

Lattice imaging of close-packed structures by high resolution electron microscopy: ABO_3 perovskite polytypes

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Abstract. Lattice imaging technique of high resolution electron microscopy has been employed to examine 4H, 6H and 9R ABO_3 perovskite polytypes. The lattice images can be correlated with the lattice periodicity and the stacking sequence of AO_3 layers and BO_6 octahedra. The study shows the utility and validity of the lattice imaging technique for the study of relatively close-packed systems.

Keywords. Lattice imaging, electron microscopy; polytypes; perovskites.

1. Introduction

Direct lattice imaging by high resolution electron microscopy can be employed to observe the structure of solid materials directly (Allpress and Sanders 1973). For crystals thin enough to approximate phase gratings, the image contrast corresponds to the projected charge density of the crystal structure under optimum defocusing condition with areas of high projected charge density being indicated by dark contrast. Thus, lattice images have been directly related to the local structure in the case of niobium oxides containing a relatively open network of metal-oxygen octahedra (Cowley and Iijima 1972, Hutchison and Anderson 1972). The success of the lattice imaging of niobium oxides depended on the fact that the projected charge density along (010) revealed channels between corner-linked octahedra. *n*-Beam image calculations (O'Keefe 1973) also confirmed the validity of correlating lattice images of niobium oxides with their local structures. Based on the studies of niobium oxides, Allpress and Sanders (1973) suggested that interpretation of lattice images of other systems might probably require the presence of voids in their projections.

In more closely packed systems where the projected charge density is less simple, experimental studies have been limited. Very recently, lattice images have been correlated with structure in the case of layered hexagonal ferrites (McConnell, Hutchison and Anderson, 1974) and ferroelectric bismuth compounds with perovskite layers (Hutchison, Anderson and Rao 1975). Encouraged by these

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studies, we considered it desirable to correlate the lattice images of a few perovskite polytypes of the general formula ABO_3 with their structures and stacking sequences. The existence of polytypes of perovskites is well-established (Goodenough and Longo 1970, Goodenough 1974) and the only electron microscope study of such systems has been on the Quaternary oxides $Ba_5W_3Li_2O_{15}$ (10 layer) and $Ba_4Ta_3LiO_{12}$ (8 layer) by Hutchison and Jacobson (1975). The present study was intended not only as a structural study of perovskite polytypes, but also to extend the realm of the lattice imaging technique by applying it to known close-packed structures.

2. Experimental

$BaCrO_3$ polytypes (4H and 6H) were prepared by high pressure synthesis starting from Ba_2CrO_4 and CrO_2 (Chamberland 1969). $BaRuO_3$ (9R) was prepared by heating BaO_2 and Ru metal at 1270 K in air (Donohue, Katz and Ward 1965). Another sample was prepared by heating the initial product of $BaRuO_3$ at 1600 K for 24 hrs and quenching it.

The samples were ground to fine powder under chloroform and mounted on carbon coated grids. A Siemens 102 electron microscope with a $\pm 45^\circ$ double tilt stage was used at an acceleration voltage of 100 kV ($\lambda = 0.0037$ nm). Thin fragments of about 10 nm thickness were oriented with the [100] axis parallel to the electron beam. A 50μ objective aperture was used to combine the primary beam with all the subcell and superlattice reflexions out to 3 nm^{-1} and micrographs recorded in a through-focus series embracing the optimum condition. Primary magnifications were 300×10^3 to 500×10^3 .

3. Perovskite polytypes

The ABO_3 hexagonal-perovskite polytypes (Goodenough and Longo 1970) are characterized by a variable stacking of close-packed, ordered AO_3 layers, the B cations occupying all the interlayer oxygen octahedra. The stacking of a AO_3 layer may be cubic or hexagonal with respect to its two neighbouring layers, depending on whether it is in the middle of an *abc* or of an *aba* sequence. If the stacking is entirely cubic, the B-filled octahedra share only corners in three dimensions to form the cubic perovskite structure (3C). If all the stacking is hexagonal, the B-filled octahedra form isolated *c*-axis chains of face-shared octahedra (figure 1) as in the case of $CsNiCl_3(2H)$. The 3C-structure can only accommodate A-cations within a size range determined by the tolerance factor, $t = (r_A + r_o)/\sqrt{2}(r_B + r_o)$.

For the ideal cubic structure, $t = 1$ and the structure is stable at atmospheric pressure within the range $0.75 < t < t_c$, where t_c is determined by the effective charge on the B cations. For $t > t_c$, hexagonal stacking of AO_3 layers is stabilized. Formation of hexagonal stacking occurs at the expense of Madelung energy and the loss of Madelung energy can be reduced by limiting the length of any face-shared chain to two or three units. Figure 1 illustrates the three most probable stacking sequences for achieving this limitation.

The 6H hexagonal structure would contain two-to-one cubic to hexagonal stacking in sequence *cchch*, while the 4H hexagonal structure would contain a one-to-one sequence *chch*. The 9R rhombohedral structure would contain the sequence

chhchh. The energy required to alternate the stacking sequence is $3/2$ as large for the 4H structure as for the 6H of 9R structure and the 4H phase is, therefore, stable over a limited range. In all these polytypes, the dimensions of the unit cell remain the same in two dimensions while the third dimension varies in length as expected.

We have studied all the three perovskite polytypes illustrated in figure 1 and their crystallographic data are given below:

$$4\text{H BaCrO}_3 \quad a = 0.566 \text{ nm}, \quad c = 0.936 \text{ nm}$$

$$6\text{H BaCrO}_3 \quad a = 0.563 \text{ nm}, \quad c = 1.37 \text{ nm}$$

$$9\text{R BaRuO}_3 \quad a = 0.575 \text{ nm}, \quad c = 2.16 \text{ nm}.$$

4. Results and discussion

An examination of figure 1 shows that the mirror plane at a hexagonally close-packed layer reverses the slope of the corner-linked BO_6 octahedra. This is accompanied by a similar reversal in the slope of the rows of A cations (Ba^{2+} in the present study). In addition to showing lattice periodicity, we would, therefore, expect the lattice images of the polytypes to show the existence of mirror planes (slope reversal) wherever hexagonal stacking is present.

In figure 2, lattice images of 4H- BaCrO_3 taken at two different defocus values are shown. Slight difference in focus between the micrographs gives rise to contrast features which are not exactly identical, although consistent with each other. The images show the lattice periodicity of 0.94 nm. Chevrons corresponding to CrO_6 octahedra and Ba^{2+} cations alternating in direction every alternate layer (0.47 nm apart) can be clearly seen in the image in figure 2(a). The idealized structure shown in the inset in figure 2(a) corresponding to the *chch* (4H) sequence compares well with the observed image.

The lattice image of 6H- BaCrO_3 is shown in figure 3. The chevrons in the thinner portion of the crystal corresponds to *chchch* (6H) sequence as can be seen by comparison with the idealized projection given in the inset. The lattice periodicity (1.37 nm) is also seen in the image, particularly clearly as the crystal becomes thicker. We found no stacking faults in the crystals of either 4H- or 6H- BaCrO_3 examined by us indicating the presence of a high degree of order.

The lattice image of 9R- BaRuO_3 is shown in figure 4 along with the electron diffraction pattern. Due to rhombohedral absences ($-h + k + l = 3n$) in the *okl* section of the diffraction pattern, very high resolution could not be attained in the lattice image. However, the 2.16 nm periodicity of the 9R structure can be clearly seen. The *chhchh* (9R) layer sequence is shown as an inset in figure 4 for purpose of comparison.

Some of the crystals of BaRuO_3 showed presence of stacking faults. Thus, the lattice image in figure 5 shows the intergrowth of 6-layer sequences along with the 9R-sequence. Lattice imaging technique is ideal to examine random occurrence of such defects in layer structures.

The lattice image of the sample of BaRuO_3 quenched from 1600 K is typical of the 4H polytype with a periodicity of 0.94 nm (figure 6). It is interesting that the 4H polytype of BaRuO_3 can indeed be obtained at room temperature by

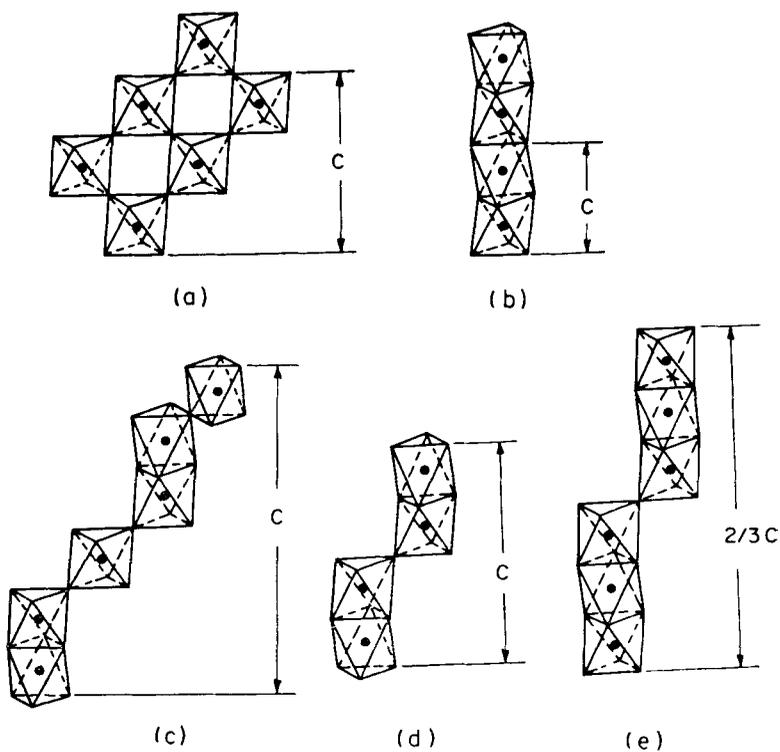


Figure 1. Representation of occupied octahedral sites (BO_6) in polytypes of ABO_3 perovskites: (a) 3C; (b) 2H; (c) 6H; (d) 4H; and (e) 9R.

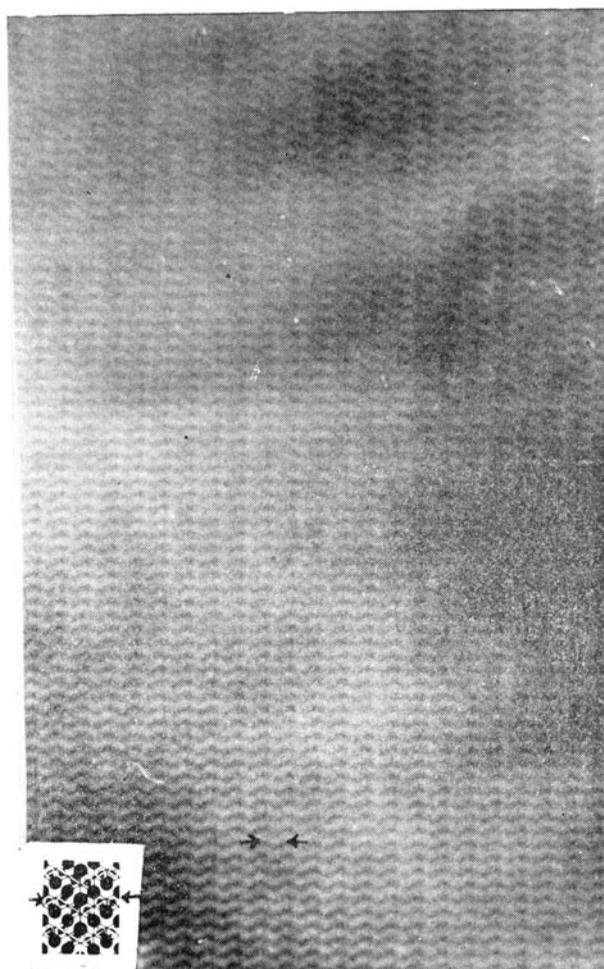


Figure 2 (a). Lattice image of 4H-BaCrO₃. Idealized projection (*chch* sequence) showing Ba²⁺ (filled circles) and CrO₆ octahedra (shaded parallelograms) is given in inset. Distance between the two arrows in the photograph is 0.95 nm.

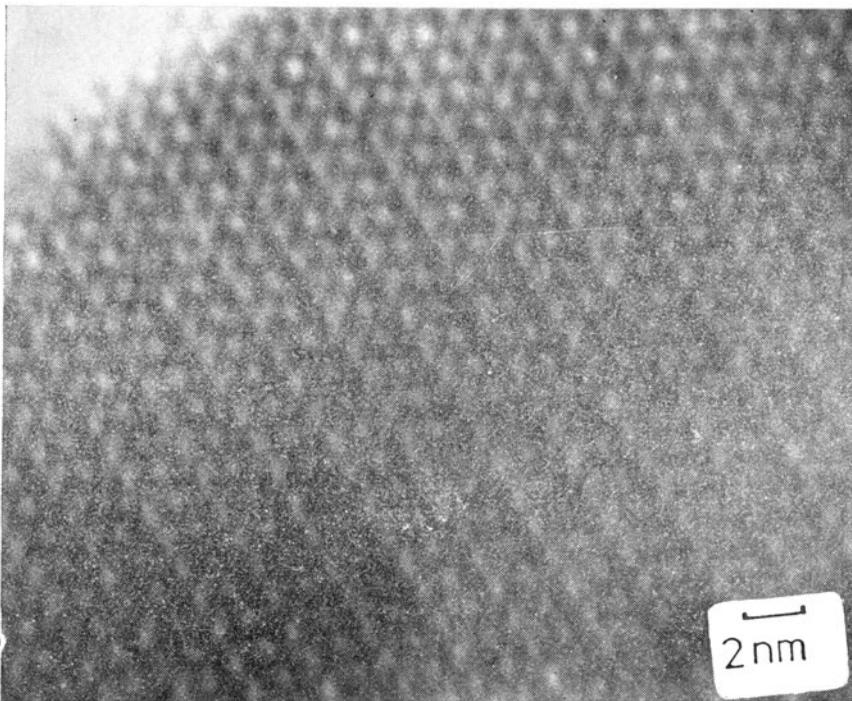


Figure 2 (b). Lattice image of 4H-BaCrO₃ at a different defocus from (a).

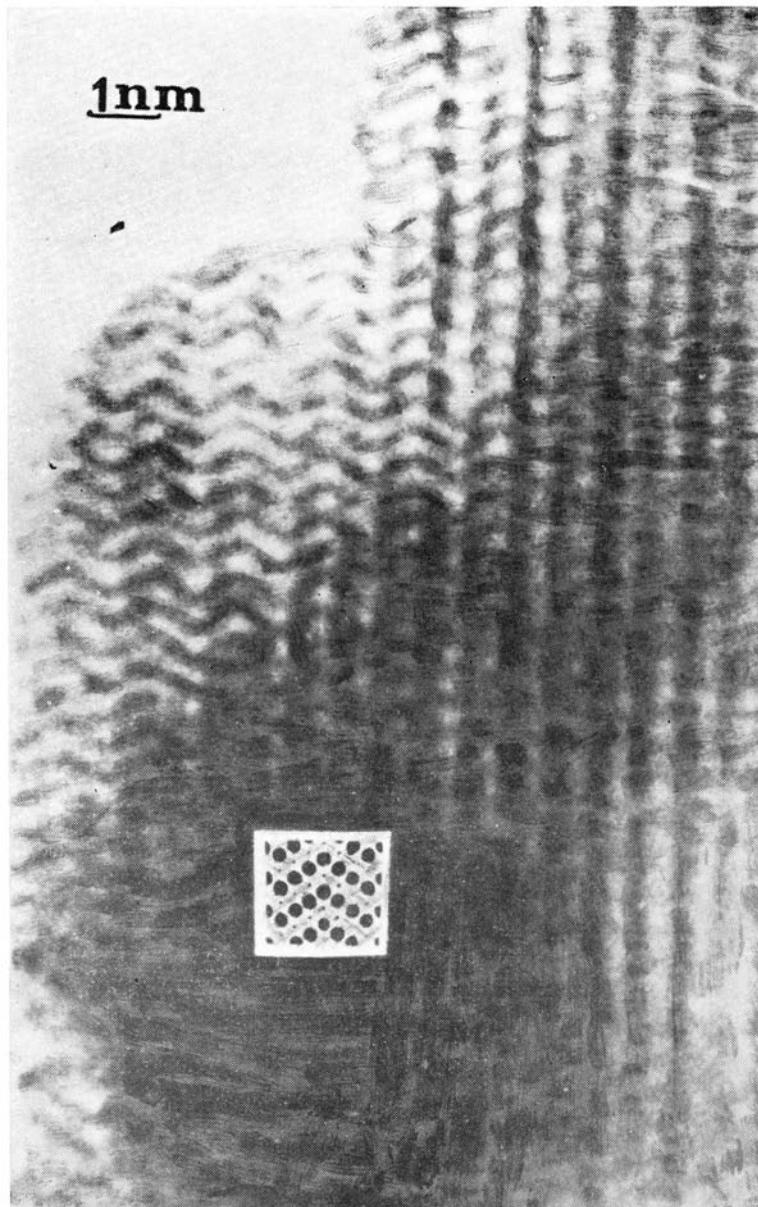


Figure 3. Lattice image of 6H-BaCrO₃ with idealized projection of the *cchch* sequence in the inset.

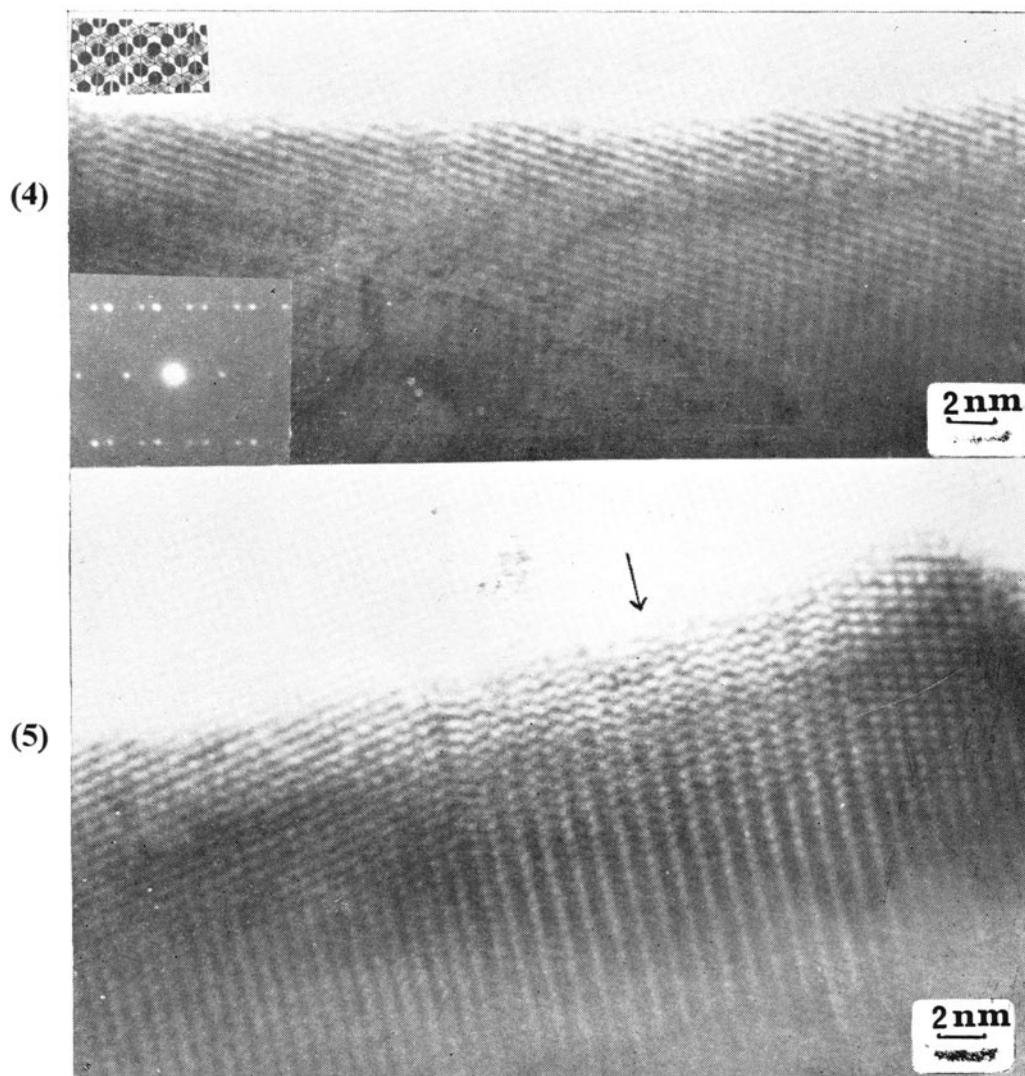


Figure 4. Lattice image of 9R-BaRuO₃ with the electron diffraction pattern showing rhombohedral absences. Idealized projection of *chhchh* sequence is also shown.

Figure 5. Lattice image of a crystal of 9R-BaRuO₃ showing 6 layer intergrowth as a stacking fault (arrowed).

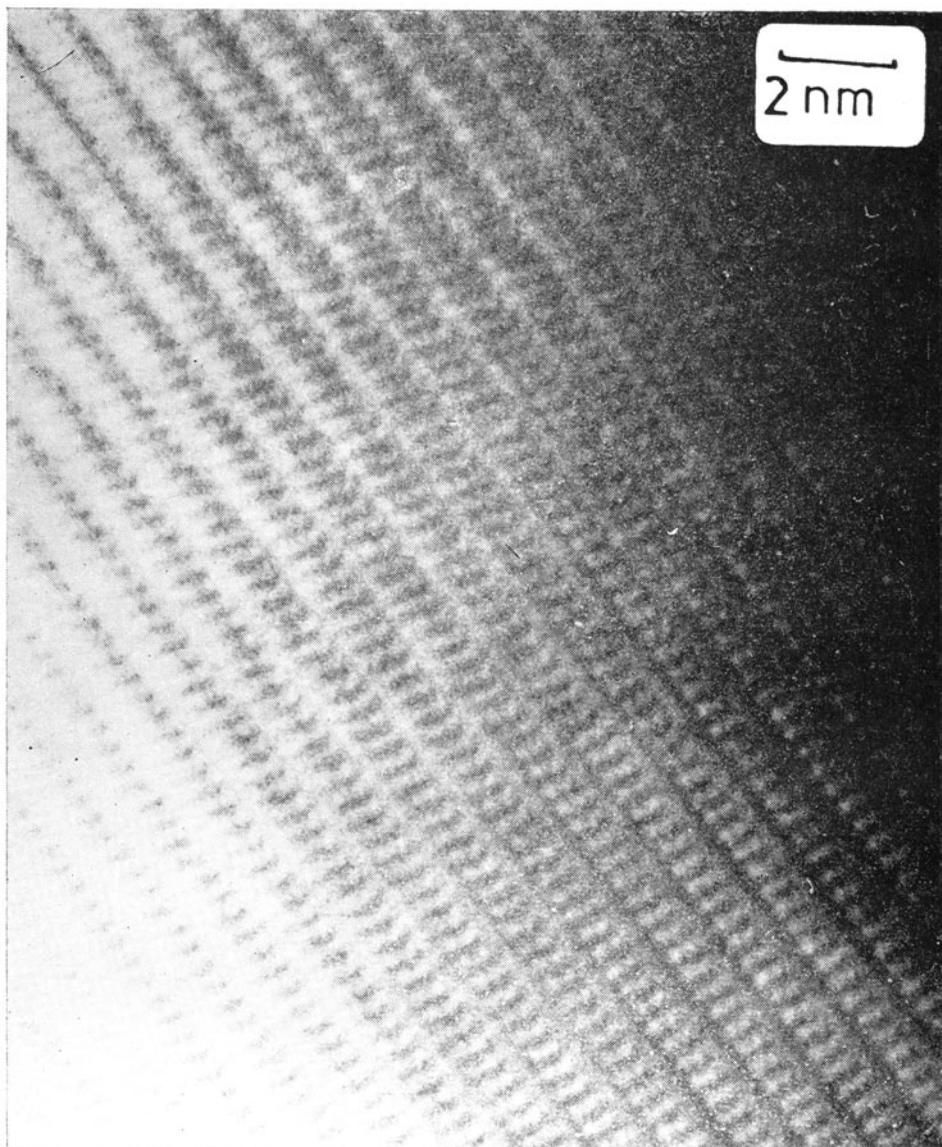


Figure 6. Lattice image of 4H-BaRuO₃ obtained by quenching a sample heated to 1600 K.

quenching the solid after the 9R polytype has transformed to 4H at high temperature. The 9R→4H transformation was not evidenced in samples quenched from 1400 K or below. It appears that the 9R → 4H transformation temperature of pure BaRuO₃ at atmospheric pressure appears to be around 1500 K. The transformation temperature is apparently lowered by substitution of Sr²⁺ for Ba²⁺. Thus, if x in Ba_{1-x}Sr_xRuO₃ is around 0.1, the 9R → 4H transformation occurs around 1300 K or lower (Donohue *et al.* 1966).

5. Concluding remarks

Lattice images of perovskite polytypes discussed above suggest that high resolution electron microscopy can provide direct information on new and complex stacking sequences in other systems. Although n -beam image calculations on densely packed structures are desirable, the present study clearly indicates the possible utility of the lattice imaging technique in favourable cases, for the study of structures of complex layered structures and so on. This feeling is further reinforced by the recent reports on the lattice imaging of 6H silicon carbide by Gai, Anderson and Rao (1975) and on the direct structure determination of BaIrO₃ (Gai, Jacobson and Rao 1976) by this technique.

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