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LETTER TO THE EDITOR

A Polytypic Study on a New Layered Perovskite Vanadate $Sr_4V_3O_{10-x}$

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The authors have discovered a new polytypic $Sr_4V_3O_{10-x}$ phase and have proposed structural models for this phase, which can be obtained by introducing double V–O layers in an ordinary Sr_2VO_4 phase. The atomic stacking difference along the *c*-direction between the ordinary $Sr_4V_3O_{10}$ phase and the new phase is discussed.

Introduction

Since the discovery of layered perovskite compounds $Sr_{n+1}V_nO_{3n+1}$, several research groups have investigated some of their physical properties, such as structural, electrical, and magnetic properties (*1–3*). It is considered that the compounds are one of the candidates for new high T_c superconductors with appropriate doping. In structural studies, Cyrot *et al.* (*1*) performed X-ray and neutron diffraction analyses on Sr_2VO_4, and they determined the refined atomic positions. In addition, Nozaki *et al.* (*2*) showed schematic unit cells for this series, i.e., n = 1, 2, and 3.

However, neither an intergrowth as shown in a Bi-based superconducting system (*4, 5*) nor a polytypic growth has been reported. Moreover, very few transmission electron microscopic (TEM) observations have been carried out for characterizing such locally irregular structures. Therefore, the authors report a study by means of TEM on the structure of a new polytypic $Sr_4V_3O_{10-x}$ phase associated with the intergrowth of an ordinary Sr_2VO_4 phase, and propose models for this new phase.

Experimental

The crystals examined in this study were prepared by the following synthesis procedure: starting materials, $SrCO_3$ and V_2O_3; sintering temperature/time, 1523 K/10 hr.; atmospheric condition, in H_2 gas. The authors obtained a Sr–V–O compound which can be considered to be composed of the new phase discovered in this study.

TEM observations were performed in the following manner in order to characterize this Sr–V–O compound from the viewpoint of crystal regularity. As the first step, the crystal was fairly crushed into powder, and

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the powder was dispersed on an amorphous carbon thin film. The observations were carried out by use of a JEM-4000FX type transmission electron microscope at an accelerating voltage of 400 kV, and multiple-beam lattice images and selected area diffraction patterns were obtained.

Results and Discussion

Figure 1 shows a high resolution micrograph taken from a beam incidence of [110]. It is well known that $Sr_{n+1}V_nO_{3n+1}$ compounds are constructed by the stacking of two types of c-planes, i.e., V–O layers and Sr–O layers (*2*). It is also well known that a zone axis HREM image of a fairly thin region taken close to the Scherzer condition often reveals the projection of cationic columns as black dots, and lighter atoms often have a fainter contrast (*6*). The HREM image in Fig. 1 is considered to be taken near the Scherzer condition, and the fainter contrast along the $[1\bar{1}0]$ direction can be associated with V–O layers indicated by small arrows. The numbers denoted with small arrows indicate the observed number of V–O layers. In the case of the ordinary Sr_2VO_4, the stacking sequence along the c-direction is

–(Sr, O)–(V, O)–(Sr, O)–(Sr, O)–(V, O)–(Sr, O)–(Sr, O)–(V, O)–(Sr, O)–,
|←——0.63 nm——→|←——0.63 nm——→|

where (V, O) and (Sr, O) indicate the V–O layer and Sr–O layer, respectively. Therefore, we can consider that the fainter c-planes, i.e., the (V, O) layers, are visible with a distance of about 0.63 nm in an HREM image taken with a beam incidence of [110] of Sr_2VO_4 (*1*). Such fainter images of the (V, O) layers with distance of about 0.63 nm are observed in a local region in Fig. 1, and the authors estimate that such regions are constructed with the ordinary Sr_2VO_4 phase; however, many regions reveal a different contrast, indicated by "2" with small arrows in Fig. 1. The authors estimate that the denoted "polytype" region in Fig. 1 can be associated with the stacking of

–(V, O)–(V, O)–(Sr, O)–(Sr, O)–(V, O)–(Sr, O)–(Sr, O)–(V, O)–(V, O)–.
|←→| Double layered ... |←→| Double layered

Figures 2(a) and (b) show schematic representations of the cationic arrangement of the "polytype" region derived from the HREM results. Both Figs. 2(a) and (b) contain double (V, O) layers inserted into two (Sr, O) layers, and the authors consider that this is the reason for the double layered fainter image indicated by "2" in Fig. 1. Moreover, the atomic models in Figs. 2(a) and (b) can be denoted as $Sr_4V_3O_{10-x}$, i.e., the $n = 3$ case, but have a different crystal structure compared with an ordinary $Sr_4V_3O_{10}$ phase (Fig. 2(c) shows the ordinary $Sr_4V_3O_{10}$ phase as in Ref.(*2*)). Thus, the authors can propose new polytypic models of $Sr_4V_3O_{10-x}$, as shown in Figs. 2(a) and (b), and the intergrowth of an ordinary Sr_2VO_4 phase is observed in the local region, as

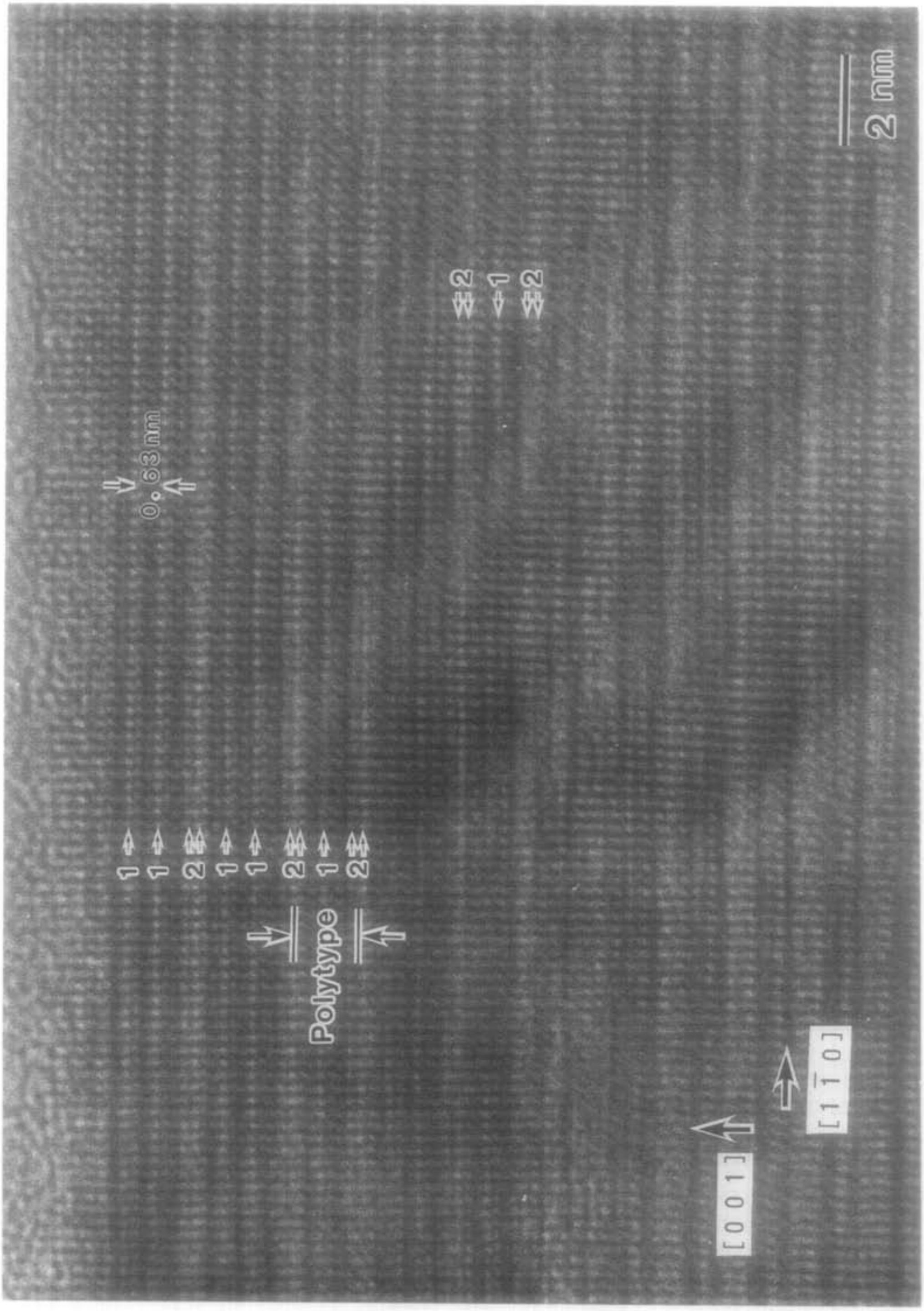

FIG. 1. Typical high resolution image taken from beam incidence of [110]. Small arrows with "1" or "2" indicate V–O layers, and the newly discovered polytypic phase is denoted "Polytype."

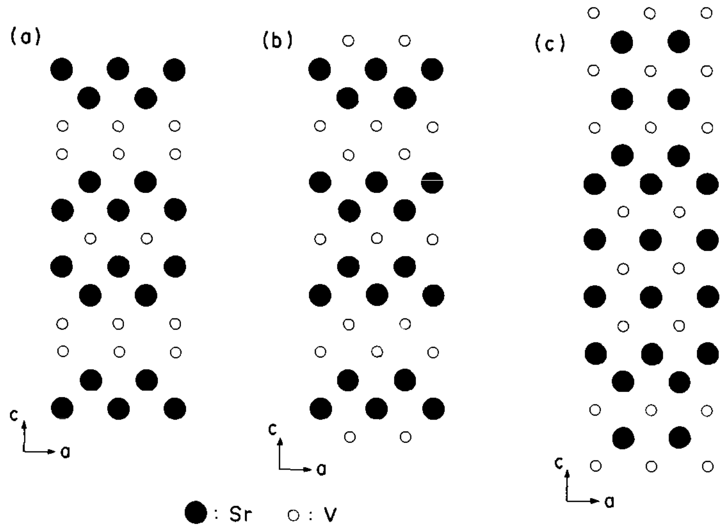

FIG. 2. (a) and (b) show possible models for new polytypic $Sr_4V_3O_{10}$. (c) shows the model of ordinary $Sr_4V_3O_{10}$ as in Ref. (2).

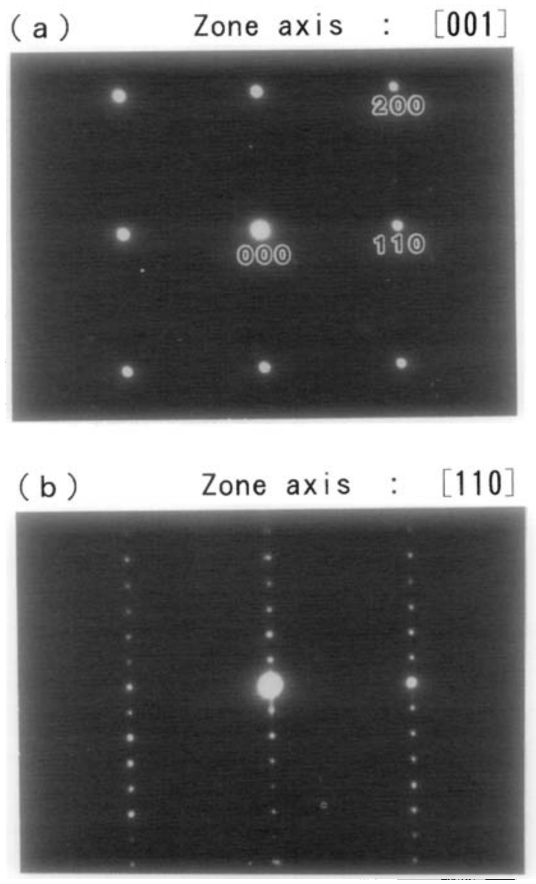

FIG. 3. Diffraction patterns from polytypic $Sr_4V_3O_{10-x}$. Zone axes of (a) and (b) are [001] and [110], respectively. Superlattice reflections are observed in these patterns.

shown in Fig. 1. The authors also estimate that the stacking of the new phase is very similar to that of the ordinary Sr_2VO_4 phase. Moreover, the relation of the stacking between the new phase and the ordinary Sr_2VO_4 phase also is similar to the structural relation between the Y–Ba–Cu–O (1–2–4) phase and the Y–Ba–Cu–O (1–2–3) phase (*7*), because the 1–2–4 phase has an excess Cu–O layer, as the new phase contains an excess V–O layer. In the case of the 1–2–4 phase, double Cu–O layers inserted into two Ba–O layers have oxygen vacancies along the *b*-axis, and this is the reason for the formation of Cu–O fences along the *b*-axis (*7*). Thus, it is possible that the double (V, O) layers in the discovered phase are constructed by the introduction of oxygen vacancies which make V–O fences in the same manner as $YBa_2Cu_4O_8$. Moreover, the oxygen content derived from thermogravimetric study was about $x = 2$ for $Sr_4V_3O_{10-x}$, and this result strongly suggests the presence of such fences. On the other hand, it is also noteworthy that the electron diffraction patterns of this new phase contain weak superlattice reflections, as shown in Fig. 3. The patterns in Figs. 3(a) and (b) were taken from the beam incidence of [001] and [110], respectively. The superlattice reflections are due to a long-range ordered structure, and they can be considered to be associated with some reasons, for example, a kind of ordered oxygen vacancies (*8, 9*). A detailed refinement of the atomic position, especially the oxygen atomic position and occupation, is now in progress.

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References

1. M. Cyrot, B. Lambert-Andron, J. L. Soubeyroux, M. J. Rey, Ph. Dehauht, F. Cyrot-Lackmann, G. Fourcaudot, J. Beille, and J. L. Tholence, *J. Solid State Chem.* **85,** 321 (1990).
2. A. Nozaki, H. Yoshikawa, T. Wada, H. Yamauchi, and S. Tanaka, *Phys. Rev. B: Condens. Matter* **43,** 181 (1991).
3. N. Fukushima, S. Tanaka, H. Niu, and K. Ando, *Jpn. J. Appl. Phys.* **29,** L2190 (1990).
4. R. Ramesh, B. G. Bagley, J. M. Tarascon, S. M. Green, M. L. Rudee, and H. L. Luo, *J. Appl. Phys.* **67,** 379 (1990).
5. Y. Matsui, S. Takekawa, H. Nozaki, A. Umezono, E. Takayama-Muromachi, and S. Horiuchi, *Jpn. J. Appl. Phys.* **27,** L1241 (1988).
6. K. Hiraga, T. Oku, D. Shindo and M. Hirabayashi, *J. Electron. Microsc. Tech.* **12,** 228 (1989).
7. R. J. Nelmes, J. S. Loveday, E. Kaldis and J. Karpinski, *Physica B+, C: (Amsterdam)* **172,** 311 (1990).
8. Y. Matsui, E. Takayama-Muromachi, and K. Kato, *Jpn. J. Appl. Phys.* **26,** L1183 (1987).
9. Y. Kubo and H. Igarashi, *Phys. Rev. B: Condens. Matter* **39,** 725 (1989).