Crystal structure of $Ba(Mg_{1/3}Ta_{2/3})O_3$ calcinated at 1400°C

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Abstract. A new phase of $Ba(Mg_{1/3}Ta_{2/3})O_3$ has been obtained by calcination at 1400°C. It belongs to the cubic $Pm3m$ with $a = 4.08840(4)$ Å and the crystal structure has been found to be the ideal perovskite by the Rietveld method from powder X-ray diffraction data.

Keywords. Calcination; crystal structure; perovskite; Rietveld method.

1. Introduction

Materials with high dielectric constant and low dielectric loss are used as dielectric resonators at microwave frequencies. It is well known that ceramics with the general formula $Ba(B'_{1/3} B''_{2/3})O_3$, where B' is divalent Zn or Mg and B'' the pentavalent Nb or Ta, have low dielectric loss at microwave frequencies (Nomura *et al* 1982; Kawashima *et al* 1977, 1983). The complex perovskite oxides have an ordered phase depending upon the charge imbalance and difference in the size of B' and B'' ions (Galasso and Pyle 1963). The degree of long-range order is influenced by the preparation method and the conditions of the heat treatments (Kawashima *et al* 1983). $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) is a low loss dielectric material with a small temperature coefficient of resonant frequency. We report here a new cubic $Pm3m$ phase of BMT obtained on calcination at 1400°C.

2. Material preparation

The starting materials $BaCO_3$(99·9% pure), Ta_2O_5(99·99%) and MgO(99·95%), obtained from CERAC Inc., USA, were mixed in the correct proportions according to the equation

$$BaCO_3 + (1/3)MgO + (2/3)Ta_2O_5 \rightarrow Ba(Mg_{1/3}Ta_{2/3})O_3 + CO_2\uparrow,$$
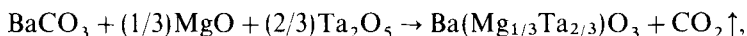
using a small quantity of distilled water. The mixing was done with agate balls in a teflon jar for 24 h. The mixture was fired at 1400°C for 10 h in air. No reaction with the crucible used was noticeable.

3. Data collection

The powder was back-pressed into a standard aluminium holder and mounted in a Philips PW1710 diffractometer equipped with a PW1877 automatic-step scanning system. Intensity data were collected at 300 K at intervals of 0·04 over the 2θ range 20–120°, with a count time of 20·0 s at each step, employing $1/2°$ divergence, $1°$

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scattering and 0·3 mm receiving slits. Ni-filtered CuKα radiation was used. The X-ray tube was operated at 40 KV and 30 mA with automatic dead-time corrections during the data collection.

4. Structure refinement and discussion

Least-squares structure refinement was carried out using the Rietveld analysis program DBWS9006-PC (Sakthivel and Young 1992). The pseudo-Voigt profile shape function was used. Twenty times the FWHM was assumed to be the range of the calculated profile. The initial values of the background parameters were determined by fitting a fifth-order polynomial to a set of carefully selected background intensities. The weight assigned to the intensity y_i at each step i in the pattern was $w_i = 1/y_i$ and the function minimized was $\Sigma_i w_i (y_{io} - y_{ic})^2$, where the subscripts o and c denote the observed and calculated quantities, respectively. The scattering factors of Ba^{2+}, Mg^{2+} and Ta^{5+} were taken from the program DBWS9006-PC and those of O^{2-} from Hovestreydt (1983).

It is known that BMT is isomorphous with $Sr(Mg_{1/3}Ta_{2/3})O_3$ (ordered trigonal $P\bar{3}m1$) (Galasso and Pyle 1963). The recorded data when subjected to the Rietveld refinement based on the model yielded the residual factors R–P = 5·42, R–Wp = 9·41 and R–Bragg = 6·78% with $a = 5·7816$ and $c = 7·0814$ Å. Ba and Ta atoms had negative thermal parameters. Further this structure was developing peaks of low intensity in the regions in which there was none. This lead us to suspect the starting model.

A careful analysis of the d-values revealed that they could be indexed on a cubic system with a lattice constant of 8·176 or 4·088 Å. The refinement was attempted assuming the structure to be isomorphous with $A_2(B' B'')O_6$ (partially ordered cubic $Fm3m$) (Galasso and Darby 1962) with an initial value of $a = 8·176$ Å. It gave the residual factors R–P = 5·30, R–Wp = 10·54 and R–Bragg = 8·58% and positive thermal factors for all the atoms.

The structure was finally attempted in the space group $Pm3m$ with the smaller unimolecular cubic cell. All the atoms occupy the special positions listed in table 1. Mg and Ta are at the body centre of the cube in the stoichiometric ratio. Refinement in this space group gave us the R factors: R–P = 3·78, R–Wp = 5·22 and R–Bragg = 3·50%. An examination of the difference plot revealed the presence of the ordered trigonal phase of BMT. The refinement was continued with the two phases. The final residual factors are given in table 1. The observed and calculated powder diffraction profiles based on the two phases are shown in figure 1. The weight of the cubic phase in the sample employed was calculated to be 91·4%.

In $Pm3m$ each Ta/Mg is at the centre of six oxygen atoms which are at the corners of a regular octahedron. The distance between Ta/Mg and O is 2·04420 (2) Å. The Ba atom has twelve oxygen atoms, each at a distance 2·89050(3) Å, forming a cubo-octahedron. This is the ideal perovskite structure, which $BaTiO_3$ has above 120°C.

The disordered cubic $Pm3m$ phase is perhaps due to the calcination temperature of 1400°C employed. Calcination at an appropriate temperature may lead to the ordered phase $P\bar{3}m1$. This shows that apart from the difference in the size of the B-cations, the calcination temperature has a crucial role to play in determining the ordering of BMT structure.

Table 1. Positional and thermal parameters in $Pm3m$ phase of BMT.

Atom	x	y	z	$B_{iso}(Å^2)$
Ba	0	0	0	0·23(5)
Mg	1/2	1/2	1/2	0·15(5)
Ta	1/2	1/2	1/2	0·15(5)
O	0	1/2	1/2	0·67(13)

$a = 4·08840(4)$ Å, $Z = 1$, dcal $= 7·63$ g/cm^3, $Pm3m$
R–P $= 3·45$, R–Wp $= 4·70$, R–Bragg $= 2·28$%;
$S = 1·98$, D–W D $= 0·77$;
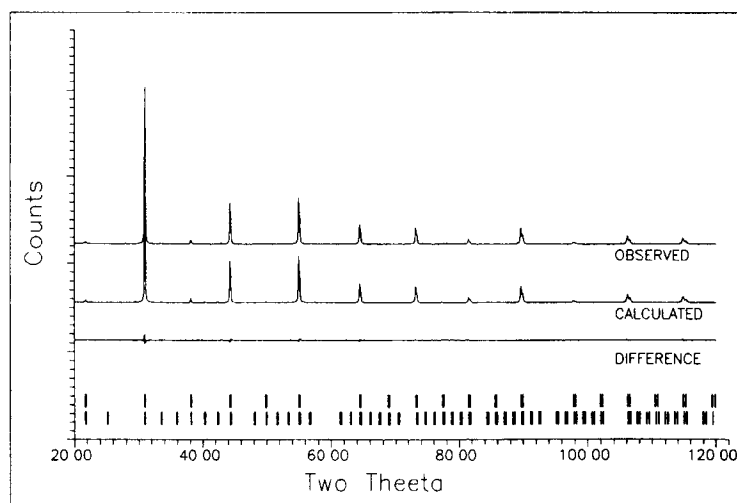Mg/Ta–O $= 6 × 2·04420(1)$ Å;
Ba–O $= 12 × 2·89050(3)$ Å.

Figure 1. Observed, calculated and difference powder diffraction profiles for BMT. The two rows of short vertical lines below the pattern represent the positions of all the possible Bragg reflections of the phases, $Pm3m$ and $P\bar{3}m1$, respectively.

5. Conclusion

A new cubic $Pm3m$ phase was established by the Rietveld profile refinement method in BMT calcinated at $1400°C$.

References

Galasso F and Darby W 1962 *J. Phys. Chem.* **66** 131
Galasso F and Pyle J 1963 *Inorg. Chem.* **2** 482
Hovestreydt E 1983 *Acta Crystallogr.* **A39** 268
Kawashima S, Nishida M, Ueda I, Ouchi H and Hayakawa S 1977 *Proc. Ferroelectr. Mater. Appl.* **1** 293
Kawashima S, Nishida M, Ueda I and Ouchi H 1983 *J. Am. Ceram. Soc.* **66** 421
Nomura S, Toyama K and Kaneta K 1982 *Jpn. J. Appl. Phys.* **21** L624
Sakthivel A and Young R A 1992 Program DBWS-9006PC for Rietveld analysis of X-ray and neutron powder diffraction patterns