High resolution TEM study of ceramic BaO·Pr₂O₃·4TiO₂

F. AZOUGH

Materials Science Centre, University of Manchester/UMIST, Grosvenor Street, Manchester, M1 7HS, UK

A. C. WRIGHT

Advanced Materials Research Laboratory, North East Wales Institute of Higher Education, Mold Road, Wrexham LLII 2LW, UK

R. FREER

Materials Science Centre, University of Manchester/UMIST, Grosvenor Street, Manchester, M1 7HS, UK E-mail: robert.freer@umist.ac.uk

Ceramic specimens of BaO·Pr₂O₃·4TiO₂ (Ba_{4.5}Pr₉Ti₁₈O₅₄) were prepared by the mixed oxide-route. The single phase products were examined by High Resolution Transmission Electron Microscopy (HRTEM). Orthorhombic symmetry, with cell parameters $a \sim 22.2$ Å, $b \sim 12.2$ Å and $c \sim 7.6$ Å, was confirmed. On the basis of space group *pnam* (No. 62) and the crystal structural data of Rawn *et al.*, good agreement was obtained between the experimental HRTEM images and images simulated by the multislice method. © 2001 Kluwer Academic Publishers

1. Introduction

Dielectric ceramics in the system $Ba_{6-3x}Ln_{8+2x}$ Ti₁₈O₅₄ exhibit high dielectric constant ($\varepsilon_r = 80-100$), low loss (Qxf = 6000–9000) and dielectric properties that are stable with respect to temperature; These properties make the ceramics suitable for electronic applications, particularly at microwave frequencies [1–7]. The compound BaO·Pr₂O₃·4TiO₂ is a member of this solid solution family. There are a number structural models [2, 7–14] for the system and although these various models differ in their detail, there is consensus that the crystal structure belongs to the tungsten bronze structure family and essentially consists of a three dimensional framework of corner-sharing perovskite-like TiO₆ octahedra joined according to a pattern similar to that of tungsten-bronze.

Gens *et al.* [8] were the first to suggest possible space groups for the solid solution phases. Based on the systematic absences observed in single crystal electron diffraction patterns of BaO·La₂O₃·4TiO₂, they reported the probable space groups as pba2 (No. 32) or pbam (No. 55). Matveeva *et al.* [9] later confirmed these results by single-crystal X-ray diffraction and X-ray spectroscopic studies of single crystal Ba_{4.5}Pr₉Ti₁₈O₅₄, reporting the same space groups. Based on data for 1990 measured peaks, Matveeva *et al.* [9] calculated atomic positions using space group pba2. Approximately 400 additional peaks, corresponding to a doubling of the period along the *z* direction were also identified, but omitted from the crystal refinement. A similar model was subsequently proposed by Roth *et al.* [10]. Ohsato *et al.* [12] also detected superlattice X-ray diffraction peaks in studies of $Ba_{3.75}Pr_{9.5}Ti_{18}O_{54}$ crystals and reported an orthorhombic lattice. The space group of their fundamental lattice agreed with that of Matveeva *et al.*, but that of the doubled cell was reported to be either pbn2₁ (No. 33) or pbnm (No. 62). By the use of X-ray diffraction methods Kolar [7] confirmed the findings of Matveeva *et al.* [9].

Azough et al. [1] studied Ba_{4.5}Pr₉Ti₁₈O₅₄ ceramic by electron diffraction. By observing systematic absences in microdiffraction patterns, they also determined the space group to be either $pna2_1$ (No. 33) or pnam (No. 62). Since these two space groups have different point symmetries, convergent-beam electron diffraction (CBED) parallel to [100] was used to distinguish between them. They concluded that the observed 2 mm symmetry of the zero-order Laue zone (ZOLZ) and the whole pattern confirmed that the space group must be pnam (No. 62). Ubic et al. [15] investigated the Nd- analogue of the solid solution in polycrystalline form by electron diffraction. They observed weak extra reflections in electron diffraction patterns, possibly due to small breaks in symmetry, and therefore suggested that the space group may be pb21m (No. 26). However, these weak extra reflections may arise from double diffraction. Rawn [13], performed Rietveld analysis of powder X-ray diffraction data of $Ba_{4.5}Ln_9Ti_{18}O_{54}$ (Ln = La and Gd) and determined the space groups to be $pba2_1$ (No. 33) for the La analogue and pnma (No. 62) for the Gd analogue. Rawn et al. [2] subsequently reported the atomic



Figure 1 Schematic representation of the crystal structure of $Ba_{(6-2x)}Sm_{(8+2x)}Ti_{18}O_{54}$ (x = 0.27) according to Rawn et al. [2].

positions for $Ba_{(6-3x)}Sm_{(8+2x)}Ti_{18}O_{54}$ (x = 0.27 using space group pnma (No. 62). The schematic representation of the structure proposed by Rawn *et al.* [2]. is shown in Fig. 1. Between the network formed by the corner-sharing Ti-octahedra are three types of channels, pentagonal, tetragonal and triangular. In general, rare earth ions occupy the rhombic channels, Ba ions fill the pentagonal channels and the remaining Ba ions share the rhombic channels. The triangular channels are empty [16].

Based on the atomic positions reported by Rawn *et al.* [2] and the space group pnam deduced by Azough *et al.* [1] we have simulated TEM images for $Ba_{4.5}Pr_9Ti_{18}O_{54}$ by the multislice method and compared results with experimental images.

2. Experimental procedures

Ceramic samples were made by the mixed oxide-route. Powders of BaCO₃, Pr₆O₁₁, and TiO₂ (Fluka Chemicals, England) were mixed in the required proportions and wet milled for 12 hours. The mixture was calcined at 1100°C for 4 hours and wet milled again for 12 hours. After drying, the powders were pressed (uniaxially) into discs of 16 mm diameter, sintered in air in the temperature range 1350°C to 1450°C and cooled at a rate of 120 C h⁻¹. Products were examined by X-ray powder diffraction using Cu K_{α} radiation (Philips PW 1800 with horizontal goniometer). Scanning electron microscopy with energy dispersive spectroscopy (Philips 505 with EDAX) was used to assess sample homogeneity. For transmission electron microscopy (TEM) samples were prepared in two ways: (i) discs of ceramic were thinned mechanically and then ion beam thinned (ION TEC, TEC 791), or (ii) pellets were crushed and ground in an agate mortar and pestle. For the latter, particles were deposited on a carbon coated copper grid. A Phillips EM430 Transmission Electron Microscope was used for lattice imaging and electron diffraction studies. Lattice images were obtained at an accelerating voltage of 300 keV by the Many Beam Imaging (MBI) method. In order to interpret the high resolution images, image simulations were prepared by the multislice method [17] using the HRTEM module of the Cerius2 package of MSI Inc. (ver. 3.0) which is an implementation of the well-known multislice technique [17]. For the [010] zone, Fourier coefficients out to 0.4 nm (96 by 192 'beams') were included to generate a sequential set of three different projected potentials each with a slice thickness of 0.255 nm. The multislice iteration retained beam indexes out to 10 by 17 within the internal 'aperture' of the algorithm. No absorption potentials were included in the calculation. Images were calculated over a range of crystal thickness (integral multiples of the crystal unit cell only) and range of defocus (0 to -110 nm) for comparison with the experimental data; a combination of manufacturer's data for the EM430 TEM, i.e. spherical aberration coefficient, $C_s = 1.2$ mm, experimental data for beam convergence (0.7 mrad) and calculated focus spread (10 nm) were employed in the simulation. Beam convergence and focal spread effects were approximated using the mutual transfer function rather than by image averaging. An objective aperture size of 0.075 nm^{-1} was used.

3. Results and discussion

X-ray diffraction and SEM analyses confirmed that the samples were single phase with the expected composition.

Selected area diffraction patterns (SADP) studies confirmed the orthorhombic crystal structure.



Figure 2 (a,b,a) experimental electron diffraction patterns along [010], [001] and [100] respectively; (d) simulated diffraction pattern for [010] orientation.



Figure 3 TEM image showing the presence of anti-phase domain boundary and a planar fault.

Fig. 2a,b,c shows electron diffraction patterns obtained for directions parallel to the three main crystallographic axes. The calculated lattice parameters are $a \sim 22.2$ Å, $b \sim 7.6$ Å and $c \sim 12.2$ Å. The simulated diffraction pattern for the [010] orientation is presented in Fig. 2d; there is good agreement with the experimental diffraction pattern (Fig. 2a).

A low magnification TEM image of the ceramic is shown in Fig. 3. No second phase was observed and

EDS analysis of individual grains confirmed sample homogeneity. Two features were observed in the grain shown in Fig. 3; a planar fault running across the grain and anti-phase domain boundaries. The presence of the anti-phase domain boundaries (APB's) indicates the occurrence of an order-disorder transformation. The latter arises by a nucleation and growth mechanism, and causes the doubling of the shortest axis. Details of the planar fault are shown in Fig. 4. It can be seen that the



Figure 4 HRTEM image of the planar fault (Fig. 3) showing a displacement vector of c/2.



Figure 5 TEM image showing anti-phase boundaries.

fault (possibly an order-disorder transformation twin) has a displacement vector of c/2. Fig. 5 is a higher magnification TEM image of a grain showing anti-phase domain boundaries. Using darkfield imaging we have deduced that these anti-phase domains have a displacement vector b/2 [1].

Fig. 6a,b,c shows experimental HRTEM images of the ceramic for [010], [001] and [100] orientations. The experimental images were taken close to the Scherzer setting (-735 Å for the instrument). This was achieved via knowledge of both the step size (60 Å) and the number of steps away from the minimum contrast at the specimen edge. These images enable the octahedral chains (Fig. 6b and c) and the cavities (Fig. 6a) to be viewed.

Detailed simulation studies concentrated on the [010] orientation, containing Ti-octahedra, and the pentago-

nal and rhombic channels (occupied by Ba and Pr). The simulated images for [010] orientation at two thickness of unit cell, i.e. one cell (7.56 Å) and 7 unit cell (53.4 Å), are shown in Fig. 7a,b in the defocus range of -400 Å to -800 Å. For both thicknesses there is a good match with the experimental image (Fig. 6a). The best match is for the thickness of 1 unit cell in the defocus range -600 Å to -800 Å. This defocus range includes the Sherzer setting at which the experimental image was obtained.

A simulated projected potential, showing electron densities, for $Ba_{4.5}Pr_9Ti_{18}O_{54}$ along [010] is presented in Fig. 8. The unit cell is outlined and the positions of ions are marked.

The experimental image for the [010] direction (from Fig. 6a) and the corresponding simulated image for a thin crystal (Fig. 7b, -700 Å) can be compared with the



(a)

Figure 6 (a,b,c) HRTEM images for [010], [001] and [100] orientation respectively. (Continued.)

100	Same	100	-			-			Contraction of the		S. and	710	See.	gane.	Seni:	Ser.	See	340		100	-	Cardina Cardina	and the second	ALC: NO
46	dere.	See.									1.00	1203	Server.	1004	Arres.	30.00		1.10		60				1
10	-Jone .	1.1.1						, mil		10000		100	and .	me	and a	and.	See		* 1	100	220		22.2	
100	Sec.	1000	(Dens)		1-5				1000	See		2-00	100	10.00		200	And a	ALC: N		100		1.000	3.28	30
	2000	Sender.	land.						1.000	(1990) (1990)	(unit	a meta	1000			100	1000	1000				1.16.2	200	100
20	1.00	(And)			1	-			ಿಂಗ್	1000		Served.	-		i antis	30.42	See.				Jest	1.00	1000	-
200	3000	Sente:	100						61 C - 2		2 - M	8 B	g mod	5.4.5	5 M B	2.2	125				6. 54	1000	and a	-
	100		Same .		1.2.3		4	1	0.446		25.2	6 - Sec.	General		1000	1000		1.000		100	and the second	6 A 10	week.	15.34
- 65	3000	Sere .	James .		0.00			See		And a	100		100	200		200	194	and the			300	(all to a	100
	Sec.	1000	diam'r.	1000			1	Sec.	Sec. 1	Abra		100	-	100	100		-				10.00	Control of	and the second	10.00
1	276	100	-	-				6.73	300	2000	200	See	Ser.	1000	5	e entre	200	1000		1.00	<u> </u>	and the	met for	pre
20	Sec.	1000	1.00	Cont 2	1	0.4		S	See.	1000	100	Same.	20446	723	100		1.44			1.14	Contra 1	10.00	14000	10.00
25	200	200	1000			1000			204	(and	2580	Same.	auth.	Sec.		1000			1000	2.00	200	6-62	848 See	00
22	22		1000	-	(margin		30.00	3 m 2	Sector	1010	Serie .	3946.	100					1.0		-			100	1
22	200	50	(Posts)	(area)		1000	200	1000		1000	Ser.	1000	1000						See.	Ser			100	
-	-	See.	<u>pres</u>	i neg		5B	and a	100	1000	100	Same	Server.	Ares 1	F	6. A		1.1		224	2	100		1000	and a
ALC: N	See.	met	100	1000			440	100	1000	200	200	1000			1		23						200	in al
MR.	3.0	Sec.	and a	100	200	200	201	Ser.	200	923	200	Ser.	and .		See. 3					200			245	de
100	- pater	1400	Sec.	And a	100	Sec.	100	See.	1000	22	200	1000	6546		Sec. 1							1.20#	200	3.0
and the	Right .	4401	and "	Bans (5.462	100	Case:	900	200	100	100	1000	6 B	and a	(mark)	in and		Sec.			100	1.3694	100	304
660	181	100	Serie.	The state	dent."	Sea.	1001	-	See.	Sere	200	The	See 8	600 C	0			1946		100		1.00		1.198
10 C	1944	See.	Sere .	100	3982	348	gent.	10%	Sec	Seat.	100	2000	0,10	and a	100	Sec. 2		100		100	100.00			100
85.	1000		and .	Acres	100	Server.	20.00	1000	Sec.	1865	20	100	200	1000	80.00	50	See.	100	2.746	1.00		5 A 4	100	(SP)
1400	South !	and a	19th Car	100	Personal States	COMP.	1000	300	See.	3.00	300	1000	1000	1000	0.46	2-2	100	a series		1.0	62. vi	1.000	100	20
350	and I	0.5	100	100	940	-99907	39445	1000	and a	(mark	-	and .	dee	100	202	100	See.	100		2.0	1.0	8- CS		100
201	Sec. 1	200	23	1000	100	100	100	3000	Seat.	1000	200	7996	3.96/	140	100	100	0.00				201-1			600
2/9	100	10.00	20	220	220	1223	Same .	200	300	1000	(mark)	HART.	april.	3746	Sect	14.4		100		S -	20 m	and the second	197	-
	2221	100	20	1000	200	100	100	25	100	1000	1000	are.	3.00	100	SHC.	2000	Seale.					98 - I	100	
a	200	200	620	620	22	22	25	100	200	100	1996	1000	34	1000	100	346	10.0	кс (1000	-
	March .	Same	Sec.	200	100	20	222	20	1000	1000	300	1000	35	100	Mar.	1996	Second							200
- /	A COMPANY	Sec.	GAR C	200	Same?	220	100	100	1000	2.3	1000	0000	6.5	100	100	100	1.00						AN.	and a
100	start-	Sec.	1966	Sec.	See. 3	Sec.	Chert	200	Sec.	See	Saul	1000	922	1000	22.	1000	Sand	See.			See.		1000	1,00
b	20.00	100	Select	Same)	Seat 1	5.16	Gran!	See.	Cane?	200	600	1000	22	000	22.5	200	1000	25	Since	a Series		1.00	3.2	300
100	Sec.	Sec.	me	and .	MAN?	der.	Solet	and -	and	Sec.	atter	100	1000	200	620	-	100	100	1000	and the second		1000		1
	19981	Seller 1	100	200	1.00	(mex.)	Send.	196R.	Same (1000	CRAP!	Sector	See.	100		222	222	100	1.00		Cum	1000	100	
and the second second	_												and the second s	the second se	the second se	the second se	And Personnelling	A REAL PROPERTY.	and the owner where the	A 8 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1				
100	Ser.	a	1000	parts .	ANS	194002	345		300	100	CORNEL,		See.	1000	Server.	Same .	3245	1000		all the second	100		5 m 18 m	100
4	and a	a	-	-	1-81	100	ČĀ.	12	and a	12	-		-	and the second	-	ANT.	1	1			5-	27		
	144	a	-	E.	50 A	The second		100	教室		140	-	112	-	115	業業業	II.	10	2.2.2					H
NIN.	18457	a	1888	1 FT N	50 A	NA I	14 14 14 14 14 14 14 14 14 14 14 14 14 1	199	(TH)	No. CO	110	1.1	1241		1324	INT	A T A A	ILLI I	1293					THE L

(b)

<u>b</u> <u>- 50 Å</u>

Figure 6 (Continued.)

-400

-500

Figure 7 Computer simulated TEM images for $Ba_{4.5}Pr_9Ti_{18}O_{54}$ as a function of defocus of the objective lens for (a) a slice thickness of 53.49 Å, and (b) a slice thickness of 7.64 Å.

-700

-600

Figure 8 Projected potential (electron density) for Ba_{4.5}Pr₉Ti₁₈O₅₄ along [010].

projected potential (Fig. 8) to enable the Ba/Pr sites to be identified. In Fig. 9, the "best fit" simulated image (Fig. 9b; based on 2×2 unit cells) is superimposed on the experimental image (Fig. 9a); the inferred sites for Ba, for Pr, and Ba/Pr are highlighted within a single unit cell. This arrangement is consistent with space group pnam (No. 62) [1, 2, 9] and the structural model of Rawn *et al.* [2].

-800

Ba sites Ln sites Ba/Ln sites

Figure 9 TEM images for $Ba_{4.5}Pr_9Ti_{18}O_{54}$ along [010] orientation: (a) experimental image, (b) simulated image (for 2×2 unit cells) for thickness of 1 unit cell and defocus of -700 Å is superimposed on top of experimental image (a). Note good match between (a) and (b). The inferred sites for Ba, Ln and Ba/Ln are highlighted within a single unit cell on the experimental image (a).

4. Conclusions

 $Ba_{4.5}Pr_9Ti_{18}O_{54}$ has an orthorhombic crystal structure with a doubled unit cell in the shortest axis, possibly due to an order-disorder transformation. This idea is supported by the observation of anti-phase domain boundaries.

Simulation of TEM images were generated for a variety of crystal thicknesses. Good agreement was obtained with the experimental images for selected focus conditions. For $Ba_{4.5}Pr_9Ti_{18}O_{54}$, the results are consistent with the space group pnam (No. 62) [1, 2, 9] and the structural model of Rawn *et al* [2].

Acknowledgement

The support of the EPSRC through research grant GR/L33306 is gratefully acknowledged.

References

- 1. F. AZOUGH, P. E. CHAMPNESS and R. FREER, J. Appl. Crystallogr. 28 (1995) 557.
- 2. C. J. RAWN, D. P. BIRNIE III, M. A. BRUK, J. H. ENEMARK and R. S. ROTH, *J. Mater. Res.* **13** (1998) 187.
- 3. R. L. BOLTON, PhD Thesis, University of Illinois (Urbana, Illinois, USA, 1968)
- KOLAR, Z. STADLER, S. GABRSCEK and D. SUVOROV, Ber. Dtsch. Keram. Ges. 55 (1978) 346.
- 5. K. WAKINO, K. MINAI and H. TAMURA, J. Amer. Ceram. Soc. 67 (1984) 278.

- 6. D. S. NISHIGAKI, H. KATO, S. YANO and R. KAMMURA, *Am. Ceram. Soc. Bull.* **66** (1987) 1405.
- D. KOLAR, S. GABRSCEK and D. SUVOROV, in Proceedings of the Third European Ceramic Society Conference (Madrid 1993), edited by P. Duran and J. F. Fernandez (Faenza Editrice Iberica, 1993) Vol. 2, p. 229.
- A. M. GENS, M. B. VARFOLOMEEV, V. S. KOSTOMAROV and S. S. KOROVIN, *Russ. J. Inorganic Chem.* 26 (1981) 482.
- 9. R. G. MATVEEVA, M. B. VARFOLOMEEV and L. S. IUYUSHEENKO, *Zh. Neorg. Khim.* **29** (1984) 17.
- R. S. ROTH, F. BEACH, A. SANTORO, K. DAVIS, J. L. SOUBEYROUX and M. ZUCCHI, Acta Cryst. A43 (1987) C138.
- F. AZOUGH, P SETASUWON and R. FREER, in "Materials and Processes for Wireless Communications," edited by T. Negas and H. Ling (American Ceramic Society, Westerville, OH, 1995) p. 215.
- 12. H. OHSATO, S. NISHIGAKI and T. OKUDA, *Jpn. J. Appl. Phys.* **31** (1992) 3136.
- C. J. RAWN, in Proceedings of Conference 'Electroceramics V', Aveiro, Portugal, 1996, Vol. 2 (University of Aveiro, 1996) p. 67.
- 14. H. OKUDERA, H. NAKAMURA, H. TORAYA and H. OHSATO, *J Solid State Chem.* **141** (1999) 336.
- 15. R. UBIC, I. M. REANEY and W. E. LEE, J. Amer. Ceram. Soc. 82 (1999) 1336.
- 16. H. OHSATO, A. KOMURA, Y. TAKAGI, S. NISHIGAKI and T. OKUDA, Japanese J. Appl. Phys. 37 (1998) 5357.
- 17. J. M. COWLEY and A. F. MOODIE, *Acta Cryst.* **10** (1957) 609.

Received 1 December 2000 and accepted 23 July 2001