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Synthesis and characterisation of doped 6H-BaTiO$_3$ ceramics

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Abstract

Hexagonal 6H-BaTiO$_3$ has been stabilised at room temperature according to the formula Ba(Ti$_{1-x}$M$_x$)O$_{3-\delta}$ where M = Mg, Al, Cr, Mn, Fe, Co, Zn, Ga, Ni and In. Solid solution ranges are reported for samples prepared by the mixed oxide route at 1400 °C. Rietveld refinement of Neutron Diffraction data for BaTi$_{0.92}$Ga$_{0.08}$O$_{2.96}$ in the space group P6$_3$/mmc shows the presence of oxygen vacancies in the hexagonally close packed layers between face sharing Ti$_2$O$_9$ dimers. All materials are dielectric insulators at room temperature with permittivity values between ~50–80. Several compositions resonate at microwave frequencies with quality factors (Q.f) between ~1300–7700 GHz.

Keywords: BaTiO$_3$; Doping studies; Electrical properties; Hexagonal perovskites

1. Introduction

Barium titanate, BaTiO$_3$, based materials are well known electroceramics that find applications as dielectric materials in capacitors and as positive temperature coefficient of resistance (ptcr) thermistors. Most research to date has focused on materials based on the ferroelectric tetragonal polymorph, t-BaTiO$_3$, due to its high permittivity[1] and because its electrical properties can be tailored to exhibit the ptcr effect. By contrast the high temperature hexagonal polymorph has not been widely investigated.

The hexagonal polymorph was first reported by Bourgeois in 1883 and crystallises in the space group P6$_3$/mmc with lattice parameters $a = 5.7238$ Å and $c = 13.9649$ Å.[2] The unit cell can be described as 6 pseudo-close-packed BaO$_3$ layers which form a (cch)$_2$ sequence, where *c* corresponds to corner sharing octahedra and h corresponds to face sharing octahedra, resulting from cubic close packing and hexagonal close packing respectively, (Fig. 1).[3]

Stoichiometric, undoped 6H-BaTiO$_3$ is reported to be thermodynamically stable above 1460 °C but can be kinetically stabilised at room temperature by rapid quenching from temperatures >1460 °C.[4] More recently, Kirby and Wechsler[5] reported 6H-BaTiO$_3$ can be quenched from temperatures >1432 °C. Investigation into the high temperature region of the BaO-TiO$_2$ phase diagram around BaTiO$_3$[5] highlighted several complexities associated with the cubic–hexagonal phase transition. For example, the cubic polymorph can persist up to ~1500 °C when a slow heating ramp rate is employed, thus demonstrating a wide metastable region for the cubic polymorph dependent on heating rate and thermal history.

Oxygen-deficient 6H-BaTiO$_3$ can be obtained at room temperature by heating at high temperatures and low oxygen partial pressures, for example in 5%H$_2$/95%N$_2$[6] or under vacuum (0.1 mbar)[3] at >1300 °C. Such treatment results in oxygen-loss that creates oxygen vacancies in the lattice. This oxygen-loss is charge compensated by partial reduction of Ti^{4+} to Ti^{3+} and produces semiconducting materials. Alternatively, doping with various transition metal ions on the Ti-sites, e.g. Fe, Mn, Co, Ni can also lead to the formation of the hexagonal polymorph at room temperature,[7] however their electrical properties have not been reported. For undoped, oxygen-deficient 6H-BaTiO$_3$ and Fe-doped 6H-BaTiO$_3$ it has been reported that oxygen is removed only from the O(1) sites in the Ba(1)O(1)$_3$ layers, Fig. 1.[3,8]

Stabilisation of doped 6H-BaTiO$_3$-based materials has been attributed to a variety of reasons, including: (i) oxygen vacancies, (ii) the electronic configuration of the dopant ion, and (iii) metal-metal bonding of cations through the face sharing octahedra.[9] None of the

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current literature has concluded which of these, if any, is the main contributor to the stabilising effect.

To date, no systematic study has been published on the type of dopants that stabilise 6H-BaTiO$_3$ or on the electrical properties of these materials. Here we report some recent results on a survey of dopants that stabilise the 6H-BaTiO$_3$ polymorph at room temperature and present some structural information and electrical property measurements on selected compositions.

2. Experimental

All samples were prepared by the mixed oxide route from appropriate quantities of carbonates or oxides of the various constituents according to the general formula Ba(Ti$_{1-x}$M$_x$)O$_{3-\delta}$ where M = Mg, Al, Cr, Mn, Fe, Co, Zn, Ga, Ni and In. Powders for phase diagram studies were mixed with acetone in an agate pestle and mortar and heat treated between 1200 and 1400 °C. Powders for the preparation of dense ceramics were made using a roller ball mill. Reagents were milled using yttria stabilised zirconia milling media in a polypropylene pot with acetone. Samples were calcined overnight at 1150 °C (Mg, Al, Cr, Zn, Ga and In) or 1300 °C (Mn, Fe, Co and Ni) remilled for 16–18 h. Pellets (8–10 mm in diameter and 2–3 mm thick) were uniaxially cold-pressed in a stainless steel die using a compaction pressure of ~200 MPa prior to sintering at 1450 °C for 2 h in air at a heating and cooling rate of 5 °C/min.

X-ray analysis for phase identification was carried out using a Stoe Image Plate (IP) diffractometer with Cu $K\alpha$ radiation. The phase purity of the powders was determined using the indexing scheme for undoped 6H-BaTiO$_3$ reported in the ICDD file, card number 34-129. Neutron Diffraction (ND) data were obtained on POLARIS at the ISIS facility at Rutherford Appleton Laboratories and refined by the Rietveld method using the General Structural Analysis System (GSAS) suite of software to establish the location of oxygen vacancies in Ba(Ti$_{0.92}$Ga$_{0.08}$)O$_{2.96}$. The density of sintered pellets was estimated from the mass and dimensions of the pellets compared to that expected from the theoretical X-ray density. Ceramic microstructures were examined by Scanning Electron Microscopy (SEM) using a Camscan Mk2 SEM operating at 20 kV. Microwave dielectric measurements of relative permittivity, ε_r, and quality factor, Q (= 1/tanδ), were performed on ceramic discs by the resonant cavity method using a network analyser, Hewlett-Packard model 8720D.

3. Results and discussion

All of the dopants studied were found to stabilise the 6H polymorph at room temperature and the solid solution limits are shown in Fig. 2. It should be stressed that these limits are temperature dependent. The results presented here are for samples that have been removed from a furnace directly from 1400 °C. A more comprehensive study of the phase equilibria associated with these dopants will be reported elsewhere.[10,11] In general, low levels of dopants, $x < 0.01$ produced phase-mixtures of the tetragonal and hexagonal polymorphs, however, for larger values of $x \sim 0.05$, single-phase materials of the hexagonal polymorph were formed. A notable exception was Fe where single-phase materials were not obtained until $x \geqslant 0.10$. Extensive solid solutions were observed for Fe- and Mn-doped materials, as has been reported previously.[7,8] It is apparent, however, that several s- and p-block elements such as Mg, Al, Ga and In can also substitute for Ti and stabilise the hexagonal polymorph at room temperature, albeit with narrower solid solution ranges.

Neutron diffraction data for Ba(Ti$_{0.92}$Ga$_{0.08}$)O$_{2.96}$ were refined using the space group P6$_3$/mmc and structural parameters from a single crystal study of undoped 6H-BaTiO$_3$[2] as a starting model. The refinement converged with a weighted R-factor, wRp, of ~2%, supporting a good quality of fit for the observed data with this model. In the final refinement, the lattice

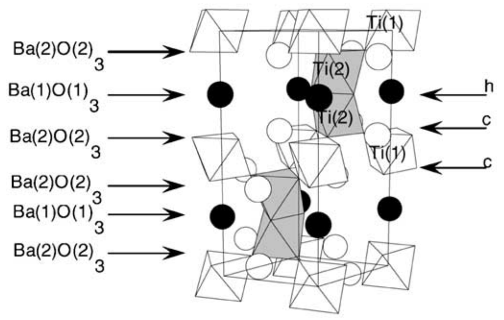

Fig. 1. The 6H-BaTiO$_3$ unit cell.

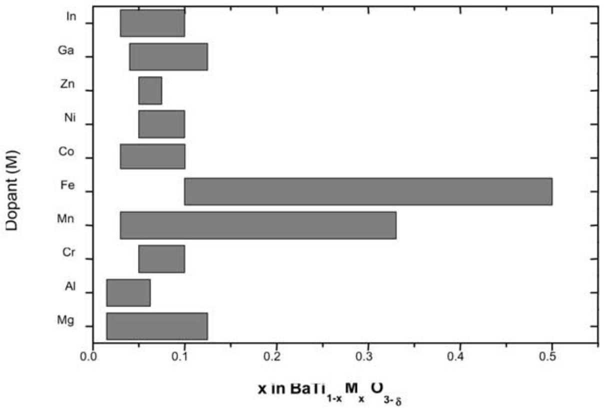

Fig. 2. Solid solution limits for Ba(Ti$_{1-x}$M$_x$)O$_{3-\delta}$ at 1400 °C.

parameters were $a = 5.72434(2)$ Å and $c = 13.99848(10)$ Å, and oxygen vacancies were located exclusively on the O(1) sites in the close packed h-Ba(1)O$(1)_3$ layers, Fig. 1. There was no apparent site preference for Ga on the Ti-sites. Details of the full structural analysis will be published elsewhere.[10]

The microstructures of ceramics formed by sintering at 1450 °C for 2 h for selected dopants with $x = 0.05$ are given in Fig. 3. All samples were > 96% of the theoretical X-ray density. In general, the microstructures consist of small, uniform grains, as illustrated in Fig. 3(a)–(c) for $x = 0.05$ Ni- Co- and Ga-doped samples, respectively. Only in the case of Mn-doped samples was exaggerated grain growth with long plate-like grains in excess of 100 μm with low aspect ratios observed, Fig. 3(d).

Impedance spectroscopy showed all ceramics to be reasonable dielectrics with room temperature resistivity > 1 MΩ cm and ε_r ranging from ~50 to 80. Microwave dielectric resonance measurements were performed to establish the Quality factor (Q.f) and ε_r of ceramics for several dopants ($x = 0.05$ or 0.08) at microwave frequencies. In general, the permittivity values are in agreement with the Impedance Spectroscopy results. The Q.f values are rather low, in the range ~1000 – 8000 GHz, Table 1. Measurements of the temperature coefficient of the resonant frequency (TCf) are in progress, however, preliminary results on Ga-doped samples show high values of ~500 ppm K^{-1}.

The results in Fig. 2 demonstrate that both transition metal ions and s- and p-block cations can be used to stabilise the hexagonal polymorph of $BaTiO_3$. The dopants can be sub-divided into two groups: those that form rather limited solid solutions, i.e. $x < 0.15$ (Mg, Al, Cr, Ni, Zn, Ga and In) and those that form extensive solid solutions, i.e. $x \geqslant 0.25$ (Mn and Fe). In the former case, the oxidation state of the cations is either II or III (with the possible exception of Cr), whereas for the latter group variable oxidation states (II, III, IV) are likely. In the first group, oxygen vacancies are required for electroneutrality and ND for the Ga-doped materials shows that oxygen is removed only from the O(1) sites in the h-Ba(1)O$(1)_3$ layers: there is no evidence of O(2) vacancies associated with corner sharing Ti(1)O$(2)_6$, octahedra. The location of oxygen vacancies on the O(1) sites is in agreement with results reported for oxygen-deficient undoped 6H-$BaTiO_3$ and for Fe-doped 6H-$BaTiO_3$ materials.[3,8]

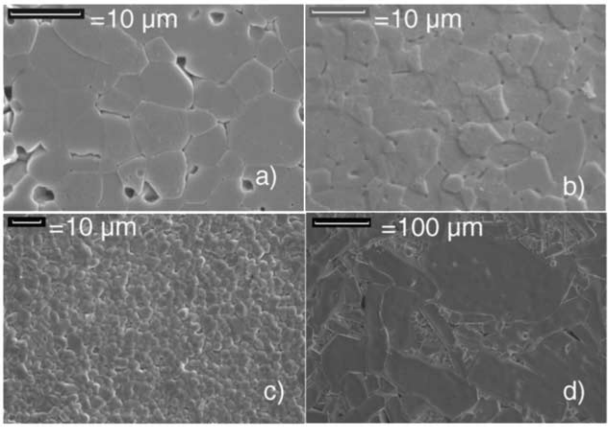

Fig. 3. SEM images of ceramic microstructures for x = 0.05 Ni-, (a), Co-, (b), Ga-, (c) and Mn- doped samples, (d).

Rietveld refinement of XRD and ND data for the other doped materials is in progress to determine any site preferences for the dopant ions and oxygen vacancies in the 6H-$BaTiO_3$ structure.[10,11] This should help to establish the oxygen content and distribution in these doped materials and also to determine the oxidation state(s) and co-ordination environments of the various dopant ions on the Ti-sites. This will be particularly important for the second group of dopants as these are known to exhibit mixed oxidation states in many perovskite-based oxides and clearly form extensive solid solutions with the 6H-$BaTiO_3$ structure, (Fig. 2). This should help in the understanding of the factors that contribute to the stability of 6H-$BaTiO_3$-based materials. In general, however, it appears that oxygen deficiency in the 6H-$BaTiO_3$ structure is primarily accommodated by preferential creation of vacancies at the O(1) sites.

Exaggerated grain growth is commonly reported for undoped and Mn-doped 6H-$BaTiO_3$ ceramics.[12,13] Under the conditions employed in this study exaggerated grain growth is observed for Mn-doped ceramics, however many of the other doped materials do not exhibit exaggerated grain growth.

The electrical properties of all the doped materials studied indicate that they are all insulating (> 1 MΩ cm) at room temperature and that many show modest microwave dielectric properties, Table 1. Although the permittivity values are high, the low Q.f and high TCf values for the compositions measured to date eliminate any potential applications of these materials as high permittivity dielectric resonators. Improvement of the Q.f values of Ga-doped materials has been achieved by processing in flowing O_2 instead of air[14] suggesting that oxygen-loss, associated with high temperature processing, may be a contributing factor to

Table 1
Microwave dielectric properties of selected 6H-$BaTiO_3$ based compositions

Sample	Frequency (GHz)	Qf (GHz)	ε_r
$Ba[Ti_{0.92}Ga_{0.08}]O_{3-\delta}$	4.20	4200	83.7
$Ba[Ti_{0.95}Mn_{0.05}]O_{3-\delta}$	4.80	7700	71.1
$Ba[Ti_{0.95}Fe_{0.05}]O_{3-\delta}$	4.02	4800	82.1
$Ba[Ti_{0.95}Co_{0.05}]O_{3-\delta}$	4.30	1300	74.1
$Ba[Ti_{0.95}Ni_{0.05}]O_{3-\delta}$	5.20	2450	55.9

the high losses in the these materials. The origin(s) of the high TCf values is currently unknown, but it may be associated with sub-ambient phase transitions. Low temperature structural and electrical studies are required to confirm this suggestion.

4. Conclusions

A wide variety of dopants can be used to stabilise 6H-$BaTiO_3$ at room temperature e.g. Mg, Al, Ga, Cr, Mn, Fe, Co, Ni, Zn, Ga and In. The variety and extent of the solid solutions formed indicates that there are likely to be several factors that influence the stability of the hexagonal polymorph. Dopants such as Mn and Fe are particularly effective in producing large solid solution ranges. This may be associated with the ability of these ions to exist in various oxidation states (II, III, IV) some of which can adopt lower co-ordination environments on the Ti-sites; however, further structural studies on these materials are required. Ga-doped materials produce oxygen vacancies on the O(1) sites in agreement with that reported for Fe-doped and oxygen-deficient undoped materials. All the doped-materials are dielectric insulators at 25 °C with $\varepsilon_r \sim 50$–80 and exhibit modest microwave dielectric properties.

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