

updating, an integral part of the refinement cycle. Structure factor computation alone requires 2.1×10^{-5} s per atom-reflection.

The completion of the model of the protein molecule and associated solvent, and the extension of the refinement to 1.8 Å resolution will be discussed in a separate publication.

The program is written in Fortran and includes documentation and patches for most common space groups. It is available from either author. Included in the package are programs for generating the reflection and ISTAB files, blocked as needed, and a program for automatic generation of parameter restraint files for polypeptides.

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SHORT COMMUNICATIONS

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Short-range ordering in $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$. By H. BRIGITTE KRAUSE, *Department of Physics, Northern Illinois University, DeKalb, IL 60115, USA* and J. M. COWLEY and JOHN WHEATLEY, *Arizona State University, Tempe, Arizona 85281, USA*

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Abstract

High-resolution electron-microscope images in conjunction with selected-area electron diffraction were used to investigate the short-range order in $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$. Intensity fluctuations of the [110] image indicated ordered domains extending over about 20 to 50 Å. Decomposition phases were observed.

atoms are generally believed to occupy the *A* metal positions while the Mg and Nb atoms are assumed to be distributed in the *B* metal positions. The questions of whether or not ordering of the *B* atoms takes place has previously been investigated with no conclusive results (Krause & Gibbon, 1971): X-ray powder measurements showed no superlattice reflections while selected-area electron diffraction yielded diffuse superlattice points in the body-centered position of the reciprocal unit cell. These results suggested either short-range ordering of the Mg and Nb atoms or slight distortions of the cubic unit cell associated with ferroelectric behavior. Electron microscopy imaging methods have now been used to distinguish between these possibilities.

$\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ crystallizes in the cubic perovskite structure with a lattice constant of 4.04 Å (Ismailzade, 1961). The Pb

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The specimens were obtained from large single crystals, grown and kindly supplied by the Bell Laboratories (Bonner & van Viter, 1967). Crystal splinters were crushed under liquid nitrogen and dispersed in acetone. Selected-area electron diffraction patterns of different orientations of the same crystal were obtained with a JEOL-100B electron microscope equipped with a tilting stage and operated at 100 kV. With a few exceptions, the particles showed the expected structure, having cubic symmetry within the accuracy of the observations with the above mentioned superlattice points in the body-centered position of the reciprocal unit cell. Because of the relatively small unit cell, high-resolution images, showing the periodicity of the crystal, could be obtained only for the three projections with the largest d spacings: [100], [111] and [110]. For those, only the diffraction pattern of the [110] projection contains superlattice points. Consequently, the images of the first two projections, shown in Fig. 1(a) and (b) display no peculiarities. A slight deviation from hexagonal symmetry in Fig. 1(b) may be attributed to a slight tilt away from the exact axial

orientation. The [110] projection, shown in Fig. 1(c), reveals local distortions of the lattice fringes and intensity fluctuations. A schematic drawing of the image intensities of ordered domains for the [110] projection is shown in Fig. 1(d).

If the intensity fluctuations were due to small local distortions of the unit cell, one would expect them to be almost invisible in the very thin crystal regions but to increase in intensity rapidly when the crystal is thick enough to give strong dynamical scattering effects (about 100 Å for 100 keV electrons). On the other hand, variations of site occupancy by Mg and Nb atoms would give appreciable intensity fluctuations for very thin crystals and these fluctuations would increase only slowly with thickness (Cowley & Iijima, 1977). Since these fluctuations occur also in the very thin regions of the crystal, one can conclude that they are the result of short-range ordering rather than of unit-cell distortions.

The evidence on the crystal thicknesses involved is indirect, since the micrographs are obtained from irregular

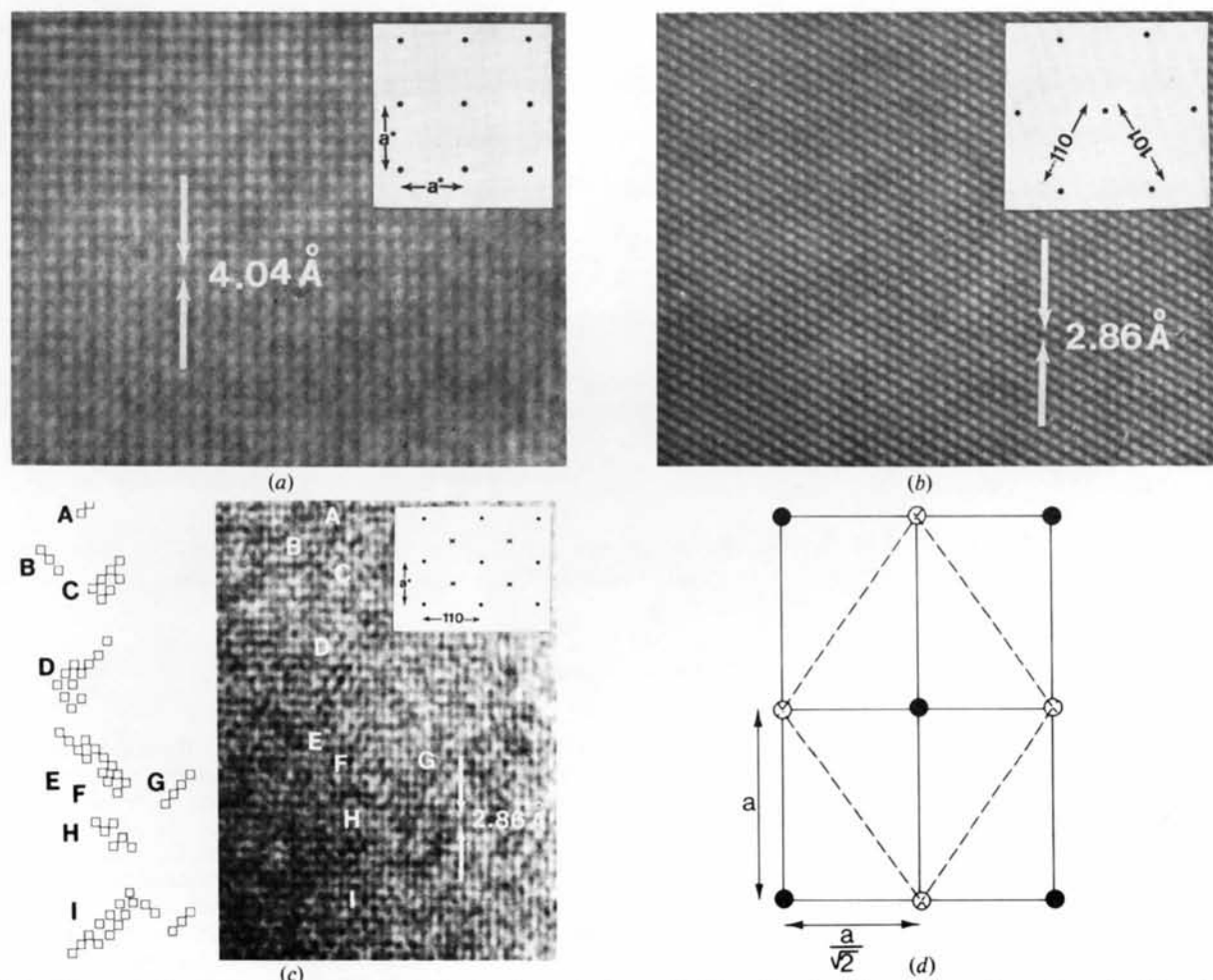


Fig. 1. High-resolution images of various crystallographic projections of $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$. The corresponding schematic diffraction patterns show: ● regular diffraction spots; × superlattice spots. (a) [100] projection. (b) [111] projection. (c) [110] projection; the schematic drawing to the left shows some ordered domains. (d) Schematic drawing of ordered region of [110] image; dashed lines connect superlattice points.

crystals, subject to radiation damage, for which detailed thickness measurements are not feasible. Our estimates on crystal thickness and the conclusions drawn are based on experience with observations on other better-behaved crystals for which thickness determinations and detailed calculations of image contrast have been made (see, for example, Iijima, 1979).

The short-range order extends over regions of about 20 to 50 Å in the [111] directions. The superlattice dimensions are expected to be $A = a\sqrt{2}$ and $\alpha = 60^\circ$ for a rhombohedral cell, or $A = 2a$ for a larger face-centered cubic unit cell. The superlattice cell volume of twice or eight times the original volume, respectively, is incompatible with the chemical composition unless one assumes that the various metals occupy both *A* and *B* positions.

Other possible origins for apparent superlattice reflections, such as spots due to twinning or fault planes, are ruled out by consideration of the diffuseness of the spots and the appearance of the images.

Because of the short-range character of the ordering, sharp superlattice spots cannot be expected to be observed and could not be detected in X-ray single-crystal photographs.

In addition to the cubic phase described above, a crystal with a distorted cubic phase was observed. The diffraction pattern and image shown in Fig. 2 suggest a cell with equal axes inclined at an angle of 100° . The ordering, in this case, is not in the [111] directions but appears to be along [110] and $\bar{1}\bar{1}0$ in accordance with a superlattice point in $(\frac{1}{2}, \frac{1}{2}, 0)$. It is not known if this cell represents a low-temperature phase of $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ or if it belongs to some decomposition product. Shortly after the image of Fig. 2 was taken, the crystal decomposed in the electron beam and recrystallized. Sudden decomposition and recrystallization was also observed with cubic crystals. Some recrystallized areas indicated different kinds of ordering patterns which may be attributed to a change in chemical composition (Fig. 3).

In addition to sudden phase changes, slow decomposition and contamination of the crystals limited the studies that could be performed on an individual crystal.

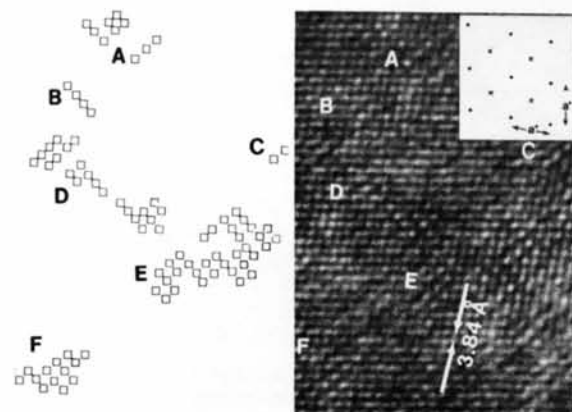
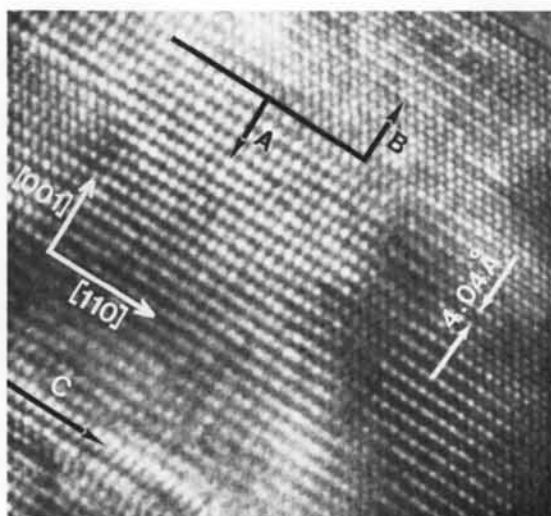
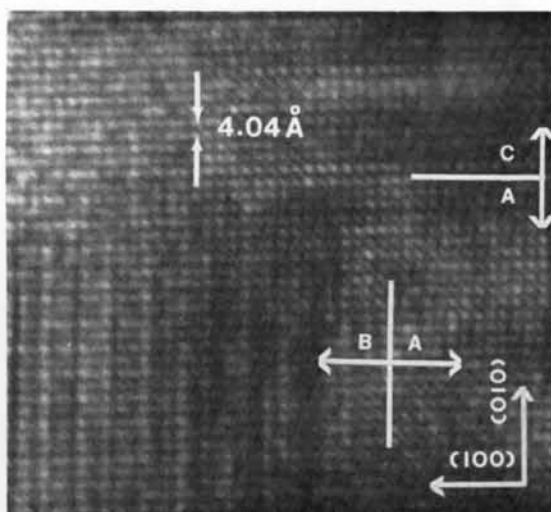


Fig. 2. High-resolution image of non-cubic phase; the corresponding diffraction pattern shows: ● regular diffraction spots; × superlattice spots. The schematic drawing to the left shows some ordered domains.



(a)



(b)

Fig. 3. (a) and (b). High-resolution images of decomposition products. *A* regular image, *B* and *C* additional ordering or irregularities.

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