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An Electron Microscope Study of Perovskite-Related Oxides in the Sr–Ti–O System

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In order to investigate the relationship between nonstoichiometry and the static dielectric constant, phases in the $SrO–TiO_2$ pseudo-binary system have been studied by X-ray diffraction and electron microscopy. Three ternary oxides were found in the temperature interval 1373–1673°K, Sr_2TiO_4, $Sr_3Ti_2O_7$, and $SrTiO_3$. In all of these oxides, nonstoichiometry seems to be taken up by coherent intergrowth of lamellae of various homologous oxides $Sr_{n+1}Ti_nO_{3n+1}$. The results are discussed in terms of the crystal chemistry of the perovskite oxides and factors which influence the magnitude of the static dielectric constant of solids.

Introduction

One of the most puzzling features of the oxides which form the so-called crystallographic shear (*CS*) phases is their limited number. They are effectively restricted to the binary oxides TiO_2, VO_2, Nb_2O_5, MoO_3, and WO_3 and to some ternary oxides in which these latter materials form the major component (*1*). Upon oxygen loss, these oxides (with the possible exception of MoO_3), appear to have no tolerance at all of significant point defect populations. Instead the crystal structure collapses upon a specific crystallographic plane (the *CS* plane) which differs from one oxide to another and also varies with the degree of oxygen loss.

Three chemical criteria have been put forward to account for why only such a limited group of materials support *CS*. Perhaps the simplest is the suggestion that the metal ion must exist in two valence states, the parent valence state and a lower one, for example, Ti^{4+} and Ti^{3+} in the Ti_nO_{2n-1} oxides. A second criterion is ionic size, and *CS* phases are generally formed by rather small cations which usually prefer octahedral coordination. The third criterion is one of geometry and requires that for a *CS* structure to form the parent lattice must be rather open and able to collapse. This feature has been discussed in terms of anion packing around cations by Tilley (*2*), Stone and Tilley (*3*), and Hyde (*4*). Neither these criteria, nor the observation that the parent *CS* oxides are transition metal oxides, has been able to explain why other materials of similar structure type do not form *CS* phases.

The central problem to be tackled is why these materials resist a point defect population within their crystal structures while other apparently similar oxides accept point defect clusters readily. The fact that the chemical approach has not been successful in this attempt suggests that physical properties may provide useful clues. It has been pointed out that one such property which is able to satisfactorily correlate the occurrence of *CS* phases is the magnetude of the static dielectric constant of these materials (*5*). Examination of compilations of dielectric constants of oxide and other materials shows that all materials showing *CS* behavior have very large values, for example ε_c for TiO_2 is about 160 (*6*) while ε for WO_3 is about 300 (*7*).

In order to follow up this suggestion a series

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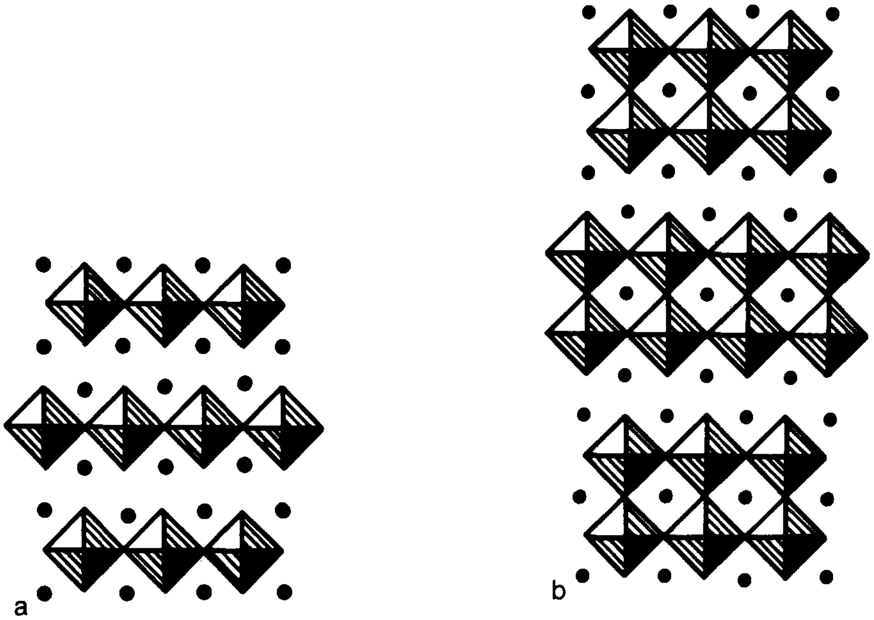

FIG. 1. Idealized representations of the structures of (a) Sr_2TiO_4, (b) $Sr_3Ti_2O_7$, (c) $Sr_4Ti_3O_{10}$, and (d) the perovskite $SrTiO_3$. The shaded squares represent TiO_6 octahedra and the filled circles Sr atoms.

of experiments were planned to study the way in which stoichiometric variation was accommodated in materials with very high dielectric constants. Consultation of standard compilations, (see, e.g., Ref. (*8*)) showed that the ferroelectric perovskites $SrTiO_3$, $BaTiO_3$, and $Ca_2Nb_2O_7$ were suitable candidates, as was PbS. Experiments on $SrTiO_3$ were underway when Portier *et al.* (*9*) reported a series of complex intergrowth phases in perovskite oxides related to $Ca_2Nb_2O_7$, which indicated that the original suggestion regarding the dielectric constant was correct. The present communication describes the microstructures found when $SrTiO_3$ is doped with SrO to produce compositions along the fully oxidized pseudo-binary phase line. It was found that intergrowth occurred, and that there was no evidence for massive concentrations of point defects, as suggested by some of the earlier literature. The findings are discussed in terms of the crystal chemistry of the perovskites.

The Pseudo-Binary SrO–TiO_2 System

In view of the vast amount of literature available on the electrical properties of $SrTiO_3$ and the fact that changes in both anion:cation and cation:cation stoichiometry can affect these properties significantly, it is somewhat surprising to find that the phase diagram of the SrO–TiO_2 system is not known with complete certainty (see, e.g., Ref. *10*). The most recent phase diagram to be found in the literature reports $SrTiO_3$ to have a composition range on the SrO-rich side of the composition $SrTiO_3$ (*11*). In addition, the three oxides Sr_2TiO_4, $Sr_3Ti_2O_7$, and $Sr_4Ti_3O_{10}$ have been reported (*12*) but none of the phase diagrams available show the existence of a phase of stoichiometry $Sr_4Ti_3O_{10}$ although the $Sr_3Ti_2O_7$ phase has been reported as having a composition range encompassing the formula $Sr_4Ti_3O_{10}$ (*11*).

The idealized structures of $SrTiO_3$ and the oxides Sr_2TiO_4, $Sr_3Ti_2O_7$, and $Sr_4Ti_3O_{10}$ are shown in Fig. 1. These oxides can all be regarded as members of a homologous series of oxides of general formula $Sr_{n+1}Ti_nO_{3n+1}$ in which $SrTiO_3$ corresponds to the composition equivalent to $n = \infty$ and SrO corresponds to the composition equivalent to $n = 0$. The intermediate oxides can therefore be regarded as ordered intergrowths between an almost complete sheet of the SrO structure and lamellae of

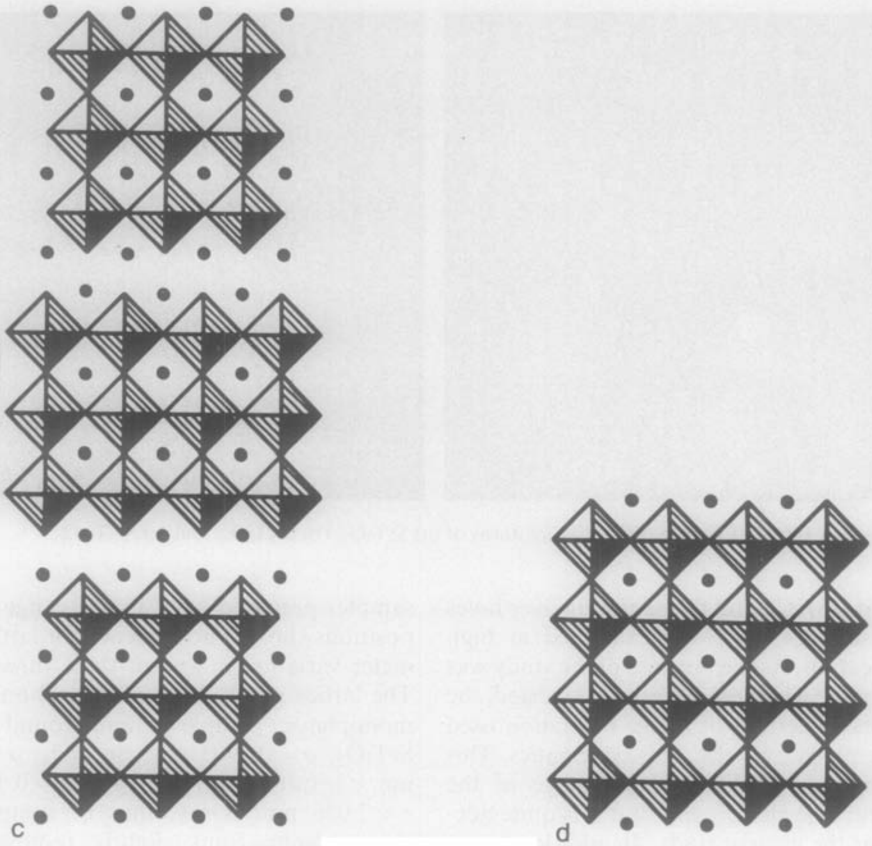

FIG. 1—*Continued*

the $SrTiO_3$ structure, or alternatively as slabs of the $SrTiO_3$ structure, *n* unit cells thick, united along planes rich in Sr.

Experimental

All specimens were prepared from high-purity powders of $SrCO_3$ and TiO_2 supplied by Johnson Matthey Ltd. Compositions of supposed $Sr_{n+1}Ti_nO_{3n+1}$ oxides with $n = 1, 2, 3, 4, 5$ and ∞ were weighed from mixtures of the starting materials, ground in an agate mortar, compacted into pellets of 4-mm diameter under a load of 2000 kg and fired on platinum foil. Heating times from 1 to 7 weeks at temperatures between 1513 and 1673°K were used. The majority of samples were reground and repelleted during this procedure. This method yielded polycrystalline samples suitable for electron microscopy.

In addition to this method, some mixtures of the starting products were mixed with an equal volume of PbF_2 in a platinum crucible and heated for 3 days at 1373°K. This method yielded quite large crystals, but the main product was always $SrTiO_3$.

Samples prepared as described were examined optically using a Zeiss Ultraphot microscope to determine their degree of homogeneity and whether they were suitable for electron microscopy. Well crystalline samples were examined further in a JEM 100B electron microscope fitted with a goniometer stage and operated at 100 kV. Electron microscope specimens were prepared by crushing selected pellets under *n*-butanol in an agate mortar and allowing a drop of the resultant suspension to dry on a net-like carbon film on a copper sup-

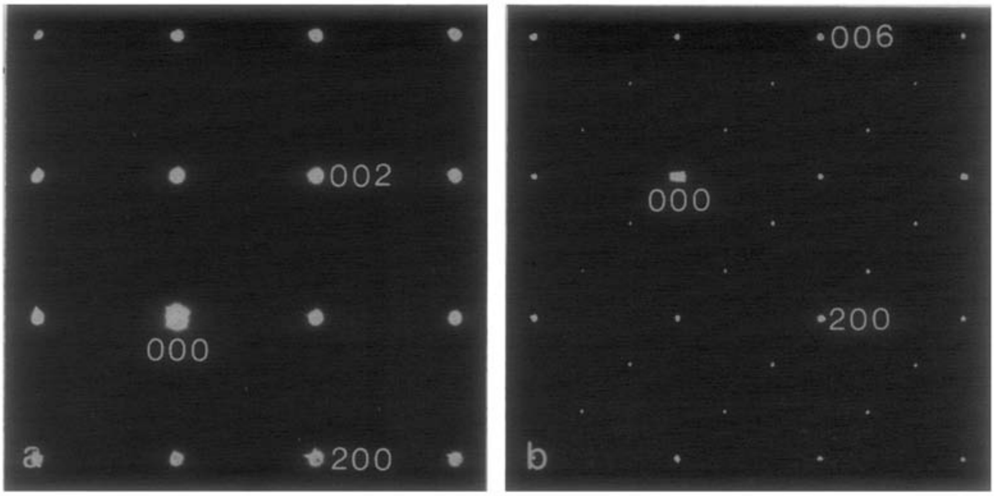

FIG. 2. Electron diffraction patterns of (a) $SrTiO_3$, (b) Sr_2TiO_4, and (c) $Sr_3Ti_2O_7$.

port grid (*13*). Crystal flakes resting over holes in the support film were examined at high magnification. As the purpose of the study was to determine whether intergrowths existed, the commonest method of image formation used was to employ only the $(00l)$ systematics. This gives only a one-dimensional image of the structural disorder present, but it is quite adequate for the present study. In addition, powder X-ray photographs of all reaction products were taken at room temperature using a Guinier–Hägg focusing camera, employing strictly monochromatic $CuK\alpha_1$ radiation ($\lambda = 0.154051$ nm) and KCl ($a = 0.62919$ nm) as an internal standard.

Results

The only ternary oxide phases discovered as end products within the temperature interval covered in these experiments by either X-ray diffraction or electron microscopy were Sr_2TiO_4, $Sr_3Ti_2O_7$, and $SrTiO_3$. No evidence was found for the existence of well-ordered crystals of the oxide $Sr_4Ti_3O_{10}$ reported earlier (*12*) or for any of the other $Sr_{n+1}Ti_nO_{3n+1}$ phases. Figure 2 shows examples of the electron diffraction patterns from $SrTiO_3$, Sr_2TiO_4, and $Sr_3Ti_2O_7$ and Fig. 3 shows well-ordered crystal fragments of this latter oxide.

A visual comparison of X-ray films from samples prepared over a wide range of compositions showed no evidence for lattice parameter variation in any of these three phases. The lattice parameters, measured on films of monophasic samples, were found to be; $SrTiO_3$, $a = 0.3903$ nm; Sr_2TiO_4, $a = 0.3886$ nm, $c = 1.2609$ nm; $Sr_3Ti_2O_7$, $a = 0.3904$ nm, $c = 2.036$ nm. X-ray films of samples with gross compositions slightly removed from these stoichiometries showed the presence of more than one phase. From this evidence it would appear that the three oxides have no appreciable composition ranges.

Although only the ternary oxides $SrTiO_3$, Sr_2TiO_4, and $Sr_3Ti_2O_4$ were identified in the final reaction products, X-ray films of incompletely reacted materials were complex and showed the presence of other so-far-unidentified phases. It is clear, therefore, that the reaction is a complex one, and studies of the mechanism of formation of the stable oxides would be of interest. However, as this is peripheral to the object of the present study it has been postponed until a later stage.

Electron microscopy revealed that in most samples a fair proportion of crystal fragments showed disorder typical of intergrowth. Figures 4–7 show typical examples. Figure 4 shows a well-ordered fragment of $Sr_3Ti_2O_7$ containing coherently intergrown lamellae of Sr_2TiO_4, giving it an overall composition

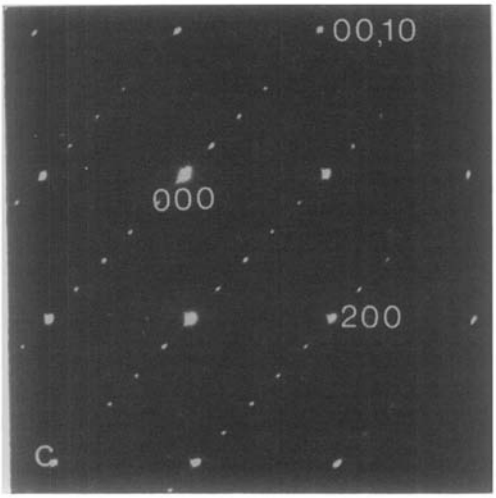

FIG. 2.—*Continued*

lower than $Sr_3Ti_2O_7$. In Fig. 5, a crystal which has a basic structure of $Sr_3Ti_2O_7$ shows considerable faulting and contains lamellae of the oxides $Sr_4Ti_3O_{10}$, $Sr_5Ti_4O_{13}$, $Sr_6Ti_5O_{16}$, and $Sr_8Ti_7O_{22}$.

The transition from $Sr_3Ti_2O_7$ to $SrTiO_3$ is shown in Fig. 6, which shows $Sr_3Ti_2O_7$ with wider fault-free regions best described as lamellae of $SrTiO_3$ coherently intergrown with the parent matrix. Finally, Fig. 7 shows two $SrTiO_3$ crystals, one containing isolated faults and one containing groups of faults corresponding to lamellae of $Sr_3Ti_2O_7$, both of which cause the crystal to have an overall composition slightly more rich in SrO than stoichiometric $SrTiO_3$. It should be noted with respect to all these micrographs, but particularly for Fig. 7a, that the real structure of these interfaces has not been determined, but it is assumed to be identical to the interfacial layers between the perovskite slabs in Sr_2TiO_4 and $Sr_3Ti_2O_7$ as shown in Fig. 1. For the purposes of this paper such an assumption seems reasonable.

Discussion

The experiments described above were not undertaken as a careful phase study of the $SrO–TiO_2$ pseudobinary system and no attempt was made to redefine the equilibrium phase

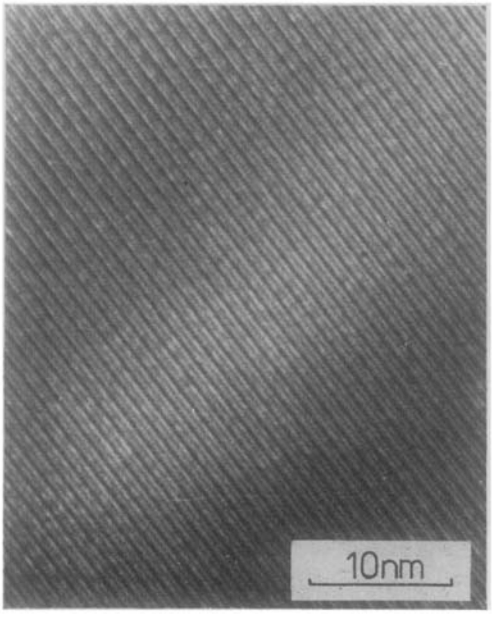

FIG. 3. (00*l*) lattice fringes in well-ordered crystals of $Sr_3Ti_2O_7$.

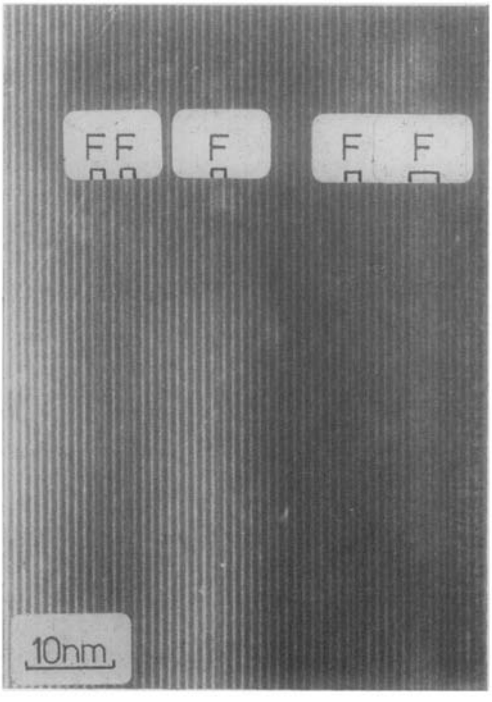

FIG. 4. $Sr_3Ti_2O_7$ crystals containing disordered intergrowths of lamellae of Sr_2TiO_4 marked F.

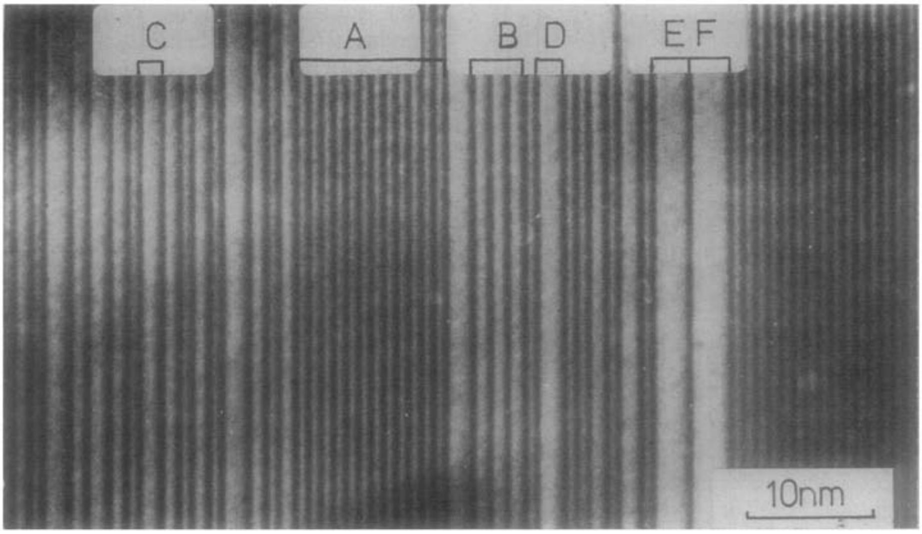

FIG. 5. A disordered $Sr_3Ti_2O_7$ crystal fragment (A) containing intergrowths of the oxides $Sr_4Ti_3O_{10}$ (B), $Sr_5Ti_4O_{13}$ (C), $Sr_6Ti_5O_{16}$ (D), $Sr_8Ti_7O_{22}$ (E) and $Sr_9Ti_8O_{25}$ (F).

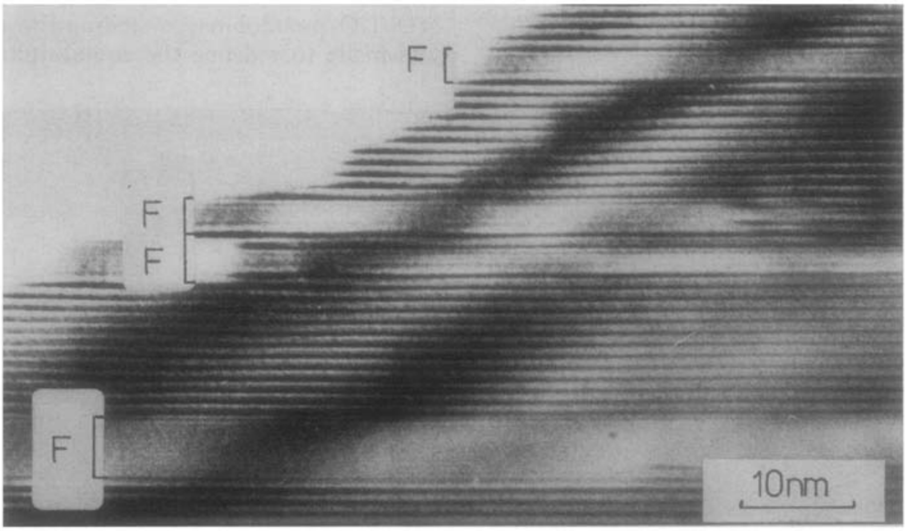

FIG. 6. An $Sr_3Ti_2O_7$ crystal containing intergrowths of $SrTiO_3$, marked F. The fragment also shows dislocations where $Sr_3Ti_2O_7$ lamellae terminate within the crystal.

diagram. Nevertheless, some information relevant to the earlier phase diagram studies has emerged. First, no ordered members of the $Sr_{n+1}Ti_nO_{3n+1}$ series were found with n greater than 2 although the occurrence of isolated lamellae which are wider than those forming $Sr_3Ti_2O_7$ suggests that such phases may form under special preparation conditions or if other cation dopants were to be used. In addition the X-ray data strongly suggests that the system does not tolerate large point defect populations as these would give rise to easily observable lattice parameter changes and to monophasic samples over considerable regions of the phase diagram. The extended homogeneity ranges of $SrTiO_3$ and $Sr_3Ti_2O_7$ re-

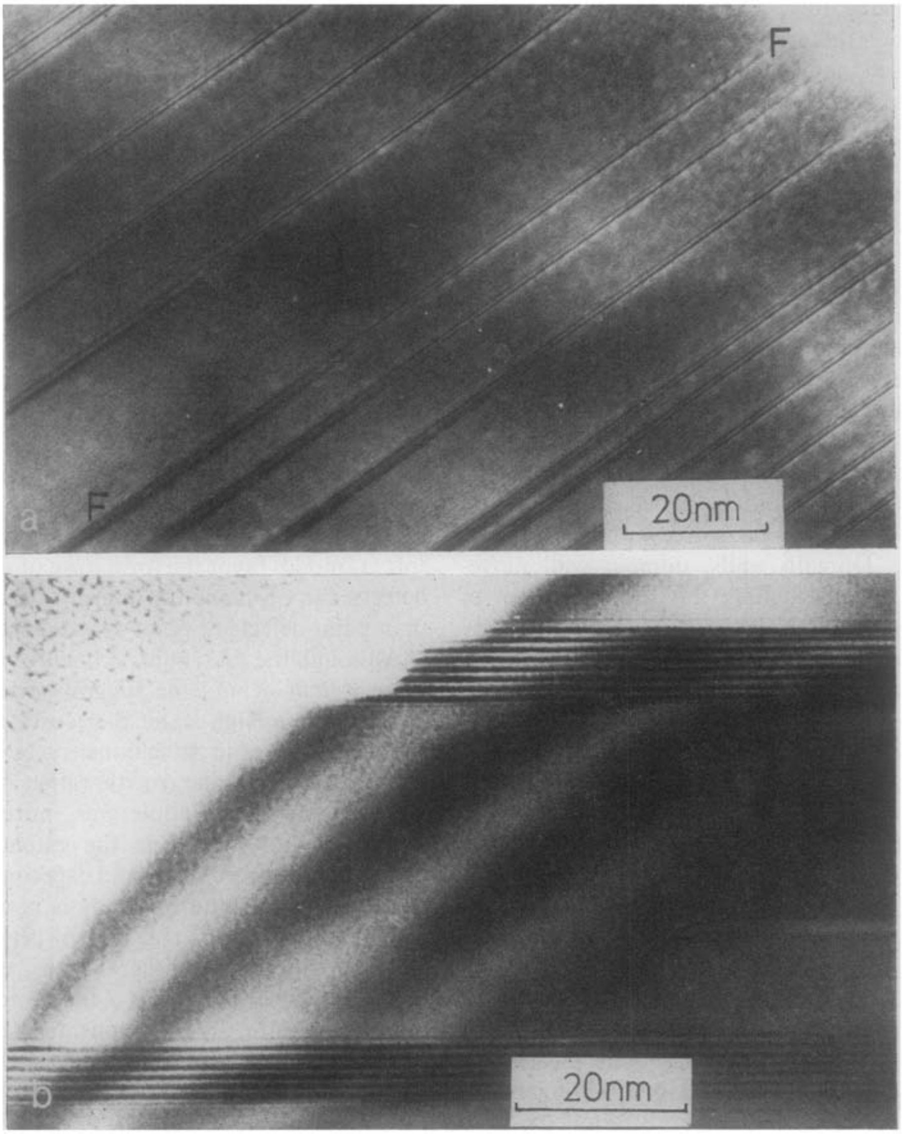

FIG. 7. (a) A crystal of $SrTiO_3$ containing isolated planar faults (marked FF). (b) A crystal of $SrTiO_3$ containing isolated bands of $Sr_3Ti_2O_7$.

ported by Cocco and Massazza are therefore unlikely to be due to excess or deficit of disordered cations. Instead, these regions are likely to be due to the coherent intergrowth of anomalously wide lamellae equivalent to slabs of various $Sr_{n+1}Ti_nO_{3+1}$ oxides in the matrix of $Sr_3Ti_2O_7$ or $SrTiO_3$.

These intergrowths can be described in a number of ways. In the case of disordered $Sr_3Ti_2O_7$ a description in terms of coherent intergrowth of other $Sr_{n+1}Ti_nO_{3n+1}$ phases is lucid. In the case of disordered $SrTiO_3$ as shown in Fig. 7a it is less useful, and a description in terms of $SrTiO_3$ containing isolated faults is more appropriate. These planar faults have not been analyzed in detail, but if we assume that they have the same structure as occurs between the perovskite lamellae in Sr_2TiO_4 and $Sr_3Ti_2O_7$ then we can see that they can be regarded as lamellae of the SrO structure, coherently intergrown with the $SrTiO_3$ structure. Alternatively these planar faults can be regarded as *CS* planes in which the $SrTiO_3$ structure has expanded rather than collapsed, and in which at each fault an extra layer of atoms of stoichiometry SrO has been added. Which description is chosen depends upon the particular macrostructure being discussed, and both chemically and structurally all are equivalent.

It is well known that the dielectric properties of crystals of $SrTiO_3$ and similar materials are somewhat hard to control experimentally. The presence of intergrowths or planar faults to some extent explains why this should be so. If stoichiometric imbalance were taken up by point defects distributed at random, the polarization of the material, particularly ionic polarization, would be expected to increase somewhat and to be isotropic throughout the crystal. Domain walls, domain wall movement, and switching of the direction of macroscopic polarization would be largely unaffected. If the crystal contains planar faults, these will clearly add a directional bias to the behavior and they are likely to impede domain wall movement and perhaps even act as pinning agents. Thus one can anticipate that careful control of stoichiometry is of extreme importance in obtaining reproducible dielectric properties in large crystals.

The experiments tend to confirm further the suggestion that materials with a high static dielectric constant resist point defect populations as a mode of structurally accommodating nonstoichiometry. In the materials we are considering, the static dielectric constant is composed of the electronic and ionic polarizability. As the electronic polarizability is not especially large in these oxides and is certainly similar in magnitude to that in related non-*CS* or in intergrowth supporting oxides, the high value of the static dielectric constant is due to the ionic polarizability term. This is, in the main, attributable to the presence of small off-center cations in the metal–oxygen coordination octahedra which form the building units of these oxides. The presence of these off-center cations not only produces the large ionic polarizability but also has a profound effect upon the lattice dynamics of the crystals. The simplest form this relationship takes is expressed by the Lyddane–Sachs–Teller relationship (*14*), which shows that a high static dielectric constant is associated with a soft (low frequency temperature dependent) transverse optical vibration mode, ω_T, of the lattice. The instability of these ω_T phonon modes is associated both with a high-static dielectric constant and also with the occurrence of ferroelectricity in crystals of sufficiently low symmetry. Barker (*14*) has shown that mode instability is strongly influenced by the local electric field within a dielectric. Certainly the presence of point defects in a solid will lead to excessive local fields in some regions of the crystal which will have a bearing on the stability of the soft ω_T modes. The interaction will be complex and has not yet been analyzed in detail, but it would seem possible that in materials with a high dielectric constant the existence of unstable soft ω_T modes favor the formation of sheets of defects, the CS planes or intergrowths, rather than point defects or point defect clusters.

Although the present experiments do throw more weight behind the suggestion that materials with a high-static dielectric constant support changes in stoichiometry by way of planar faults or intergrowth rather than by way of point defect populations, more studies are needed to determine the extent of its validity both theoretically and experimentally. At present a program of study is now under way in which $SrTiO_3$ and related perovskites are being doped with other cations, or being reduced to stoichiometries ABO_{3-x} to ascertain whether, in these circumstances, planar faults are formed. In addition, attempts are being made to approach the problem theoretically from the point of view of crystal lattice dynamics. These results will be reported in the future.

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