JOURNAL OF SOLID STATE CHEMISTRY **121,** 324–331 (1996)
ARTICLE NO. 0044

Phase Formation in the $Nd_2Ti_2O_7$–$SrTiO_3$ System at 1350°C in the Presence of V_2O_5, CuV_2O_6, or $SrCuO_2$

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Received April 10, 1995, in revised form September 22, 1995; accepted October 3, 1995

The system $Nd_4Ti_4O_{14}$ (=$Nd_2Ti_2O_7$)–$SrTiO_3$ has been studied by powder X-ray diffraction and electron microscopy. The samples were prepared by normal ceramic methods and contained one of the additives V_2O_5, CuV_2O_6, or $SrCuO_2$. Each of these additives caused the reaction to take place at greatly increased rates compared to that without additives. The major products were $Nd_4Ti_4O_{14}$ and $SrTiO_3$, which were formed in 8 hr at 1350°C. The vanadium in the additives formed $NdVO_4$ while the other components were incorporated into the product phases. The $Nd_4Ti_4O_{14}$ was generally well ordered but the $SrTiO_3$ showed a complex microdomain microstructure which was associated with a variety of changes in the unit cell observed by X-ray diffraction. Heating for several days caused the $SrTiO_3$ to revert to the normal cubic form, at which point the microdomain structure was lost. © 1996 Academic Press, Inc.

INTRODUCTION

Crystallographically $Nd_2Ti_2O_7$ belongs to a small group of $A_2B_2O_7$ oxides that includes $La_2Ti_2O_7$, $Ca_2Nb_2O_7$, and $Sr_2Nb_2O_7$ (1). The structure of these materials can be thought of as built up from layers of perovskite-like sheets which are four BO_6 octahedra in thickness bounded by {110} planes relative to a cubic perovskite parent. In all of these materials the larger A cations occupy positions within the perovskite sheets and at the interface between them. The structure of $Nd_2Ti_2O_7$ is shown in Fig. 1.

It has long been recognized that a homologous series of related oxides can be constructed, at least hypothetically, by variation of the thicknesses of the perovskite slabs. The formula of the series is $A_nB_nO_{3n+2}$, where the subscript n is equal to the thickness of the perovskite-like slabs measured in octahedra. The oxides of interest here are thus representatives of the $n = 4$ member of the series. To emphasize this structural feature we have found that it is often preferable to use the formula $A_4B_4O_{14}$ rather than $A_2B_2O_7$ to describe these phases and we follow this practice here.

The real structures of these materials display a variety of distortions which include A and B cation displacements and tilting of the BO_6 octahedra. These are responsible for a number of important physical properties exhibited by perovskite-related compounds in general (2). In particular several oxides show high-temperature ferro- and piezoelectric behavior and some, including $Nd_4Ti_4O_{14}$, display potentially important opto-electronic properties (3, 4). Recently investigations on the similar $La_4Ti_4O_{14}$–$LaTiO_3$ system have shown that varied electrical behaviour accompanies the structural changes taking place as the stoichiometry is altered (5, 6).

Although $Nd_4Ti_4O_{14}$ is of considerable interest, phase relations in systems between $Nd_4Ti_4O_{14}$ and other perovskite structure ABO_3 oxides have not been widely studied with the exception of the $Nd_4Ti_4O_{14}$–$CaTiO_3$ system (7–10). Because of the interest in layered perovskites, both from the point of view of physical properties and crystal chemistry we have investigated the phases occurring in the $Nd_4Ti_4O_{14}$–$SrTiO_3$ system. As $Nd_4Ti_4O_{14}$ and $SrTiO_3$ are both refractory oxides, reactions were expected to proceed very slowly. In a previous paper we have given details of the phases found in this system when samples were melted as part of a preparation procedure designed to overcome this problem (11). An alternative technique, the incorporation of small quantities of rate-enhancing additives into the system is described here. The additives chosen were V_2O_5, CuV_2O_6, or $SrCuO_2$. All are low-melting compounds and would be expected to form liquid phases, which are known to increase sintering rates in solids. The oxide V_2O_5 was chosen because it has well-known spreading and surface wetting properties. $SrCuO_2$ was selected because (unpublished) results in our laboratory had shown that this was a good sintering aid for the formation of ordered Aurivillius phases. CuV_2O_6 was chosen to see if the surface wetting properties combined with the Cu might give superior results to $SrCuO_2$. The results of this study are described and discussed.

EXPERIMENTAL

The starting materials were Nd_2O_3, (99.99%, Alfa Industries) and CuO, TiO_2, V_2O_5, and $SrCO_3$ of Specpure qual-

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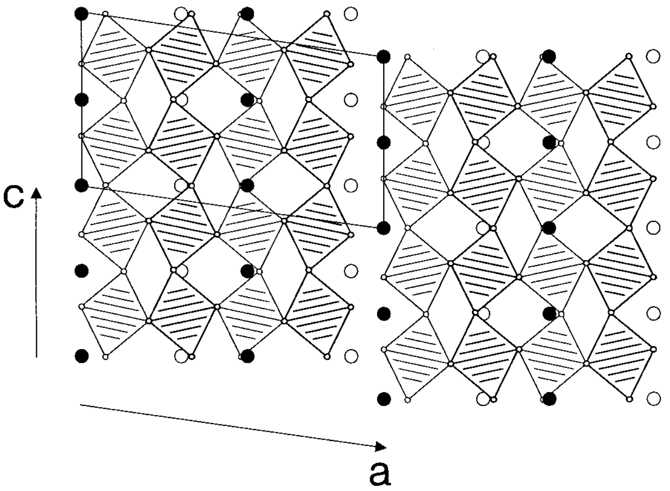

FIG. 1. Projection of the structure of $Nd_2Ti_2O_7$ ($Nd_4Ti_4O_{14}$) along [010]. The circles represent Nd atoms at two different heights and the shaded diamonds represent TiO_6 octahedra. In some structure determinations the a-axis is double that shown here.

ity (Johnson Matthey). The additive-assisted preparations used Nd_2O_3, SrO, and TiO_2, and one of the additives V_2O_5, CuV_2O_6, or $SrCuO_2$. The oxide TiO_2 and additive V_2O_5 were employed in the as-supplied form without further modification. The oxide SrO, because of its tendency to absorb CO_2 from the atmosphere, was prepared immediately prior to use by calcining $SrCO_3$ in an open crucible at 1150°C for 8 hr. CuV_2O_6 was prepared by heating together a 1 : 1 molar ratio of CuO and V_2O_5 in an open crucible to 600°C for 8 hr. $SrCuO_2$ was prepared by arc melting a 1 : 1 molar ratio of SrO, prepared as above, and CuO, according to standard procedures (11).

The compositions prepared all fell along the $Nd_4Ti_4O_{14}$–$SrTiO_3$ line in the phase diagram if the additives are ignored and corresponded to the hypothetical oxides $Nd_nSr_{n-4}Ti_nO_{3n+2}$ with $n = 4, 4.5, 5, 5.5$, and 6. Additionally preparations at some other compositions were occasionally made to clarify aspects of the reactions taking place. Appropriate weights of the reactants were mixed with 5 wt% of one of the additives. The mixtures were then ground thoroughly and compressed to form pellets 10 mm in diameter and 3–5 mm thick. Stacks of two pellets of each mixture were placed onto a sheet of freshly cleaned platinum foil resting on a ceramic tile inside a chamber furnace. The pellets were heated at 200°C/min to 800°C and maintained at this temperature for 30 min before heating at 50°C/min to the reaction temperature of 1350°C. The pellets were maintained at the reaction temperature for 8 hr and were then air quenched to room temperature. After reaction the bottom pellet was discarded as a precaution against platinum contamination.

A further set of samples were prepared in an identical fashion but subjected to extended heating times. In these cases the pellets were removed from the furnace after 3 days heating at 1350°C, reground, pressed, and heated to give a total of 7 days at 1350°C. This was repeated once more so that pellets were subjected to a final heating time of 14 days at 1350°C. Some preparations were also made in the absence of additive. These samples were heated for 7 days without any intermediate treatment.

After reaction each sample was examined by powder X-ray diffraction using a Guinier–Hägg focusing camera employing monochromatic $CuK\alpha_1$ radiation and KCl as an internal standard ($a_0 = 0.62923$ mm at 25°C). Lattice parameters were refined using least-squares techniques. Samples were also examined by scanning and transmission electron microscopy. For transmission studies, fragments of the pellets were crushed under n-butanol in an agate mortar. A drop of the resultant suspension was placed onto a copper grid that had previously been coated with a holey carbon film. Fragments of the crystal were examined in a Jeol 200CX transmission electron microscope fitted with a goniometer stage operating at 200 kV and equipped with a LaB_6 filament. For scanning electron microscopy, samples were examined in a Jeol 35CF microscope fitted with energy and wavelength dispersive analysis facilities. Samples were gold coated to avoid problems associated with electrostatic charging.

RESULTS

Powder X-Ray Diffraction

No additives. Samples with an overall composition $Nd_nSr_{n-4}Ti_nO_{3n+2}$ with $n = 4, 4.5$, and 5 were used for these preliminary experiments. X-ray diffraction showed that no significant reaction had taken place after 7 days at 1350°C beyond the production of a small amount of Nd_2TiO_5. The major materials present were the starting oxides. No $Nd_4Ti_4O_{14}$ had formed.

Additive reactions. Irrespective of the starting composition, $Nd_4Ti_4O_{14}$ and, when appropriate, $SrTiO_3$ were formed after heating for 8 hr at 1350°C. No traces of the starting oxides or Nd_2TiO_5 were observed on the X-ray films.

The $Nd_4Ti_4O_{14}$ patterns were in good agreement with that given in the JCPDF file (entry 33-942). The refined lattice parameters for $Nd_4Ti_4O_{14}$ were typically (from a sample corresponding to the composition $Nd_4Ti_4O_{14}$ with V_2O_5 as additive) $a_0 = 1.3001 \pm 0.0001$ nm, $b_0 = 0.5460 \pm 0.0001$ nm, $c_0 = 0.7680 \pm 0.0001$ nm, and $\beta = 98.62 \pm 0.04°$. These values compare favorably with the reported values $a_0 = 1.3008$ nm, $b_0 = 0.54648$ nm, $c_0 = 0.7679$ nm, and $\beta = 98.56°$. No significant variations in the powder pattern of this phase were found across the phase range and no trace of an orthorhombic modification of $Nd_4Ti_4O_{14}$ was observed.

TABLE 1
X-Ray Phase Analysis

Composition, n^a	Phases	$SrTiO_3$ parameters nm
	CuV_2O_6 8 hr	
4	$Nd_4Ti_4O_{14}$, $NdVO_4$, (TiO_2)	
4.5	$Nd_4Ti_4O_{14}$, $NdVO_4$, $SrTiO_3$(cs)	0.7699
5	$Nd_4Ti_4O_{14}$, $NdVO_4$, $SrTiO_3$(cs)	0.7711
5.5	$Nd_4Ti_4O_{14}$, $NdVO_4$, $SrTiO_3$(c)	0.3856
6	$Nd_4Ti_4O_{14}$, $NdVO_4$, $SrTiO_3$(cs)	0.7078
	CuV_2O_6 3, 7, 14 days	
5.333	$Nd_4Ti_4O_{14}$, $NdVO_4$, $SrTiO_3$(c)	0.3861
6	$Nd_4Ti_4O_{14}$, $NdVO_4$, $SrTiO_3$(c)	0.3870
7	$Nd_4Ti_4O_{14}$, $NdVO_4$, $SrTiO_3$(c)	0.3870
	V_2O_5 8 hr	
4	$Nd_4Ti_4O_{14}$, $NdVO_4$, ((TiO_2))	
4.5	$Nd_4Ti_4O_{14}$, $NdVO_4$, $SrTiO_3$(cs)	0.7700
5	$Nd_4Ti_4O_{14}$, $NdVO_4$, $SrTiO_3$(cs)	0.7702
5.5	$Nd_4Ti_4O_{14}$, $NdVO_4$, $SrTiO_3$(c)	0.3856
6	$Nd_4Ti_4O_{14}$, $NdVO_4$, $SrTiO_3$(cs)	0.7708
	$SrCuO_2$ 8 hr	
4	$Nd_4Ti_4O_{14}$	
4.5	$Nd_4Ti_4O_{14}$, $SrTiO_3$(t)	$a = 0.3890^b$
5	$Nd_4Ti_4O_{14}$, $SrTiO_3$(t)	$a = 0.3870$, $c = 0.3900$
5.5	$Nd_4Ti_4O_{14}$, $SrTiO_3$(t)	$a = 0.3878$, $c = 0.3899$
6	$Nd_4Ti_4O_{14}$, $SrTiO_3$(st)	$a = 0.3860$, $c = 0.7816$
	$SrCuO_2$ 3, 7, 14 days	
4.333 (3 days)	$Nd_4Ti_4O_{14}$, $SrTiO_3$(st)	$a = 0.3849$, $c = 0.7892$
4.33 (7, 14 days)	$Nd_4Ti_4O_{14}$, $SrTiO_3$(c)	0.3895 (7 days)
6 (3 days)	$Nd_4Ti_4O_{14}$, $SrTiO_3$(st)	$a = 0.3853$, $c = 0.7790$
6 (7, 14 days)	$Nd_4Ti_4O_{14}$, $SrTiO_3$(c)	0.3893 (7 days)
7 (3 days)	$Nd_4Ti_4O_{14}$, $SrTiO_3$(st)	$a = 0.3845$, $c = 0.7788$
7 (7, 14 days)	$Nd_4Ti_4O_{14}$, $SrTiO_3$(c)	0.3884

[a] n refers to the formula $(Sr, Nb)_nTi_nO_{3n+2}$.

[b] The lines were not intense enough to determine a value for c_0.

The $SrTiO_3$ powder pattern displayed a degree of variation. In some preparations X-ray powder pattern corresponded closely to the normal cubic form reported in the literature. This modification will be referred to as $SrTiO_3$(c). In other preparations a low-angle line was seen which could be incorporated into a cubic pattern if a unit cell approximately double that of normal $SrTiO_3$ was assumed. This modification will be called $SrTiO_3$(cs). Other preparations resulted in a powder pattern which showed that the phase was tetragonal with a cell of dimensions similar to those of the normal cubic modification. This will be referred to as $SrTiO_3$(t). The final modification was also tetragonal, but with a double cell similar to the $SrTiO_3$(cs) material. This will be referred to as $SrTiO_3$(ts). It was also found that the unit cell was slightly contracted compared with that reported in the literature. The X-ray powder diffraction phase analysis is summarized in Table 1 and considered in detail below.

5 wt% CuV_2O_6 additive. The $n = 4$ samples heated for 8 hr contained $Nd_4Ti_4O_{14}$, $NdVO_4$, and a trace of TiO_2 (rutile). All phases had patterns which agreed with those reported in the literature and the JCPDS files. No lines could be detected in the powder patterns which could be attributed to CuV_2O_6. In the case of the other preparations, $Nd_4Ti_4O_{14}$ and $NdVO_4$ were present together with $SrTiO_3$. No TiO_2 could be found on these other preparations. No differences could be found between the powder patterns of $Nd_4Ti_4O_{14}$ and $NdVO_4$ from one film to another apart from the gradual change in intensity expected as the phase range was traversed. In the $n = 4.5$, 5, and 6 preparations the $SrTiO_3$(cs) modification was found. In the $n = 5.5$ sample $SrTiO_3$(c) was present. The lattice parameter of the $SrTiO_3$ was slightly smaller than that recorded in the literature.

The X-ray diffraction results for the samples heated for the longer times of 3, 7, and 14 days were identical to those of the shorter heating time preparations with the single exception that only $SrTiO_3$(c) was observed. This also had a slightly smaller cell than that reported for pure $SrTiO_3$.

5 wt% V_2O_5 additive. The X-ray powder diffraction results for these samples were identical to the equivalent CuV_2O_6 additive preparations. Longer periods of heating were not utilized because of this similarity.

5 wt% $SrCuO_2$ additive. For the $n = 4$ composition, only $Nd_4Ti_4O_{14}$ was present. In the other preparations only two phases were observed, $Nd_4Ti_4O_{14}$ and $SrTiO_3$. In the $n = 4.5$, 5, and 5.5 preparations the $SrTiO_3$ was present as $SrTiO_3$(t) while in the $n = 6$ preparation it was $SrTiO_3$(st).

The X-ray powder diffraction results for the samples heated for 3, 7, and 14 days showed that the $SrTiO_3$ patterns evolved in a consistent fashion. After 3 days total heating time the X-ray patterns of this phase were characteristic of $SrTiO_3$(st) and after 7 days total heating time the material conformed to the $SrTiO_3$(c) parent structure.

Scanning Electron Microscopy

Scanning electron microscopy was mainly used to determine whether the additives were present after reaction rather than for morphological studies. Nevertheless it was found that in all cases well-formed crystals made up the bulk of the samples. In none of the preparations were discrete crystals or other phases found which analyzed to a composition identical to an additive phase. Instead the elements which comprised the additive for any particular sample were found to be distributed fairly evenly throughout the sample. In the cases of CuV_2O_6 and V_2O_5 the overall amounts of Cu and V found were identical to those originally incorporated into the preparation within the accuracy of the technique. In the case of $SrCuO_2$ the amount of Cu remaining after reaction was a little less than that originally incorporated into the sample. The Sr could not be determined uniquely because of interference with that already present as $SrTiO_3$.

Transmission Electron Microscopy

$Nd_4Ti_4O_{14}$. A small difference was observed between fragments of $Nd_4Ti_4O_{14}$ formed in the presence of CuV_2O_6 and V_2O_5 as opposed to those produced with $SrCuO_2$. Most of the fragments of $Nd_4Ti_4O_{14}$ obtained from the CuV_2O_6 and V_2O_5 preparations exhibited a measure of disorder along the long axis of the unit cell. This was revealed by uneven contrast on the micrographs, as shown in Fig. 2a, taken from a preparation using CuV_2O_6 as the additive. The disorder was also manifested on the diffraction patterns by diffuse streaking along and parallel to a^* and by a doubling of the spot spacing in alternate rows of diffraction maxima running parallel to a^*. Inspection of the contrast on these micrographs revealed that the disorder was due to microtwinning with (100) acting as the composition plane. The twins were sometimes seen to be aggregated into larger bands, as shown in Fig. 2b, which was also taken from a preparation utilizing CuV_2O_6. The degree of disorder and twinning observed in the fragments of $Nd_4Ti_4O_{14}$ formed in the presence of $SrCuO_2$ additive was found to be considerably less and so is not illustrated here.

No order or disorder was found in any of the fragments examined which could be interpreted as due to slabs of a perovskite type wider than those characteristic of $Nd_4Ti_4O_{14}$.

$SrTiO_3$. The $SrTiO_3$ crystal fragments presented a similar picture regardless of the sample preparation method used. In the samples heated for 8 hr most crystal fragments exhibited contrast indicative of a microdomain substructure. Similar microdomain structures arose in the (sc), (t), and (st) forms of $SrTiO_3$. The microdomains consisted of regions of altered contrast lying along two orthogonal directions. We show two examples in Figs. 3a and 3b. The relative extent of the microdomains varied from one crystal fragment to another and the two examples shown are representative of many others, each of which is slightly different from the others in the extent and arrangement of the microdomain texture. When crystal projections which were at an angle to the cubic axes were examined the microdomains appeared as irregular patches in the regular fringe patterns of the matrix.

All the electron diffraction patterns showed extra reflections compared to that expected for cubic $SrTiO_3$. As examples, the diffraction patterns corresponding to the images shown in Fig. 3 are included in Figs. 4a and 4b. The intensities of the additional spots in the diffraction patterns varied in a way that was consistent with the amount of microdomain material present and the underlying symmetry of the structure as determined from the X-ray powder patterns.

In all samples diffraction patterns similar to those expected from normal $SrTiO_3$ were also found. In such cases the micrographs did not show microdomain contrast. In the samples which were annealed for long times this was the normal state of affairs and microdomains, or the remnants of this contrast, were only rarely seen.

DISCUSSION

One of the principal conclusions of this study was that no $A_nB_nO_{3n+2}$ phases with n greater than 4 were found. Moreover, no wider spacings were found as defects within the matrix of $Nd_4Ti_4O_{14}$, which could be considered to be evidence for the incipient formation of the $n = 5$ or higher phases. This result is likely to reflect the temperatures employed, that is, thermodynamic considerations, as we have found that the phases $SrNd_4Ti_5O_{17}$, $Nd_5Ti_5O_{17}$, and $Nd_6Ti_6O_{20}$ form in arc-melted preparations (11, 12). This is supported by the fact that $Nd_4Ti_4O_{14}$ formed in just 8 hr and no other phases formed even after 14 days, strongly suggesting that it is not kinetic factors which are a problem in the synthesis of high-n phases.

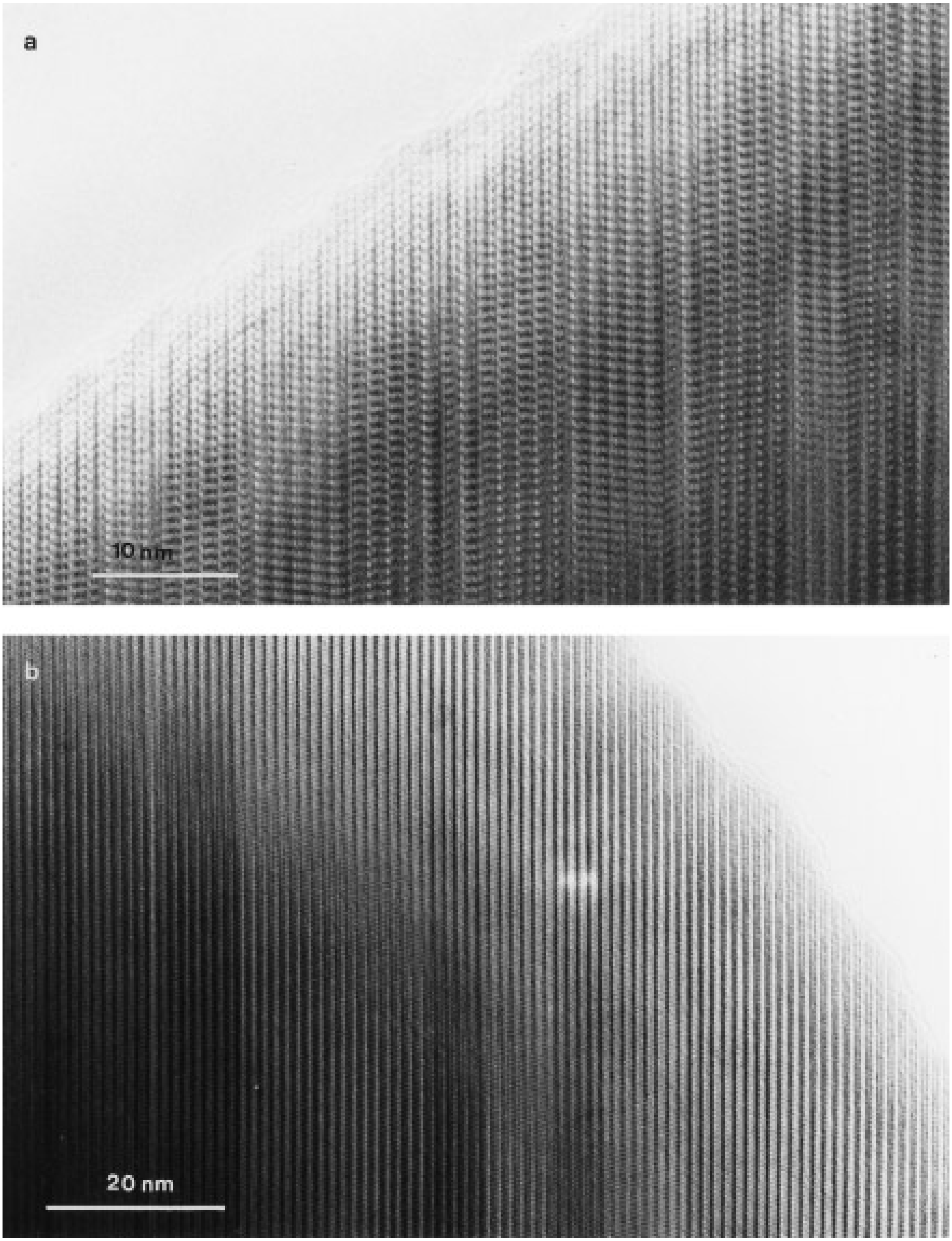

FIG. 2. Micrographs of $Nd_4Ti_4O_{14}$ ($n = 4$) prepared using CuV_2O_6 additive. (a) Preparation conditions: 8 hr at 1350°C. The uneven contrast is due to microtwinning across (100) planes, imaged as dark lines running vertically in the photograph. (b) Preparation conditions: 14 days at 1350°C. The twins are aggregated into bands, imaged as strips of darker contrast running vertically.

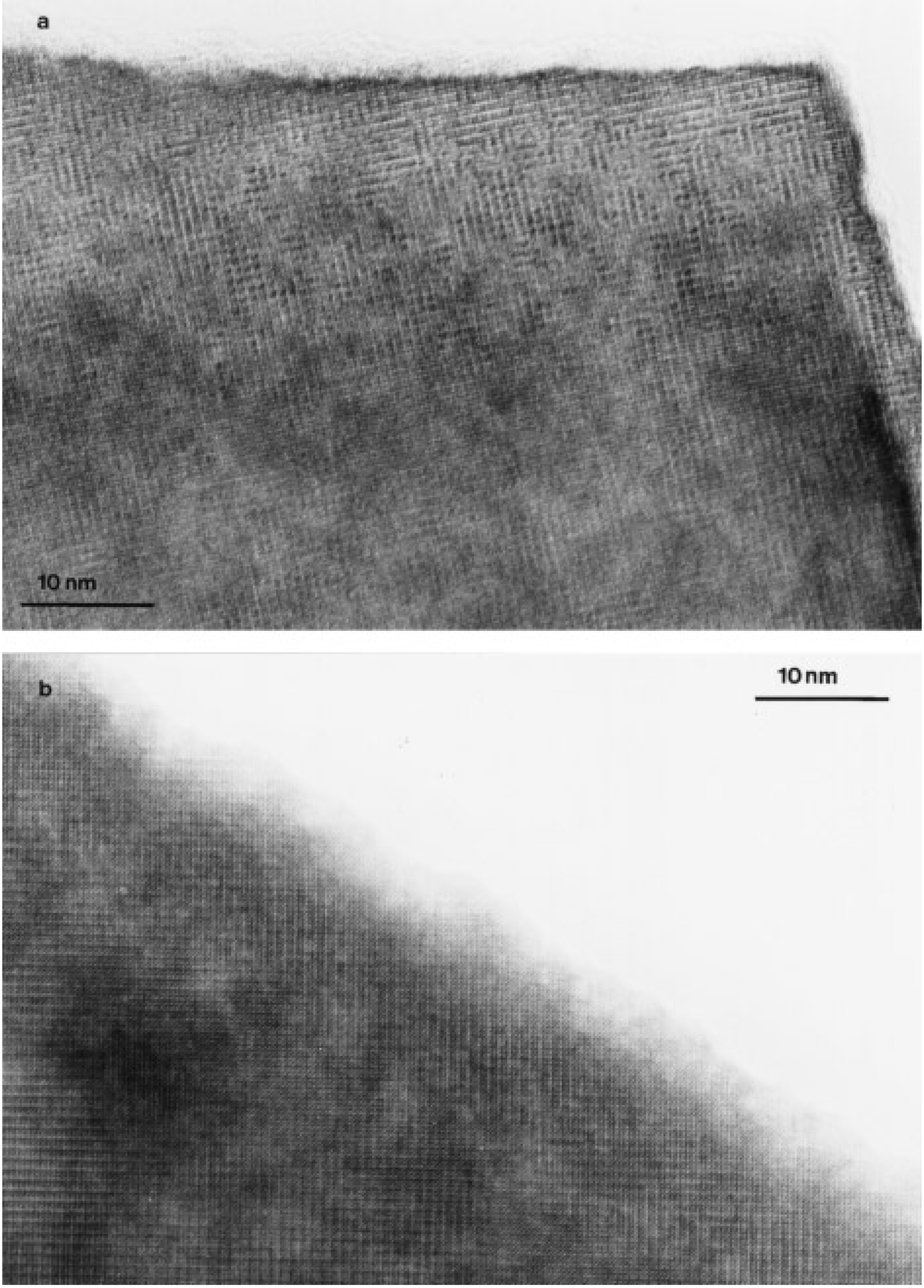

FIG. 3. Micrographs showing two different forms of microdomain contrast in $SrTiO_3$. (a) Preparation conditions: V_2O_5 additive, 8 hr at 1350°C. (b) Preparation conditions: CuV_2O_6 additive, 8 hr at 1350°C.

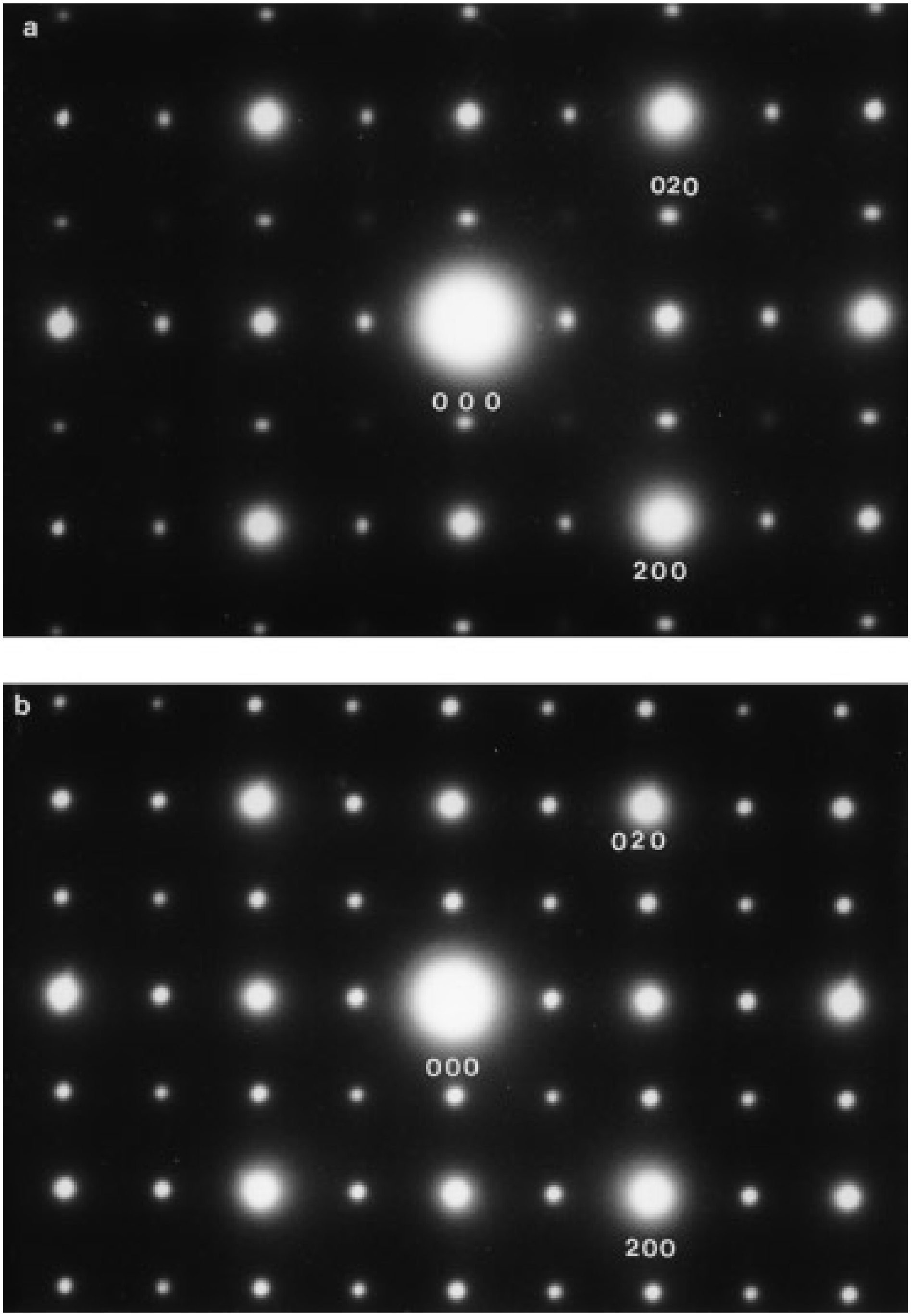

FIG. 4. (a,b). Diffraction patterns from the images shown in Fig. 3a and 3b, respectively. It is seen that the intensity distribution of the superlattice reflections varies considerably between the two patterns. The indices refer to the $SrTiO_3$ subcell.

A second important finding was that the reactions proceeded to form mainly $Nd_4Ti_4O_{14}$ and $SrTiO_3$ and that the presence of all of the additives, V_2O_5, CuV_2O_6, and $SrCuO_2$, increased the rate of the reaction considerably compared to that without additives. As far as the kinetics of the reaction are concerned, a time of 8 hr gave an apparently complete reaction in the presence of all additives while 7 days in the absence of additives gave virtually no reaction at all. The fact that $Nd_4Ti_4O_{14}$ formed readily in all preparations at 1350°C suggests that an even lower temperature could have been employed in the synthesis. The lower temperature limit for this reaction was not investigated, however. Even so, the reaction conditions used compare favorably with those reported in the literature.

For example, $Nd_2Ti_2O_7$, $La_2Ti_2O_7$, and $Sr_2Nb_2O_7$ typically require temperatures in excess of 1600°C for their formation.

We have no information on the mechanism by which the reaction rate was increased so drastically. However, the additives were chosen because of their low melting points and it is likely that a transient liquid phase plays a role in the kinetics. The importance of gas-phase transport is not eliminated, though, and is worthy of further investigation.

The additives utilized in this study were not observed after reaction as discrete phases. The fact that no second phase at all was found when $SrCuO_2$ was used as the additive, even for the $n = 4$ preparations, indicates that this must be incorporated into the $Nd_4Ti_4O_{14}$ structure. Probably the Sr enters the Nd sites and the Cu enters the Ti sites. As the charges are balanced no other defects are needed. A similar situation is also likely to hold with $SrTiO_3$. $SrCuO_2$ could readily be incorporated without the necessity of forming cation counter defects, if the additional Sr population enters Sr sites and the Cu occupies Ti sites. The well-known tolerance of the perovskite structure for substitution supports this view.

For the V_2O_5 and CuV_2O_6 additives, $NdVO_4$ formed as a side-product. The formation of $NdVO_4$ indicates that neither V_2O_5 or CuV_2O_6 could be incorporated into $Nd_4Ti_4O_{14}$ or $SrTiO_3$ readily. This is possibly due to the fact that such incorporation would involve substitution on the Ti sites and the necessity of generating energetically unfavorable counter defects in the A sites. However, small amounts of incorporation have not been ruled out by the present study.

The metastable superstructures formed in the $SrTiO_3$ phase present features very similar to those reported in a study of the $SrTiO_3$–$La_{2/3}TiO_3$ system (13). These authors found powder patterns almost identical with our (sc) type for samples close to compositions of $30\%SrTiO_3 : 70\%La_{2/3}TiO_3$ and interpreted their observations as indicative of vacancy ordering on the A cation positions. Although this makes a suitable model for the $SrTiO_3$ formed in our preparations, we do not have sufficient information on the presence or absence of additives in our materials to draw further conclusions at present. However, it is reasonable to conclude that the decrease in the lattice parameter of the $SrTiO_3$ is due to substitutions taking place perhaps in conjunction with vacancy formation. One likely scheme would involve the incorporation of Nd^{3+} on the A sites and Cu^{2+} on the B sites.

The microdomain contrast observed in the $SrTiO_3$ material would arise naturally if small regions of different symmetry are coherently grown into the perovskite matrix. In all of the cases described the normal cubic matrix is converted to some extent into material of lower symmetry. The alternative ways in which these lower symmetry variants can be disposed in the structure would then give rise to the microdomain motifs seen. Similar microdomains have been observed in $LaTiO_3$ in contact with $La_5Ti_5O_{17}$ (6). Modeling of these structures is not practical until the exact defect structure of each material is obtained. Further studies of the microdomain structure of $SrTiO_3$ are needed to clarify the remaining uncertainties. These will be reported in the future.

ACKNOWLEDGMENTS

J.S. is indebted to the School of Engineering, University of Cardiff, for the provision of a grant which made this study possible.

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