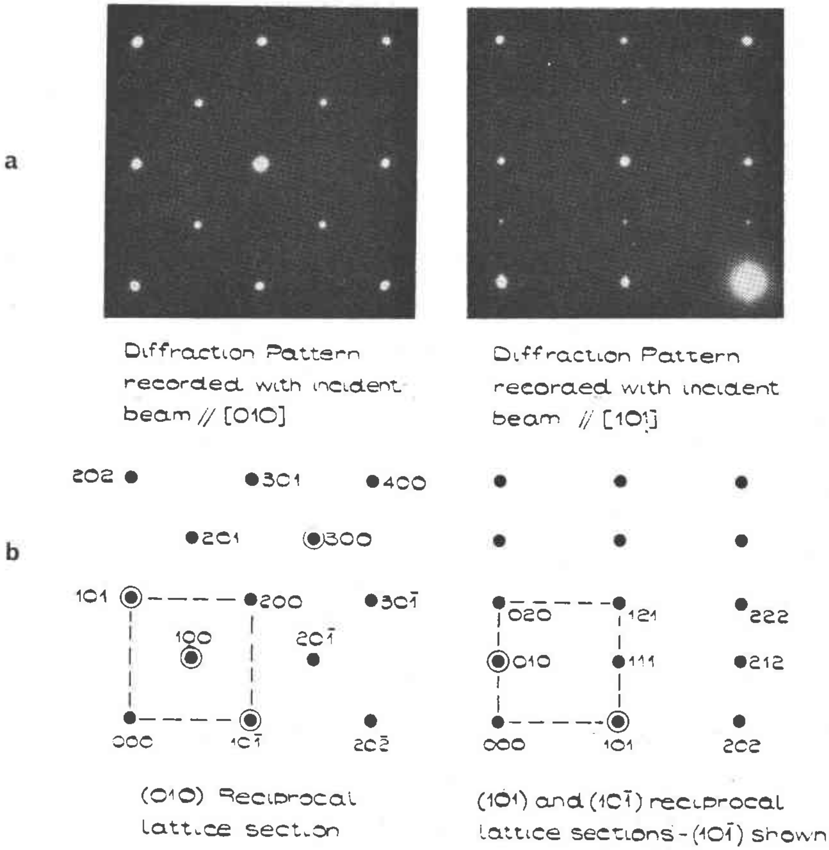

Fig. 2. (a) Prominent electron diffraction patterns from $NaMgF_3$ crystals with electron beam directions parallel to $[010]_O$ and $[10\bar{1}]_O$.

(b) Reciprocal lattice planes for $NaMgF_3$ identified with the diffraction patterns of (a). Encircled points are equivalent to diffraction spots which appear via a multiple diffraction effect.

been identified with the reciprocal lattice sections of Figure 2b, in which the encircled lattice points correspond to diffraction spots which do not appear in X-ray diffraction patterns but occur in Figure 2a by multiple diffraction of electrons (Hirsch *et al.*, 1965). The electron diffraction patterns are formed with electron beam directions parallel to $[010]_O$ and $[010]_O$ or $[10\bar{1}]_O$[1] which for the high temperature cubic structure correspond to $[010]_C$ and $[100]_C$ or $[001]_C$. The corresponding diffraction patterns for the cubic form would therefore be indistinguishable, consisting of the four-fold symmetric pattern of the more intense spots of Figure 2a. The extra allowed reflections arise from displacements of ions in the cubic perovskite structure. These extra reflections permit a distinction to be made between $[010]_O$ and $[101]_O$ diffraction patterns which is relevant to the analysis of micro-twinning in the following section.

TRANSFORMATION TWINNING

Images corresponding to the selected area diffraction patterns of Figure 2a were recorded before degradation of the structure in the electron beam prevented the observation of fine structure in the crystal fragments. Figures 3a and 3b, images of thin plate-shaped fragments, correspond to an electron diffraction pattern (Fig. 2a) with $[010]_O$ parallel to the electron beam which is perpendicular to the plate face. Fine parallel bands were observed in the large number of plate shaped crystals examined. Image contrast for these bands is extremely sensitive to specimen tilting through immeasurably small angles and produces systematic contrast reversal for adjacent bands. This behaviour is characteristic of adjacent bands constituting crystal parts in which very small differences exist in orientation or length for the reciprocal lattice vector of the imaging reflection. The trace of interface plane between the crystal parts lies in $[101]_O$ or $[101]_O$ directions. Images for plates at various angles of specimen tilt about these directions indicate that the interfaces are perpendicular to the plate faces (in Figures 3a and 3b) and therefore parallel to $(10\bar{1})_O$ and $(101)_O$. These planes correspond to $(001)_C$ and $(100)_C$ which are the preferred cleavage planes for the $NaMgF_3$ crystal fragments. Dark field electron microscopy using the various diffracted electron beams shows that adjacent bands contribute to all diffraction spots in the pattern of Figure 2, *i.e.*, they appear to be crystallographically equivalent but possess very small relative misorientations.

The observed fine structure is interpreted as alternate bands of twin related crystal with twin composition plane $(101)_O$ or $(10\bar{1})_O$. The ortho-

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[1] The subscripts O and C refer to orthorhombic and cubic indices respectively.

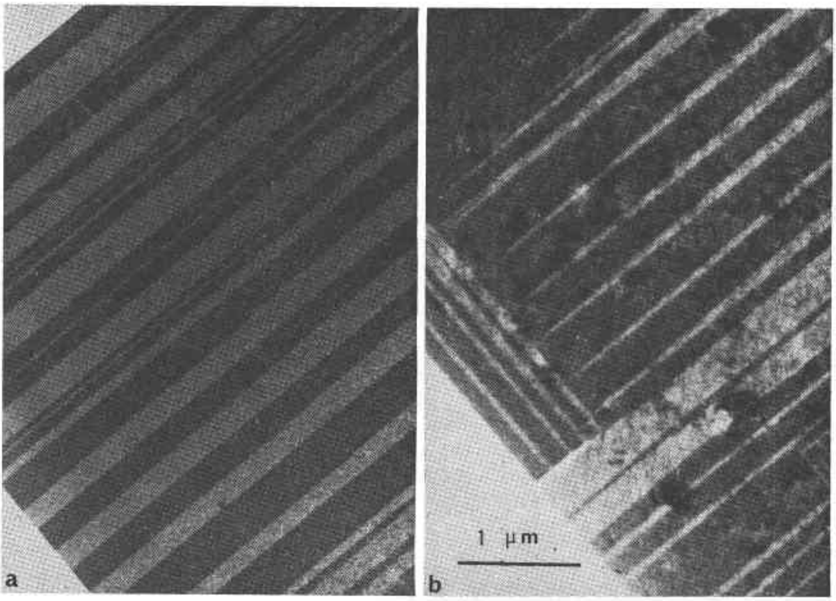

FIG. 3. (a) & (b) Images, corresponding to the diffraction pattern with electron beam parallel to $[010]_O$, showing micro-twinning with composition plane $(101)_O$. In (b) two, crystallographically equivalent, sets of twins are visible.

rhombic distortion due to inequality of *a* and *c* axes, (Fig. 1) is too small to be resolved in selected area diffraction patterns, (there is a 2.5 percent difference in these lattice vectors) but is detectable by sensitive variation in image contrast. The presence of twinning and choice of twinning plane may be rationalised as follows. The plate shaped $NaMgF_3$ phase is constrained, during transformation from the growth temperature (820°C) by the presence of a second phase and by interconnection with adjacent plates in differing orientation, in a manner similar to a single grain in a polycrystalline aggregate. A homogeneous distortion to orthorhombic symmetry of a plate-shaped crystal would result in a large strain energy associated with atom displacements near to the interface with the surrounding solid. This may be avoided if the direction of the asymmetric distortion is different in alternate small regions of crystal to produce a macroscopically undistorted interface. The geometrical features of this process are illustrated in Figure 4. A contraction of the *a* axis relative to the *c* axis (referring to the resulting orthorhombic unit cell) may be accomplished by a shear distortion parallel to $(100)_C$ or $(001)_C$. These planes then form coherent twin interfaces between orthorhombic crystals with different directions of unit cell vector.

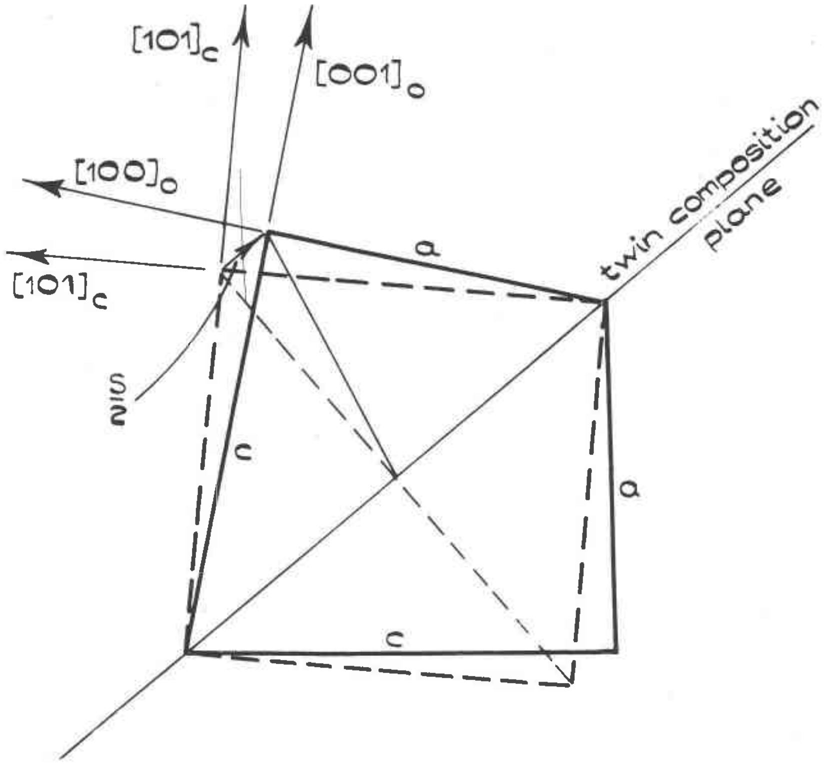

FIG. 4. Illustrating the relation between twin composition plane, orthorhombic unit cell axes *a* and *c* and directions in the parent (pseudo-cubic) structure. The vector S/2 indicates one half of the twinning shear displacement for the orthorhombic crystal (displacements exaggerated for clarity).

This description for the crystallographic transformation of (initially cubic) single crystals of $NaMgF_3$ resembles that of a diffusionless (martensitic) transformation. A phenomenological description in terms of martensitic transformation theory (Wechsler, Liebermann, and Read, 1953) involves a 'lattice' deformation, to provide the crystallographic change, coupled with a 'lattice invariant' deformation to satisfy the condition for a macroscopically undistorted interface between the transforming region and the matrix phase. For the neighborite transformation the lattice deformation involves an expansion of the lattice along the orthorhombic (product) *c* axis relative to the *a* axis. In this particular case the transformation is not completed via a homogeneous distortion but requires ion 'shuffles' (motion over distances small compared with inter-ion spacings) to accomplish the complex distribution characteristic of the suggested space group. The lattice invariant deformation is that of twinning, leaving the crystal symmetry unchanged, with a twin distribution sufficient to produce the macroscopically undistorted interface for the crystal plate. The twinned crystal should therefore occupy about 50 percent of the volume, be of small and constant width, and homogeneously distributed in the crystal plate. In a formal description of the twinning mode occurring in a transformed crystal the following crystallographic elements may be identified:

$$K_1 \text{ plane} = (101)_O, \qquad K_2 \text{ plane} = (\bar{1}01)_O,$$
$$\eta_1, \text{ direction} = [\bar{1}01]_O, \qquad \eta_2 \text{ direction} = [\bar{1}0\bar{1}]_O$$

An equivalent set corresponding to the second twin band orientation (Fig. 3b) is possible.

The above comparison with 'martensite' crystallography indicates successive operation of the two deformations, but the 'lattice' and 'lattice invariant' deformations may occur simultaneously. The lattice deformation then occurs in alternate regions in different but crystallographically equivalent directions in the parent (pseudo-cubic) phase which are initially perpendicular. The interface between alternate regions is a coherent twin plane and is derived from a mirror symmetry plane $(001)_C$ or $(100)_C$ in the parent structure (Fig. 1). However, since the lattice parameter variations occur in a continuous manner with progress of cooling from the growth temperature it is probable that the crystal initially distorts homogeneously. Twinning is nucleated at a critical 'undercooling' below 760°C, which will be a function of crystal size and environment (constraint). With a decrease in temperature the width of twin related bands decreases, associated with an increase in the twinning (transformation) shear. Examples of the enhanced 'constraint' effect in producing large twin densities are provided near the interface with differently oriented crystals (Fig. 3b). Evidence for the progressive nature of twin formation and mechanism for microstructural development is provided by the frequent observation of twins with lenticular cross sections which terminate within the crystal plate and are often associated with visible obstacles to their propagation. These tapered cross sections are typical of deformation twins and arise from the attempt to retain the twin interface parallel to a coherent twin boundary and reduce the 'accommodation' shear strain at the twin periphery.

The above analysis neglects the effect of a small degree of tetragonality of the crystal before transformation which is progressively increased during cooling from the growth temperature. A similar analysis for this distortion shows that potential strain accommodation twinning should occur on $\{110\}_C$ planes which are inclined at 45° to the composition planes for 'orthorhombic twinning.' Such twins do not occur indicating, in agreement with the lattice parameter changes monitored by Chao *et al.*, (1961), that this distortion is comparatively small.

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