JOURNAL OF
Materials
CHEMISTRY
Communication

A new relaxor ferroelectric, $Ba_2LaTi_2Nb_3O_{15}$

Caroline A. Kirk, Martin C. Stennett, Ian M. Reaney and Anthony R. West

Department of Engineering Materials, The University of Sheffield, Mappin Street, Sheffield, UK S1 3JD

Received 14th May 2002, Accepted 25th June 2002
First published as an Advance Article on the web 4th July 2002

Ceramic samples of the tetragonal tungsten bronze $Ba_2LaTi_2Nb_3O_{15}$, containing B-site disorder of Ti,Nb, have a maximum permittivity of 250–300 at $T_c \approx 200$ K and frequency-dependent permittivity below T_c, characteristic of relaxor behaviour.

There has been much recent interest, particularly in the publications of Chen and co-workers,[1,2] in a number of tetragonal tungsten bronze (TTB)-related compositions in the systems BaO–RE_2O_3–TiO_2–$(Nb,Ta)_2O_5$ (RE = rare earth) as possible high permittivity microwave dielectrics. It is not clear whether there is a single TTB composition in each system, or whether a range of solid solutions exists; a number of compositions have been synthesized and their properties measured. The electrical properties all appeared to show permittivities at microwave frequencies in the region 80–170; however, samples were often multiphase. Structural studies by Rietveld refinement of X-ray data have shown inconsistent results; two space groups were used. In addition to these recent reports on microwave dielectric properties, the phase $Ba_2LaTi_2Nb_3O_{15}$ is included in a tabulation of possible ferroelectric materials by Lines and Glass.[3] The Curie temperature, T_c, is given as −80 °C, but the data carry a question mark, indicating their uncertainty.

Our interest is to synthesise new materials with high permittivity, both ferroelectric and non-ferroelectric, and to understand the factors that control the properties so as to permit their fine tuning. Given the possible existence of such phases in the systems BaO–RE_2O_3–TiO_2–$(Nb,Ta)_2O_5$ with TTB-related structures, we have commenced a systematic study of phase formation, crystal structures and electrical properties. Here, we report permittivity data over a wide temperature range on a ceramic composition, $Ba_2LaTi_2Nb_3O_{15}$, which show it to be a low temperature relaxor ferroelectric. At higher temperatures, >200 K, the material exhibits temperature-dependent permittivity and a Curie–Weiss response, consistent with incipient ferroelectric behaviour and a large positive temperature coefficient of permittivity, likely to cause difficulties in its possible application as a microwave dielectric.

Samples were synthesised by solid state reaction in Pt boats of mixtures of $BaCO_3$, La_2O_3, Nb_2O_5 and TiO_2. Dried reagents were weighed, mixed and fired at 1000 °C for 4 h to eliminate CO_2, followed by 1250 °C overnight, 1300 °C overnight and 1350 °C for 12 days. After each firing stage, the samples were removed from the furnace, cooled and ground. During final firing at 1350 °C, the samples were also removed after 4 days and reground. For permittivity measurements, pellets of crushed powder were pressed uniaxially at 1 ton cm^{-2} and sintered at 1350 °C for 2 days. X-Ray powder diffraction (XRD) measurements on powdered and crushed pellet fragments were carried out with a Stoe Stadi P diffractometer, employing Cu-Kα_1 radiation and using a small linear position-sensitive detector. To collect data suitable for Rietveld refinement, a slow step-scan was employed with a total collection time of 14 h over the 2θ range 10–120°. The GSAS Rietveld refinement package was used.[4]

For impedance measurements, electrodes were fabricated from gold paste, which was coated on to opposite pellet faces, dried and fired at 800 °C. These were attached to the Pt leads of a 2-terminal conductivity jig, which was inserted into a horizontal tube furnace or, for low temperature measurements, into an Oxford cryostat. Permittivity data at selected frequencies were extracted from frequency scans of the sample impedance using Solartron 1250/1286 instrumentation. Data were corrected for the blank, parallel capacitance of the sample holder.

The XRD data for $Ba_2LaTi_2Nb_3O_{15}$ were fully indexed on a tetragonal unit cell; $a = 12.4317(6)$, $c = 3.9262(2)$ Å. All peaks were indexed and there was no evidence of any second phase(s) present. We conclude, therefore, that the sample was phase-pure by XRD.

Rietveld refinement of the XRD data was carried out initially in the space group *P*4/*mbm* (no. 127), with the final parameters listed in Table 1 and a profile fit in Fig 1. The refinement is satisfactory in all aspects. The B sites appear to contain Ti and Nb in statistical ratio. For the framework sites, it is impossible to distinguish between La and Ba from XRD data, since these have essentially the same scattering power. However, previous studies[5] using neutron diffraction on related compositions indicated that the A sites are fully ordered. In addition, bond valence calculations and inspection of the bond lengths Table 2 both point to a fully ordered structure with La on the 2a sites and Ba on the 4g sites.

Space group *P*4/*mbm* has mirror planes at $z = 0, 0.5$. There is no evidence from the U_{iso} values that any of the atoms should be displaced off the mirror planes; all U_{iso} values are small and positive, including the U_{aniso} parameter along *c* (not shown). In addition, difference Fourier maps showed no evidence of residual electron density to either side of the cations along *c*.

The space group *P*4/*mbm* is centrosymmetric and, therefore, could not exhibit ferroelectricity. An alternative, related, space group which is non-centric is *P*4*bm*. This is a lower symmetry space group and a satisfactory structure refinement was also achieved in this space group. The main structural difference concerns the displacement of cations in the *c* direction away from the mirror plane positions at $z = 0$ and 0.5 in space group *P*4/*mbm*. The *z* parameters of all atoms are also indicated in Table 1. It can be seen that the cations are displaced significantly by several times the esds, but only small displacements of the oxygens are seen. At this stage, we cannot confirm whether the displacements associated with this lower symmetry space group are valid, since the improvement in the profile fits was observed to be very small and the refined *R* parameters were only marginally lower than in the space group *P*4/*mbm*. It is questionable, therefore, whether the slight improvement in *R* factors can be justified because of the large increase in the number of refinable parameters that was used (30 compared to 21). In order to confirm the structural details,

DOI: 10.1039/b204667a

Table 1 Refined atomic positions and thermal parameters of $Ba_2LaTi_2Nb_3O_{15}$ in space group *P*4/*mbm*;[a] also shown, in the final column, are the *z* co-ordinates when refined in *P*4*bm*[b]

Name	*x*	*y*	*z*	U_{iso}/Å^2	Occ.	Wyckoff	*z* (*P*4*bm*)
La(1)	0	0	0	0.0162(6)	1.0	2a	0.985(9)
Ba(2)	0.1715(1)	0.6715(1)	0	0.0324(6)	1.0	4g	0.975(4)
Nb(1)	0	0.5	0.5	0.028(1)	0.6	2c	0.455(2)
Ti(1)	0	0.5	0.5	0.028(1)	0.4	2c	0.455(2)
Nb(2)	0.0751(2)	0.2163(2)	0.5	0.0161(5)	0.6	8j	0.467(5)
Ti(2)	0.0751(2)	0.2163(2)	0.5	0.0161(5)	0.4	8j	0.467(5)
O(1)	0	0.5	0	0.023(8)	1.0	2d	0.98(4)
O(2)	0.2831(8)	0.7831(8)	0.5	0.016(5)	1.0	4h	0.531(9)
O(3)	0.073(1)	0.2013(8)	0	0.021(3)	1.0	8i	0.98(2)
O(4)	0.3431(8)	0.0082(6)	0.5	0.008(3)	1.0	8j	0.517(8)
O(5)	0.1368(8)	0.0659(9)	0.5	0.018(4)	1.0	8j	0.52(1)

[a] CHI2 = 1.047, wR_p = 8.63%, R_p = 6.80%. [b] CHI2 = 1.040, wR_p = 8.60%, R_p = 6.77%.

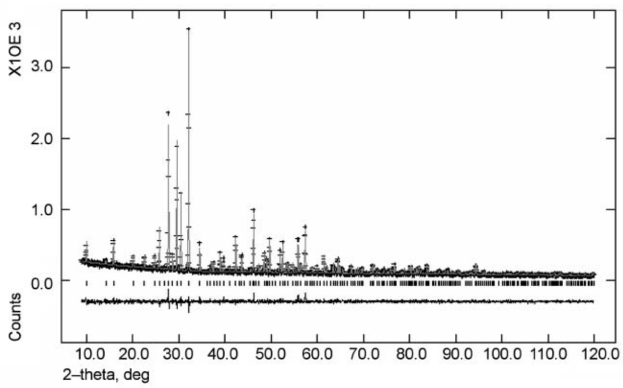

Fig. 1 Observed, calculated and difference profiles of the XRD data for $Ba_2LaTi_2Nb_3O_{15}$.

Table 2 Bond lengths in $Ba_2LaTi_2Nb_3O_{15}$

	Bond length/Å		Bond length/Å
La(1)–O(3)	2.660(10) × 4	Nb(1)/Ti(1)–O(1)	1.962(2) × 2
La(1)–O(5)	2.722(6) × 8	Nb(1)/Ti(1)–O(4)	1.953(10) × 4
Ba(1)–O(1)	3.014(2)		
Ba(1)–O(2)	2.775(10) × 2	Nb(2)/Ti(2)–O(2)	1.949(5)
Ba(1)–O(4)	2.828(6) × 4	Nb(2)/Ti(2)–O(3)	1.971(1) × 2
Ba(1)–O(3)	3.201(13) × 2	Nb(2)/Ti(2)–O(4)	1.886(9)
Ba(1)–O(3)	3.422(13) × 2	Nb(2)/Ti(2)–O(5)	2.020(12)
Ba(1)–O(5)	3.354(7) × 4	Nb(2)/Ti(2)–O(5)	2.011(12)

and in particular the space group, neutron diffraction studies over a range of temperatures are planned. A projection of the TTB structure of $Ba_2LaTi_2Nb_3O_{15}$ on the *ab* plane is shown in Fig 2.

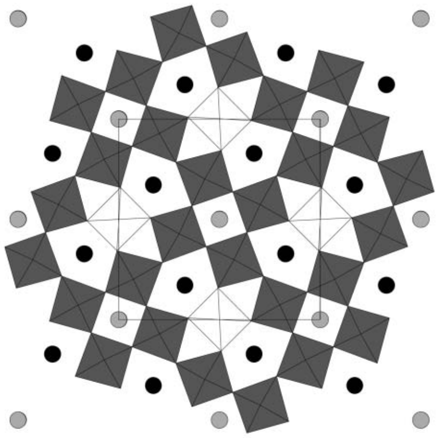

Fig. 2 *ab* Projection of the crystal structure of $Ba_2LaTi_2Nb_3O_{15}$.

Fixed-frequency permittivity data are shown at three frequencies in Fig 3. The data show a classic relaxor ferroelectric response, with frequency-independent permittivities at high temperatures that gradually increase to a maximum whose temperature is frequency dependent but is in the range 200–220 K. Below the maximum, the permittivity shows a large frequency dispersion, which decreases significantly at much lower temperatures.

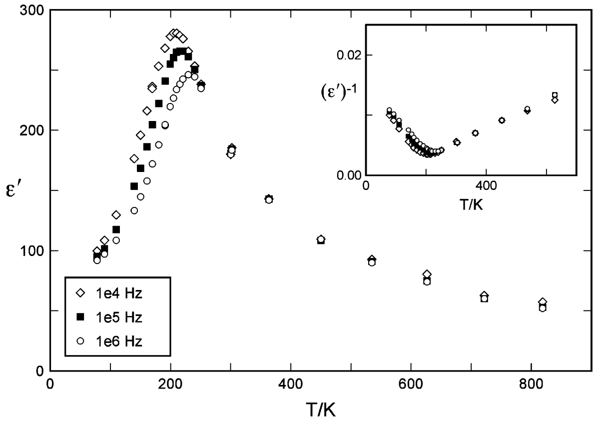

Fig. 3 Permittivity *vs.* temperature of $Ba_2LaTi_2Nb_3O_{15}$; the inset shows a Curie–Weiss plot of ε^{-1} *vs.* *T*.

The same permittivity data are replotted in Curie–Weiss format as an inset to Fig 3. The high temperature data are essentially linear and extrapolate to a T_o of approximately 100 K, which is 100–120 K below T_{max}. From the same set of impedance data, it was possible to extract sample resistances, but only at the highest temperatures. For example, at 820 K, the sample resistance was estimated to be 2×10^7 Ω cm, but at lower temperatures, the resistance was much greater and was beyond the range of measurement for the instrumentation. Hence, at all temperatures below 800 K, the material is essentially a high permittivity dielectric with no significant dc conductivity.

These results have significant bearing on the possible utilisation of this phase as a microwave dielectric. At room temperature, the permittivity increases rapidly with decreasing temperature (Fig 3) and the material, therefore, has a large negative temperature coefficient of permittivity, τ_ε, making it unsuitable for applications where temperature-independent permittivity is needed. Manipulation of the phase transition temperature by suitable compositional modification may well, however, enable tuning of τ_ε.

Continuing studies, as yet unpublished, indicate that $Ba_2LaTi_2Nb_3O_{15}$ is not a stoichiometric line phase of fixed composition, but can have a variable La to Ba ratio, variable Ti to Nb ratio and variable O content. The precise solid solution mechanism(s) and the influence of these on the properties remain to be determined.

Acknowledgements

We thank the EPSRC for support and D. C. Sinclair for advice on impedance measurements.

Notes and references

1 X. M. Chen and J. S. Yang, *J. Eur. Ceram. Soc.*, 1999, **19**, 139–142.
2 X. M. Chen, C. L. Liu, J. S. Yang and Y. J. Wu, *J. Solid State Chem.*, 1999, **148**, 438–441.
3 M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials*, Oxford University Press, London, 2001.
4 A. C. Larson and R. B. von Dreele, *Report No. La-Ur-86-748*, Los Alamos National Laboratory, NM, USA, 1998.
5 C. A. Kirk and A. R. West, unpublished results.