

We suggest that the Glazer notation is particularly suited to the derivation and description of twin boundaries because it provides a concise and unambiguous means of enumerating the various structural models for each composition plane. A single, simple example will serve to illustrate the potential of this system.

Lamellar (twin) boundaries

The simplest boundary which was encountered is shown in Fig. 7(a). The perovskite domains are related to each other by a rotation of 180° about the normal to $(101) = (001)_{pc}$. Only one structure may be postulated in which the Ca, Ti and O positions of the individuals coincide exactly at the interface. This is illustrated by the (single layer) polyhedral drawing in Fig. 7(b) (labelled model 1).

Several other models, which also involve this twin law, are possible. However, in these instances Ca and O displacements are required. One such example (model 2 in Fig. 7b) is given.

Alternatively, these models may be conveniently and completely represented - both octahedral layers are indicated - by listing the octahedral tilt patterns (Fig. 7c); the pseudocubic axes are $a' = [0\bar{1}0]$, $a' = [10\bar{1}]$ and $a' = [\bar{1}0\bar{1}]$. These tilt sequences can be obtained by inspection from drawings of the octahedral motifs.

Discussion

It is interesting that of the several pseudocubic axes present in perovskite only those which involve rotation about $\langle 100 \rangle_{pc}$ are utilized for twinning. However, interface surfaces were observed on planes of the forms $\{101\} = \{001\}_{pc}/\{100\}_{pc}$, $\{010\} = \{010\}_{pc}$ and $\{121\} = \{110\}_{pc}/\{011\}_{pc}$. Not surprisingly, many of the observed twin boundaries were very complicated as a result of extremely fine-scale intergrowth on the several pseudosymmetric interfaces. The variation in octahedral tilt pattern across the composition planes

may simply be considered as a coherent interface between domains of the well known perovskite polytype, or as extremely thin regions of other hettotypes. The latter description is particularly compelling in those instances where lamellar defects are introduced (Fig. 7a).

It is proposed that perovskite in SYNROC will incorporate trivalent rare-earth elements and tetravalent actinide elements (Ringwood *et al.*, 1981). A wide-ranging study of perovskite containing 2-6 at.% of these elements failed to reveal any change in twin behaviour or the presence of cation ordering to yield superstructures.

The authors wish to thank K. D. Reeve, E. J. Ramm, D. M. Levins and J. L. Woolfry (AAEC) for the provision of SYNROC specimens. We are grateful to Dr S. E. Kesson and W. Hibberson (ANU) for preparing very many rare-earth- and actinide-doped perovskite samples. Natural perovskite minerals were very kindly supplied by Dr W. Birch (National Museum of Victoria) and Mr P. Tandy (British Museum of Natural History). TJW gratefully acknowledges the financial support of a Postdoctoral Fellowship from the Australian Institute of Nuclear Science and Engineering. RLS would like to thank Professor Sir Peter Hirsch FRS for the provision of laboratory facilities at Oxford.

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Acta Cryst. (1985). **B41**, 98-101

Constitution and Structure of Synthetic Hollandites, an Electron and X-ray Diffraction Study

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(Received 1 December 1983; accepted 15 October 1984)

Abstract

Synthetic hollandite compounds of composition $A_x M_{4-2x}^{IV} N_{2x}^{III} O_8$ ($A = \text{Sr, Ba}$; $M = \text{Ti, Sn}$; $N = \text{Al, Cr, Ga, In}$) studied by electron and X-ray diffraction have been found to be stable only within certain ranges of

x , depending on the M and N ions. The lower value of x is never less than 0.54, the upper x level is about 0.73. Higher x seems to be correlated with larger radii of M and N . The A ions are accommodated along tunnels, giving rise to an incommensurate superstructure. A simple vacancy modulation wave is proposed

to explain the diffraction patterns. Correlation among tunnel sequences varies widely, also depending on the nature of the M and N ions.

Introduction

Hollandites may be characterized as oxides of composition $A_xM_{4-x}N_yO_8$ (Byström & Byström, 1950). The M and N ions are octahedrally coordinated. In this paper we use the shorthand notation $A,M/N$ hollandites. Detailed single-crystal X-ray structure determinations of mineral and some synthetic hollandites (Post, Von Dreele & Buseck, 1982; Sinclair, MacLaughlin & Ringwood, 1980; Cheary, Hunt & Calaizis, 1981), and also electron-microscopy studies (Bursill & Grzanic, 1980; Cadee & Prodan, 1979), have recently appeared.

Assuming Ba,Ti/Ga hollandite to be stable in the range $0.4 < x < 0.66$, Bursill & Grzanic propose an elaborate structural model, based on the intergrowth of several superstructures. At x close to 0.5 two $5c$ sequences (Ba-O-Ba-O-O and O-Ba-O-Ba-Ba) and one $2c$ sequence (Ba-O) are combined to result in an averaged superperiod with $m = 2.405$, where m is the ratio between the repeat period of the modulation, p , and the basic lattice period in the same direction, *i.e.* c in our case. From a physicochemical point of view it is hard to imagine that sequences containing both adjacent vacancies and adjacent Ba sites would be stable.

Trying to reproduce their results we observed that in mixtures that should result in $x < 0.56$, rutile (TiO₂) was always present.

Experimental

We tried to prepare hollandites, $A_xM_{4-x}N_{2x}O_8$ ($A = \text{Sr, Ba}$; $N = \text{Ti, Sn}$; $M = \text{Al, Cr, Ga, In}$ and $x = 0.5$ or 0.8), by heating N_2O_3 and MO_2 with the corresponding amount of ACO_3 at 1573 K for several days. The products were ground and examined by X-ray powder diffraction (using a Philips PW 1050 diffractometer) and electron microscopy. Only the hollandites listed in Table 1 were found. Electron diffraction patterns, mostly of the $\langle 110 \rangle$ zone, were recorded using a Siemens Elmiskop 102 electron microscope, fitted with a double tilt and a lift cartridge, operating at 100 kV. High-resolution images were obtained with a Jeol 200CX electron microscope, equipped with a 10° double tilt and operating at 200 kV.

Results

It was found that for all compounds (see Table 1) stable hollandites exist only for $x > 0.5$ (more than 50% of the potential A sites filled); X-ray powder diffraction shows that for x values below the lower

Table 1. *Composition limits of the hollandites A, M/N (A = Sr, Ba; M = Ti, Sn; and N = Al, Cr, Ga, In) which could be prepared and the radii of M and N according to Shannon & Prewitt (1969)*

	x_{\min}	x_{\max}	$r(M)$	$r(N)$
Ba, Ti/Al*	0.58 (1)	0.64 (1)	0.605 Å	0.53 Å
Ba, Ti/Cr	0.56 (1)	0.67 (1)	0.605	0.615
Ba, Ti/Ga	0.58 (1)	0.66 (1)	0.605	0.62
Ba, Sn/Cr	0.67 (1)	0.69 (1)	0.69	0.615
Ba, Sn/Ga	0.66 (1)	0.71 (1)	0.69	0.62
Ba, Sn/In	0.67 (1)	0.73 (1)	0.69	0.79
Sr, Ti/Cr	0.62 (1)	0.65 (1)	0.605	0.615

* Cheary, Hunt & Calaizis (1981) report that Ba, Ti/Al hollandite in Synroc *B* has the composition $x = 0.57$.

limit the intended composition is not obtained, but MO_2 is still present in the sample.

The electron diffraction pictures show satellites in the c^* direction around the basic diffraction spots. Their spacing is consistent with a truly incommensurate modulation of the structure, caused by the Ba-vacancy sequence along the tunnels and perhaps a correlated $M-N$ ordering.

The modulation vector $\mathbf{p} = m\mathbf{c}$ can be correlated with x if we assume that along the tunnels, sequences of xp filled and $(1-x)p$ vacancies occur, and that the vacancies are isolated (no pairs) (Fig. 1). A pattern of sharp incommensurate superlattice spots, similar to those observed, is obtained in calculation if the modulation waves along $0, 0, z$ and $\frac{1}{2}, \frac{1}{2}, z$ are in phase (see Fig. 2, where calculated patterns for several different phases between $0, 0, z$ and $\frac{1}{2}, \frac{1}{2}, z$ are given). Clearly only structures with corrugated sheets of vacancies yield patterns corresponding to those observed (Fig. 3).

Fig. 4 shows that the superperiod in the c direction is always well defined. The spots, however, are smeared in planes in reciprocal space perpendicular to c^* . The extent of smearing depends on the type of compound. In one instance (Ba,Sn/Cr) sheets of diffuse intensity occur in these planes. In the case of Ba,Ti/Ga hollandite the superspots are sharp. It may be inferred that the correlation distance among the tunnels varies for different hollandites.

The model yields a relationship between the superperiod m and the Ba fraction x . Since $(1-x)p = (1-x)mc = c$, we have $x = 1 - (1/m)$. This gives a

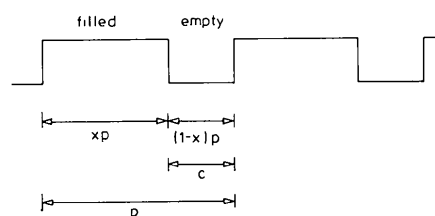


Fig. 1. Occupation wave (period p) describing the large-ion sequence in hollandites. The period of the host lattice is c , x is the proportion of occupied to available sites.

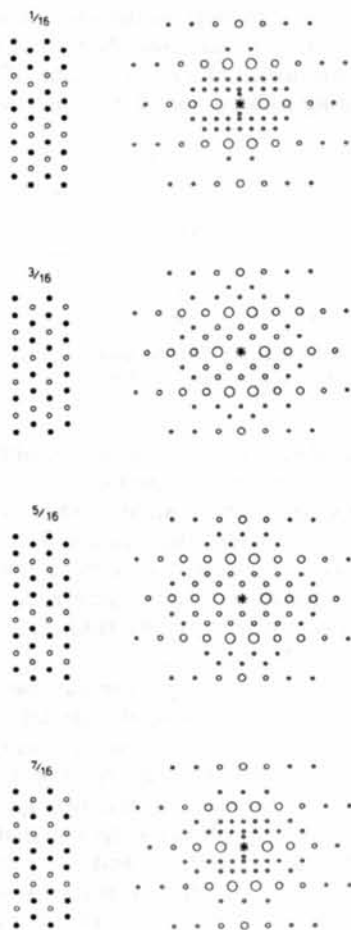
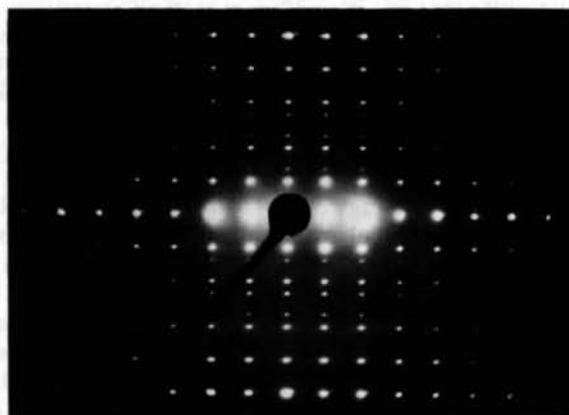


Fig. 2. Various ways of filling neighboring tunnels for $x = \frac{5}{8}$. In these models the tunnels are strictly correlated. The body-centered sites are related by a shift $\frac{1}{16}, \frac{3}{16},$ etc. times the overall period. The diagrams on the left represent projections along [110]. Full circles occupied, open circles vacant sites. On the right are the calculated [100] diffraction patterns.

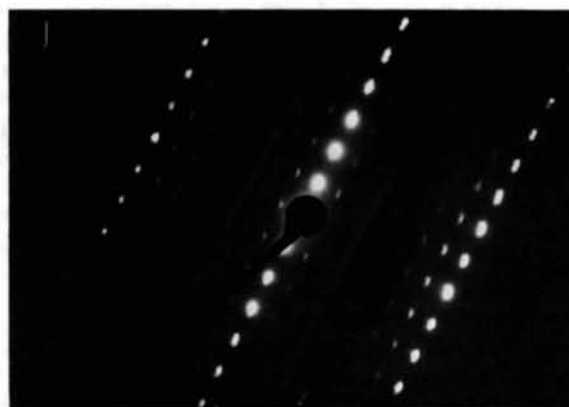


Fig. 3. Typical observed [100] electron diffraction pattern of a hollandite.

second argument in favor of our conclusion about the lower x limit. Attempts to produce hollandites with $x < x_{\min}$ always resulted in products for which the electron diffraction patterns showed an m value corresponding to x_{\min} . Table 1 shows the lower and



(a)



(b)



(c)

Fig. 4. [110] electron diffraction patterns of (a) Ba,Ti/Ga, (b) Ba, Sn/In and (c) Ba, Sn/Cr showing several degrees of smearing due to loss of correlation among the tunnels.

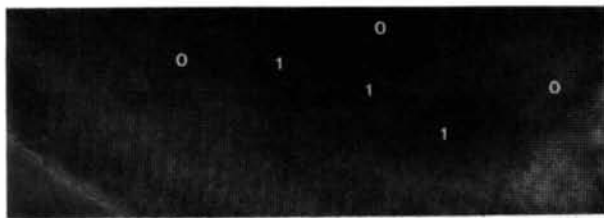


Fig. 5. A high-resolution image of $\text{Ba}_{0.6}\text{Ti}_{2.8}\text{Al}_{1.2}\text{O}_8$ (beam direction [110]) showing regions of high (0) and low (1) correlation between the tunnels. The tunnels run in the vertical direction. Note the blurring in regions 1.

upper levels of x , derived from electron diffraction pictures.

Discussion

We have found that stable hollandites exist only for $x > 0.54$. This was inferred from the fact that attempts to produce compositions with lower x resulted in the presence of $M^{\text{IV}}\text{O}_2$ and that we never observed superperiods consistent with lower values by continuously varying x between 0.46 and 0.54.* Direct images might be used to discriminate, but a number of

* Note: $x = 0.5 + y$ and $x = 0.5 - y$ will tend to produce electron diffraction patterns with reflections at the same positions, though differing in intensities.

Acta Cryst. (1985). **B41**, 101-108

Tilt and Tetrahedra Distortions in the Zeolite A Framework

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(Received 13 April 1984; accepted 30 November 1984)

Abstract

A geometrical analysis of the zeolite A framework concerning the effects of the deviations from ideal geometry on the lattice parameter, the coordinates of the framework atoms and the $T\text{-O-T}$ angles has been undertaken with the restriction of only one T atom present. The total deviation of the real framework from a hypothetical one, consisting of ideal TO_4 tetrahedra parallel to the unit-cell edges, has been decomposed into three contributions: (i) a cooperative rotation (tilt) of the tetrahedra about axes parallel to $\langle 100 \rangle$; (ii) distortions of the O-T-O angles of the

channels will be superimposed and contrasts will be blurred, unless high correlation among filling sequences along the tunnels exists. Fig. 5 is a [110] high-resolution image of the well ordered (Ba,Ti/Ga) hollandite with $x = 0.6$ showing ordered and disordered regions.

According to Bursill & Grzinic (1980), Ba,Ti/Ga hollandite with $x = 0.4$ and 0.5 (0.8 and 1.0 in their formulation based on 16 O atoms) has $m = 2.375$ and $m = 2.405$ (our formulation, superperiod mc). In our model this corresponds to $x = 0.578$ and 0.584 , both values being close to 0.58 .

This research was partly financed by the Commission of the European Communities. The authors are indebted to the workers of the Laboratory for High Voltage Electron Microscopy, Antwerp, for facilities.

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TO_4 tetrahedra; (iii) bond-length distortions of the tetrahedra. The $\text{O}(1)$ atom has been used to differentiate (i) from (ii). The main results obtained are: (i) the lattice parameter passes through a maximum on varying the tilt angle; $\angle[T\text{-O}(1)\text{-}T]$ increases, $\angle[T\text{-O}(2)\text{-}T]$ (beyond a maximum) and $\angle[T\text{-O}(3)\text{-}T]$ decrease with increasing tilt angle; (ii) the angular tetrahedron distortion is explained as being composed of two contributions, one of which is determined by the framework composition, the other depending essentially on the interchangeable cations. The mapping of 30 zeolite A species reveals that most of these scatter about a relaxed state with almost maximal lattice parameter and minimal deviations of the $T\text{-O-T}$ angles from their mean value. Deviations from the relaxed state - by decreasing or increasing

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