

SYNTHESIS AND STRUCTURE OF COPPER- AND YTTRIUM-RICH $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ SUPERCONDUCTORS

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Copper- and yttrium-rich modifications of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductors have been synthesized using a liquid nitrogen quench followed by annealing. In both types of cation-rich materials the starting material is highly disordered but upon annealing the extra copper or yttrium precipitates out in the form of planar defects normal to the c axis which on annealing at higher temperatures start to coarsen from single plane defects to multiple plane defects and become better ordered normal to the c axis. In all cases X-ray diffraction gives an average orthorhombic structure. The existence of these defects appears to have no effect upon the sharpness of the superconducting transition for specimens annealed to 800°C, leads to a small broadening of the transitions in specimens annealed at 700°C, while the specimens annealed at 300°C show only a hint of superconducting behavior. This supports the view that these materials are one- or two-dimensional superconductors normal to the c axis with only a small contribution to the bulk superconductivity along the c axis.

1. Introduction

From extensive phase diagram studies using primarily X-ray methods, e.g. [1,2], it is now well established that the superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ is a point compound. At the same time, there has also been a number of reports using high resolution electron microscopy of planar defects containing either an extra plane of copper [3-9] and/or rare earths [10,11]. In particular, in our own work on the gadolinium superconductors [8,9], thin film materials [12] and in *one* grain of liquid nitrogen quenched $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ [8] these defects can be very common, and by using a fast quench we have been able to produce trigonal phases with different metal atom ordering [8,13]. Since X-ray diffraction techniques will as a rule be quite insensitive to the presence of planar defects, an unanswered question is whether such defects and cation non-stoichiometry in general

exists undetected in many samples, and whether it plays a role in degrading the superconducting properties either in the short or long term. For instance, additional copper or rare earth elements can be expected in time to precipitate out and if they decorate grain boundaries could lead to long term degradation of the current carrying capabilities or alter the mechanical properties making the boundaries more brittle.

The exact source of the cation non-stoichiometry and planar defects is at present unclear. Van Tenderloo and Amelinckx [5] and Zandbergen et al. [6] have pointed out that copper-rich defects can occur in specimens left in air for several weeks which from our results [8] is due to leaching of the barium from the structure and similar defects can also occur due to mechanical deformation or ion beam damage [8]. Although these processes are possible sources of the defect structures, it does not follow that the only way

that they can be formed is by a damage process. For instance, our original work [14] on the superconductors indicated that order-disorder reactions were possible, and, reinforced by the observation of trigonal phases [8,13], implies that cation disorder may have a more intrinsic source.

In this paper we report a method of preparing both copper-rich and yttrium-rich superconductors which explains the role of additional cations in the perovskite superconductors; they are not simply artifacts or due to damage but represent the early stages of precipitation of excess of either of these cations.

In both cases the extra metal forms planar defects normal to the c axis which show indications of coarsening and ordering when annealed at higher temperatures, very similar to Guinier-Preston zones. The materials appear to follow what is in essence an age-hardening process, with the additional cations precipitating out from a metastable solid solution as planar defects which can be several thousand ångströms in length. Electrical measurements indicate that the superconducting transition is still very sharp even with a very high concentration of these defects.

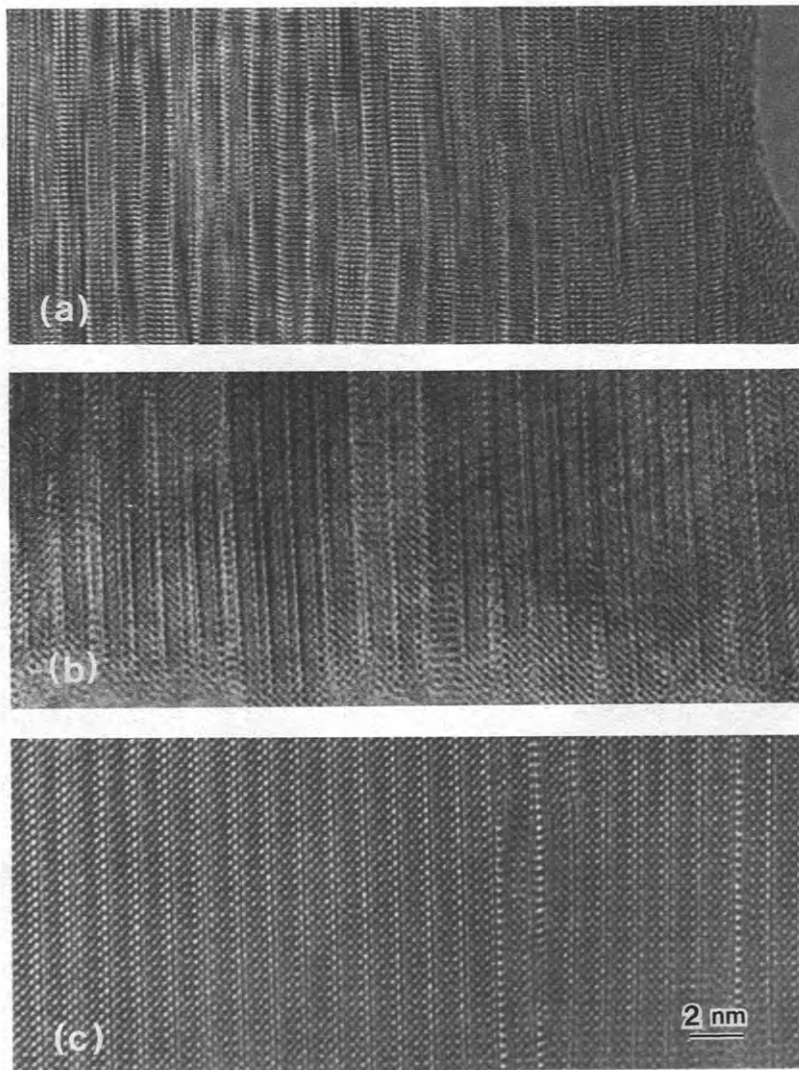


Fig. 1. High resolution images of $\text{YBa}_2\text{Cu}_3\text{O}_7-x$: (a) the as-quenched material; (b) after annealing at 300°C ; and (c) after annealing at 700°C .

2. Experimental method

The starting point of the synthesis was to follow the standard firing/grinding procedure using compositions $Y_{1.1}Ba_2Cu_3O_{7-x}$ and $YBa_{2.2}Cu_3O_{7-x}$ with an annealing temperature of 940°C and an initial firing of 20 hours in air. (We have also used the same procedure for a composition of $YBa_{2.2}Cu_3O_{7-x}$ but to date have not been able to produce barium-rich phases; instead phase separation giving barium copper oxide was observed.) The materials were then liquid nitrogen quenched and three different samples were annealed in oxygen at 300°C for a week, 700°C for 72 hours and 800°C for 48 hours, respectively.

To characterize the specimens, both X-ray diffraction and high resolution electron microscopy were employed. For the X-ray work, a diffractometer with a Cu-K α source was used. For the high resolution electron microscopy specimens were prepared by very gentle grinding between two glass plates (to minimize mechanical deformation), mounted dry onto holey carbon films and then examined using a Hitachi H-9000 electron microscope operated at 300 kV. In general, specimens were freshly prepared before microscopy analysis to avoid problems with water vapor damage of old specimens. Image simulations were performed using the NUMIS suite of programs on an Apollo workstation ring to characterize the materials.

3. Results

The as-quenched material (see fig. 1a) showed a highly defective structure with disorder of the *c* axis periodicity. Based upon our earlier studies of fast quenched materials [8,13] we can understand these results as due to a disordering of the metal atoms in the basic perovskite 3.8 Å unit cell; at 940°C the triple perovskite lattice is not well established but is only established on cooling. There may well be a solid solution range at higher temperatures where either (and probably both) additional copper and yttrium is dissolved in the 123 phase. After annealing to 300°C, (see fig. 1b), the triple perovskite ordering was established. X-ray measurements indicate that this material has an average orthorhombic composition

Table I

Average lattice parameters as determined by X-ray measurements of the various annealed specimens. Note that from the X-ray data alone there is no way of determining that the materials contain numerous planar defects, or that the orthorhombic 300°C annealed material is not a bulk superconductor; it is in fact the "most" orthorhombic material.

	Annealing temperature	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)
Cu-rich	300	3.821	3.885	11.675
	700	3.833	3.880	11.644
	800	3.835	3.885	11.659
Y-rich	800	3.828	3.884	11.655

(see table I). The high resolution results show that there is still substantial disorder with only limited ordered regions. As the material is annealed to higher temperatures (see fig. 1c) the material becomes better ordered and planar defects extending several thousand ångströms normal to the *c* axis are present as shown in fig. 2. This, and all the other electron microscope images herein show the typical structure of the material, rather than that found in only a few grains, and is not an artifact of mechanical deformation or other damage to the material. Analysis of the images (see fig. 3a) indicates that the copper planar defects have the same basic structure as reported elsewhere [7-9], which is shown in fig. 3b, with the two copper planes occurring predominantly in the basal plane between two barium sites (rather than between barium and yttrium) with a translation vector between the two planes of either $\frac{1}{6}[301]$ or $\frac{1}{6}[031]$. The excess yttrium is accommodated in a very similar fashion as shown in fig. 4a with the structure shown in fig. 4b. Although perhaps not completely apparent in the images shown, there is no danger of confusing the copper- and yttrium-rich defects; the latter show substantially higher contrast and occur at different positions with respect to the adjacent perovskite framework. For the 800°C annealed copper specimens there are indications of coarsening leading to defects composed of three copper planes as shown in fig. 5. Although we cannot rigorously prove this interpretation from the image contrast, both the spacing, contrast level and the absence of single plane copper defects in the region of these larger defect structures support this interpretation.

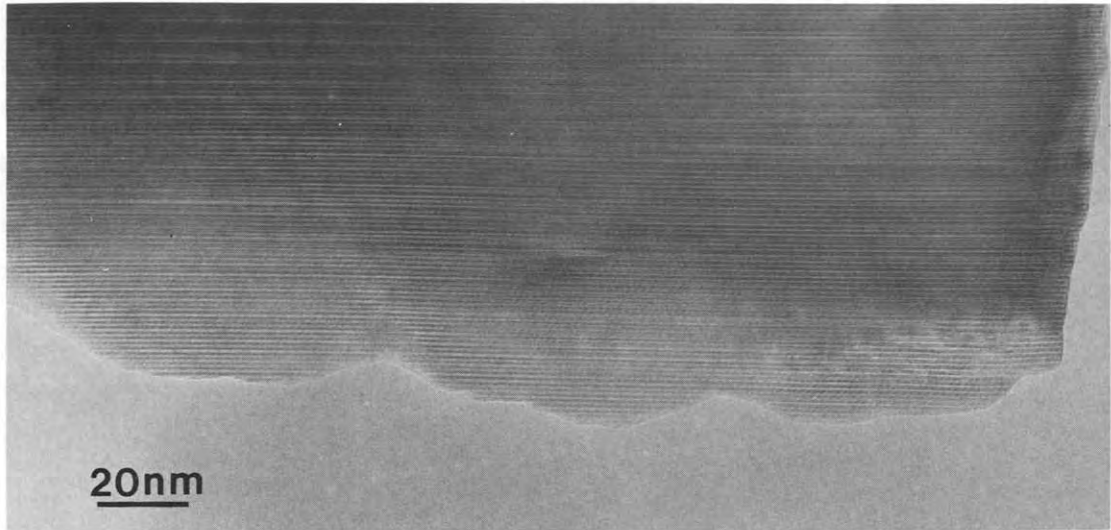


Fig. 2. Low magnification image of the copper-rich material annealed to 800°C. The image shows a typical region containing numerous copper-rich defects running across the figure. The planes are continuous over at least several thousand ångströms.

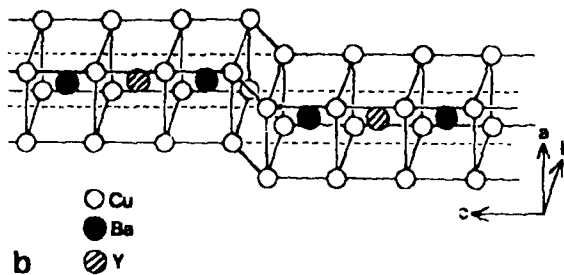
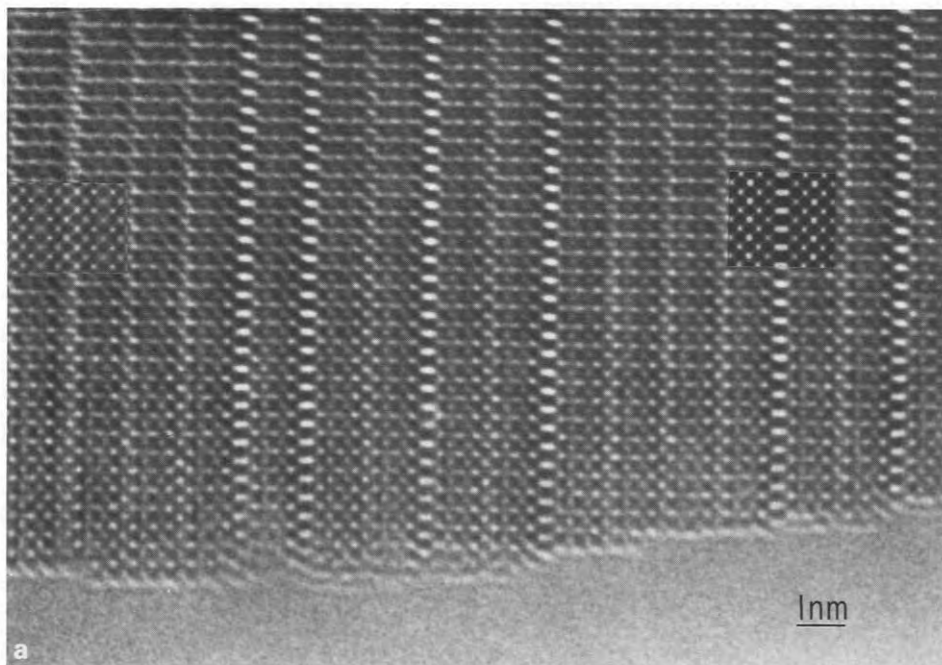


Fig. 3. High resolution image (a) and structure model (b) of the copper-rich defects taken from the 800°C annealed specimen with a calculated image inset. The image contrast correlates well with that reported elsewhere [7-9].

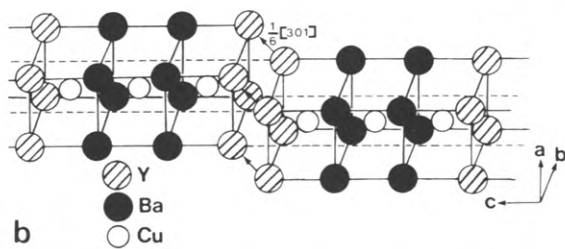
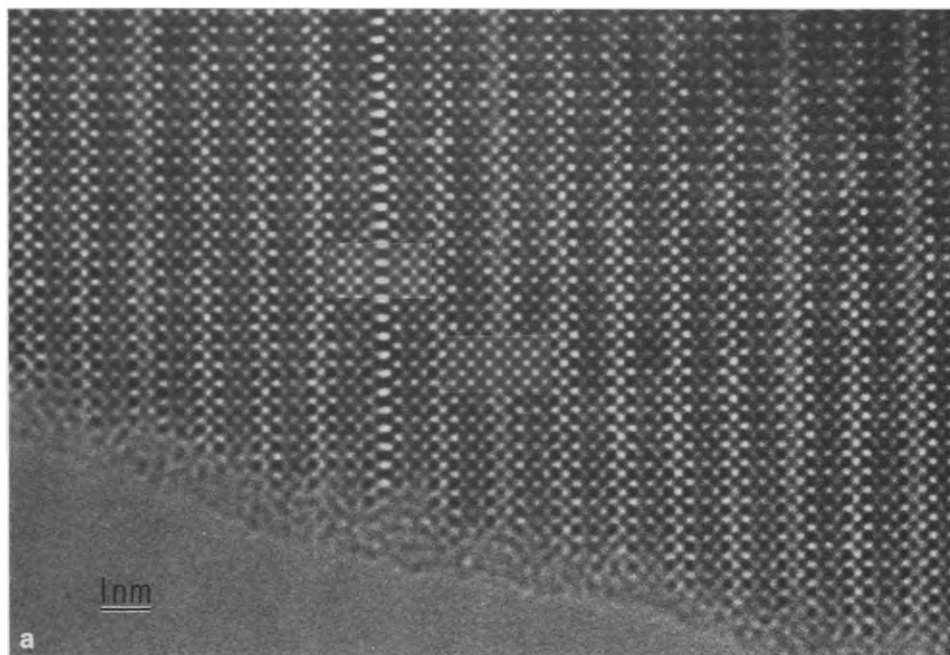


Fig. 4. High resolution image (a) with image simulations (inset) and structure model (b) for the yttrium-rich defects.

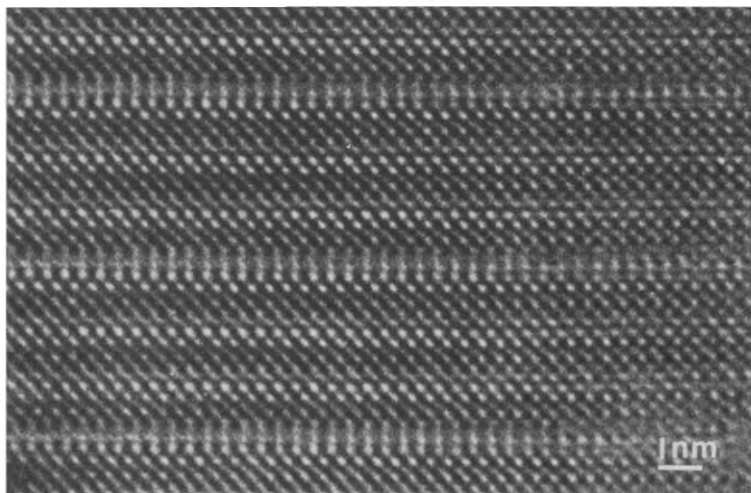


Fig. 5. Area of the 800°C annealed copper-rich specimen showing wider defects which contain 3 copper planes.

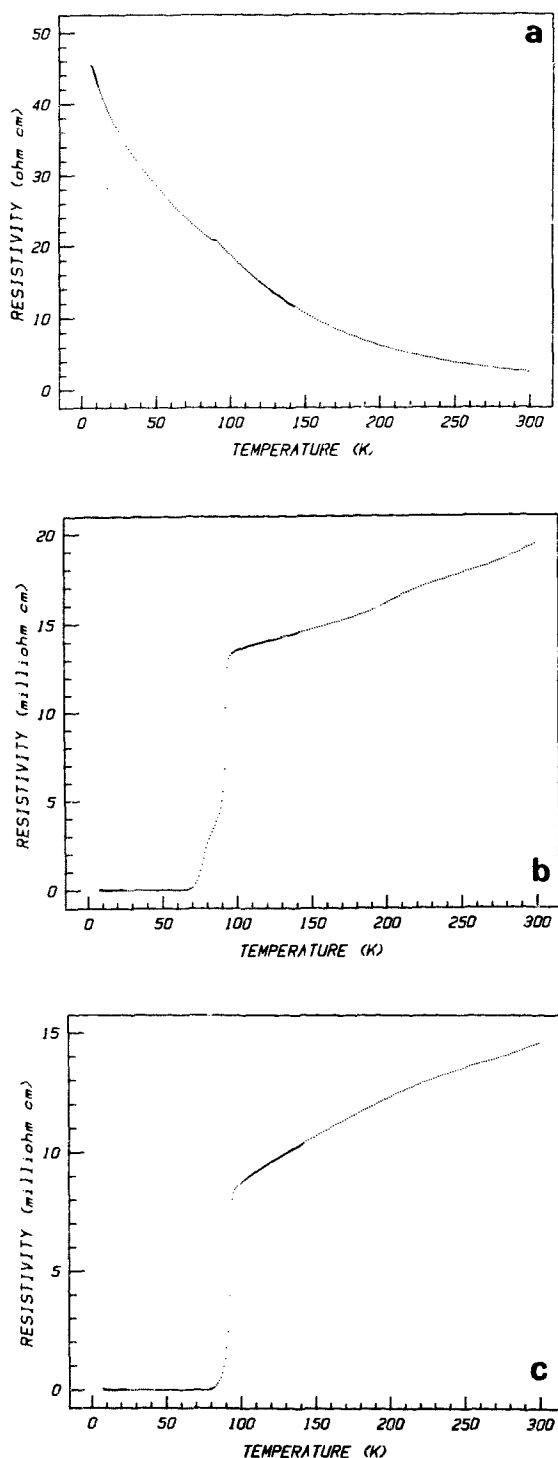


Fig. 6. Resistivity measurements: (a) 300°C annealed specimen, (b) 700°C annealed specimen, and (c) 800°C annealed specimen.

tation. The density of the copper- or yttrium-rich planes was consistent with the initial starting composition, and the total excess cation concentration appeared to remain essentially constant during the annealing. However, we cannot completely rule out the possibility that a small fraction of the excess cations has phase separated, but we can definitely state that the majority of the excess cations have not. For instance, in the case of the yttrium-rich material, substantial quantities of the green phase ($\text{Yb}_2\text{BaCuO}_5$) were not apparent in either X-ray or electron diffraction patterns, and the material was primarily "single phase" $\text{Y}_{1.1}\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$.

In many respects the most surprising result was the width of the superconducting transition using four point resistance measurements on fresh pellets which is shown in fig. 6. For the 300°C anneal the material is almost completely semiconducting, with only a small indication of a superconducting transition around 90 K, while the 700°C samples show a small tail and in the 800°C samples the transition is very sharp. Experiments to analyze in more detail the superconducting properties from Meissner measurements are in progress which may reveal more information.

4. Discussion

One clear conclusion from this work is that copper and/or yttrium planar defects may be very common in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconducting system, and may well be a source of systematic errors in property measurements. For instance, we feel that the conclusions of experiments where other elements have been substituted into the superconductors, e.g. ref. [15], have to be considered as suspect since it is not clear that these elements have in fact replaced the copper; they may be present as planar defects or even precipitates and it does not appear that this has been tested. The fact that annealing at 800°C for 48 hours does not eliminate (by phase separation) the excess metal explains their quite common observation by high resolution electron microscopy. The surprising result that we see no change in the superconducting transition width for the 800°C specimens implies that the superconduction is quite strongly localized normal to the *c* axis, and is not effected by the existence

of disruptions to the lattice 10 or 20 Å away. The quenching of the transition in the 300°C samples indicates that disrupting the ordering normal to the *c* axis strongly effects the bulk superconductivity, although there may be small superconducting domains which are electrically disconnected. Further experiments to explore this and, among other properties, the mechanical characteristics of these materials are in progress.

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References

- [1] G. Wang, S.-J. Hwu, S.N. Song, J.B. Ketterson, L.D. Marks, K.R. Poeppelmeier and T.O. Mason, *Adv. Ceram. Mater.* 2 (3B) (1987) 313.
- [2] R.S. Roth, K.L. Davis and J.R. Dennis, *Adv. Ceram. Mater.* 2 (1987) 303.
- [3] H.W. Zandbergen, G. Van Tenderloo, T. Okabe and S. Amelinckx, *Phys. Status Solidi*, 102 (1987) 45.
- [4] G. Van Tenderloo, H.W. Zandbergen, T. Okabe and S. Amelinckx, *Solid State Commun.*, 63 (1987) 969.
- [5] G. Van Tenderloo and S. Amelinckx, *J. Electron Microsc. Techn.* 8 (1988) 285.
- [6] H.W. Zandbergen, R. Gronsky and G. Thomas, *Phys. Status Solidi a*, preprint.
- [7] H.W. Zandbergen, R. Gronsky, K. Wang and G. Thomas, *Nature* 331 (1988) 596.
- [8] L.D. Marks, D.J. Li, H. Shibahara and J.P. Zhang, *J. Electron Microsc. Techn.* 8 (1988) 297.
- [9] H. Shibahara, S.J. Hwu, K.R. Poeppelmeier and L.D. Marks, *J. Solid State Chem.*, submitted.
- [10] A. Ourmazd, J.C. Spence, J.M. Zuo and C.H. Li, *J. Electron Microsc. Techn.* 8 (1988) 251.
- [11] H.W. Zandbergen, G.F. Holland, P. Tejedor, R. Gronsky and A.M. Stacey, *Adv. Ceram. Mater.* 2 (1987) 688.
- [12] H. Shibahara, D.J. Li, J.P. Zhang and L.D. Marks, in preparation.
- [13] D.J. Li, J.P. Zhang, J.P. Theil and L.D. Marks, in preparation.
- [14] L.D. Marks, J.P. Zhang, S.-J. Hwu and K.R. Poeppelmeier, *J. Solid. State Chem.* 69 (1987) 189.
- [15] G. Xiao, M.Z. Cieplak, A. Gavin, F.H. Streitz, A. Bakhshai and C.L. Chien, *Phys. Rev. Lett.* 60 (1988) 1446.