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Structural investigation of the phase transition in perovskite titanate containing additives

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The phase transformation from tetragonal to cubic for perovskite $BaTiO_3$ containing Dy_2O_3 and Ho_2O_3has been studied by X-ray diffraction and infrared absorption spectra. The high-angle reflections (4 1 1) and (4 2 2) from the cubic phase give a set of doublets of the two wavelengths $K_{\alpha 1}$ and $K_{\alpha 2}$. In the tetragonal structure each doublet is split into a set of partly overlapping doublets. The high broadening of absorption bands in the infrared spectra of heavily doped samples is attributed to symmetry changes from tetragonal to cubic.

1. Introduction

The properties of ferroelectric ceramics in a given system are largely determined by the method of preparation, by type and concentration of dopant, and by the sintering temperature used. In a certain composition, such properties as insulation resistance, breakdown voltage and mechanical hardness are greatly influenced by phase structure changes at room temperature. Many modifications of $BaTiO_3$ ceramics have been developed using several different effects and oxide additives [1–3]. However, in these reports, very little is said about the effect of additives on the structural changes of the perovskite $BaTiO_3$ lattice at room temperature.

Yamaji *et al.* [4] has studied the effect of Dy doping (concentrations up to 1.2 at %) and sintering parameters on the dielectric properties of $BaTiO_3$ ceramics. Tennery and Cook [5] have investigated the effect of 0.005–0.003 mole fraction of Ho_2O_3 on some physical properties of $BaTiO_3$ ceramics. They stated that no deviation from the normal room temperature tetragonal system is observed.

It is clear from these data, that no systematic study regarding the effect of Dy_2O_3 or Ho_2O_3 doping (concentrations up to 6 mol %) on the structural changes of $BaTiO_3$ at room temperature have been reported. This is the subject of the present investigation.

2. Experimental procedure

Samples were prepared following the usual ceramic technique described in [5, 6]. The starting materials were $BaCO_3$, TiO_2 and Dy_2O_3 or Ho_2O_3 (Merck). Additives of Dy_2O_3 or Ho_2O_3 were varied from 0.01 to 6 mol % in $BaTiO_3$. The raw materials were mixed by dry and wet mixing and the mixture was calcined at 1000 °C for 3 hours. The pressed discs were sintered at 1300 °C for 2 hours. X-ray powder diffraction patterns were taken by Ni filtered CuK_α radiation using a philips X-ray diffractometer. For peak profile analysis, the speeds were chosen to give a good resolution of 4 cm per degree of Bragg angle. The high-order reflections at 88 °C to 161.5 °C were recorded to measure the lattice constants.

The method of Rachinger was used to derive the position of the unresolved lines $K_{\alpha 1}$ and $K_{\alpha 2}$ [7] and the lattice constants were calculated by the extrapolation method, using the functions $1/2\ [(\cos^2\theta/\sin\theta) + (\cos^2\theta/\theta)]$.

The infrared (IR) absorption spectra of the prepared samples were measured at room temperature from 200–2000 cm^{-1}. The sample concentration was 3 mg of $BaTiO_3$ mixed with 700 mg *KBr* powder and pressed into discs. The spectra were recorded employing a Beckman instrument GMBH Munchen-Bel Nachbestellung spectrophotometer.

Results and discussion

3.1. X-ray diffraction studies

X-ray diffraction analysis shows that the addition of Dy_2O_3 or Ho_2O_3 with concentration up to 6 mol % gives no additional lines representing either dopant or any other unwanted phases such as Ba_2TiO_4, $BaTi_3O_7$ or $BaTi_4O$g. A similar conclusion was obtained by Eror and Smyth [8], for $BaTiO_3$ with Ra_2O_3 additions of concentration up to 20 at %.

To test the effect of Dy_2O_3 or Ho_2O_3 additions on the crystal structure of $BaTiO_3$, the group of reflection planes (1 1 4) and (2 2 4) were chosen to study their splitting. These groups of lines are very sensitive to the different structure modifications of $BaTiO_3$ [9]. The cubic structure gives a set of doublets formed by reflections from the same phase of the two wavelengths $K_{\alpha 1}$ and $K_{\alpha 2}$. In the tetragonal structure each doublet is split into a set of partly overlapping doublets. In Figs. 1 and 2, an example of these high-angle reflections, i.e., $(2 2 4)_{\alpha 1}$, $(2 2 4)_{\alpha 2}$, $(4 2 2)_{\alpha 1}$, $(4 2 2)_{\alpha 2}$,

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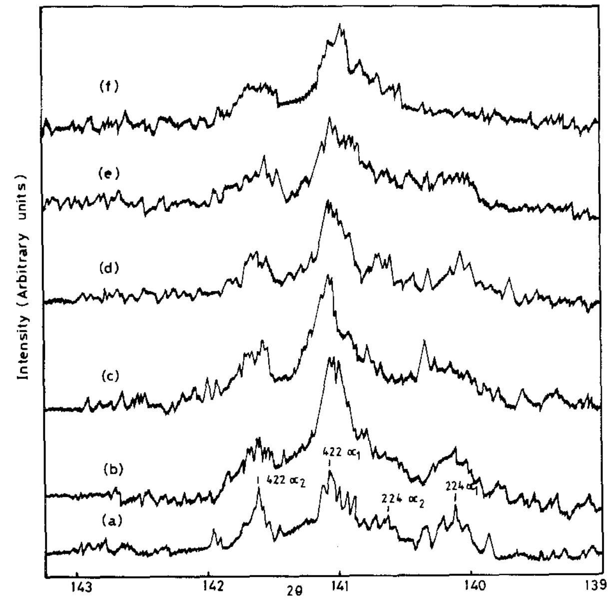

Figure 1 Diffractometer tracing of the components of the group of 4 2 2 lines of $BaTiO_3$ ceramics with different Dy_2O_3 additions, (a) undoped $BaTiO_3$, (b) + 0.01 mol %, (c) + 0.1 mol %, (d) + 0.5 mol %, (e) + 2 mol %, (f) + 6 mol %.

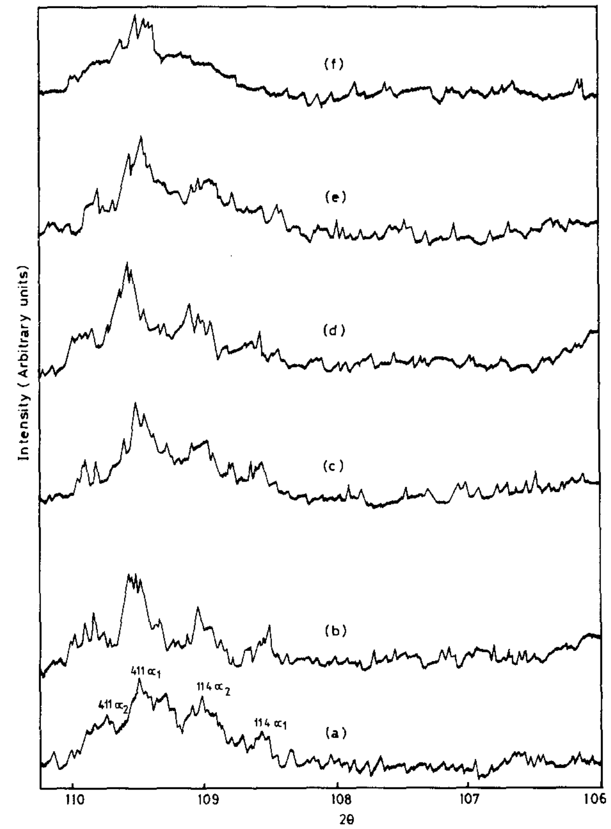

Figure 2 Diffractometer tracings of the components of the group of 4 1 1 lines of $BaTiO_3$ ceramics with different Ho_2O_3 additions. (a) undoped $BaTiO_3$, (b) + 0.01 mol %, (c) + 0.1 mol %, (d) + 0.5 mol %, (e) + 2 mol %, (f) + 6 mol %.

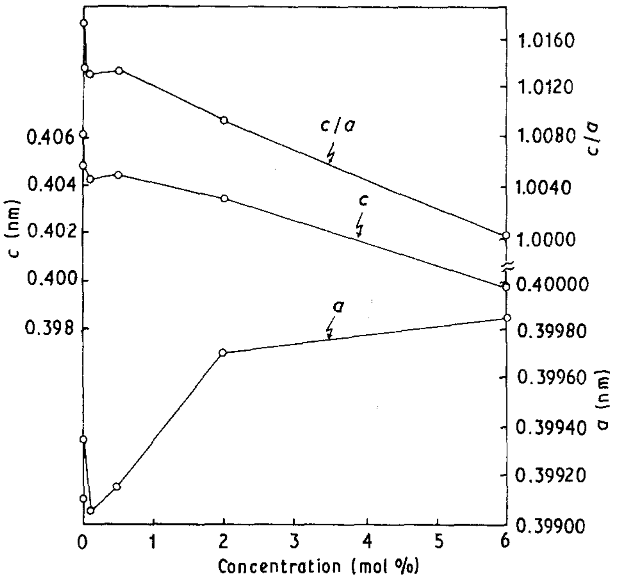

Figure 3 Lattice constants of $BaTiO_3$ as a function of Dy_2O_3 dopant concentration.

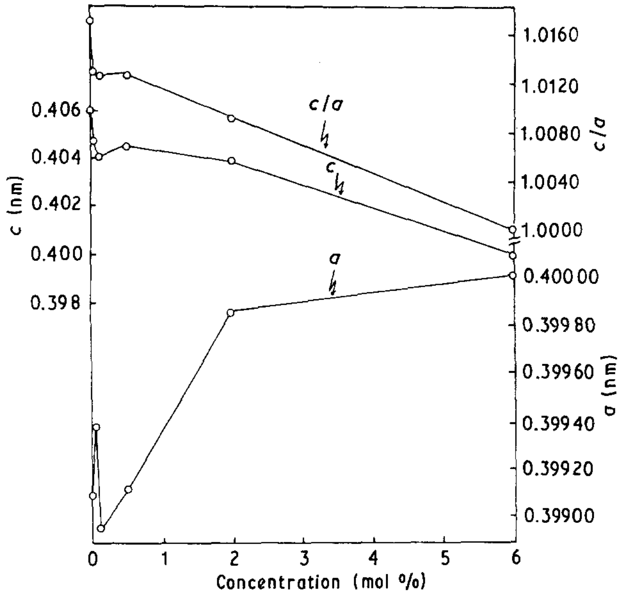

Figure 4 Lattice constants of $BaTiO_3$ as a function of Ho_2O_3 dopant concentration.

$(1\,1\,4)_{\alpha1}$, $(1\,1\,4)_{\alpha2}$, $(4\,1\,1)_{\alpha1}$ and $(4\,1\,1)_{\alpha2}$ of undoped and doped $BaTiO_3$ samples are given. It is clear from these peak profiles that the splitting of the doublet (4 2 2) and (4 1 1) is still present for all doped samples except those containing 6 mol % Dy_2O_3 or Ho_2O_3. This indicates that specimens doped with 6 mol % Dy_2O_3 or Ho_2O_3 become nearly cubic. To confirm this view, calculations of lattice parameter values *a* and *c* corresponding to tetragonal or cubic systems were carried out. At least eight peaks from high angle reflection lines in which $K_{\alpha1}$, and $K_{\alpha2}$ are split were measured for each point. The results of lattice parameter measurements *a*, *c*, *c/a* and unit cell volume, *V*, are shown in Tables I and II and represented in Figs. 3, 4, 5 and 6.

It is clear from these results that the values of the lattice parameters of tetragonal undoped $BaTiO_3$ are in close agreement with those obtained by other authors [10, 11]. The great similarity between the values of *a*, *c*, *c/a* and *V* of the two types of dopant Dy and Ho is expected since the ionic radii of both dopants are very close, namely 0.099 and 0.097 nm for Dy^{3+} and Ho^{3+}, respectively. Also, it can be observed from Figs. 5 and 6 that there is a fluctuation in the value of the unit cell volume (*V*) of $BaTiO_3$ due to Dy_2O_3 or Ho_2O_3 additions. This might be attributable to the different possibilities of substitutions of dopant in cation sites of $BaTiO_3$. These can be summarized as follows.

(i) The replacement of a Dy^{3+} ion (ionic radius 0.099 nm) in a Ba^{2+} (ionic radius 0.135 nm) site

TABLE I. Symmetry, lattice parameters and unit cell volume of specimens of BatiO$_3$ doped with different concentrations of Dy$_2$O$_3$.

Content of Dy$_2$O$_3$ (mol %)	Symmetry	a (nm)	c (nm)	c/a	V (Å^3)
0	Tetragonal	0.39910	0.40608	1.0174	64.680
0.01	Tetragonal	0.39935	0.40480	1.0136	64.557
0.1	Tetragonal	0.39905	0.40425	1.0130	64.373
0.5	Tetragonal	0.39915	0.40445	1.0132	64.437
2	Tetragonal	0.39970	0.40345	1.0093	64.455
6	Cubic	0.39985	0.39985	1	63.928

TABLE II Symmetry, lattice parameters and unit cell volume of specimens of BaTiO$_3$ doped with different concentrations of Ho$_2$O$_3$.

Content of Ho$_2$O$_3$ (mol %)	Symmetry	a (nm)	c (nm)	c/a	V (Å^3)
0	Tetragonal	0.39910	0.40600	1.0174	64.680
0.01	Tetragonal	0.39938	0.40466	1.0132	64.545
0.1	Tetragonal	0.39895	0.40396	1.0125	64.294
0.5	Tetragonal	0.39912	0.40438	1.0131	64.416
2	Tetragonal	0.39986	0.40383	1.0099	64.567
6	Cubic	0.40005	0.40005	1	64.024

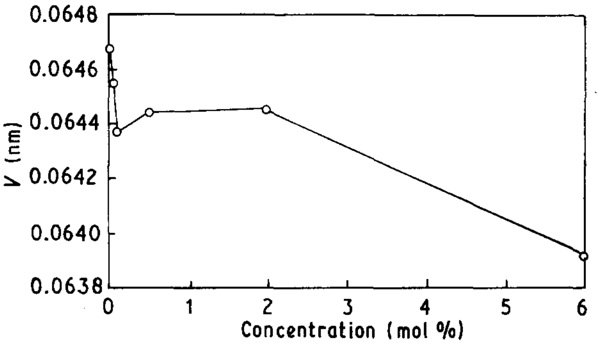

Figure 5 Effect of Dy$_2$O$_3$ additions on the unit cell volume of BaTiO$_3$ ceramics.

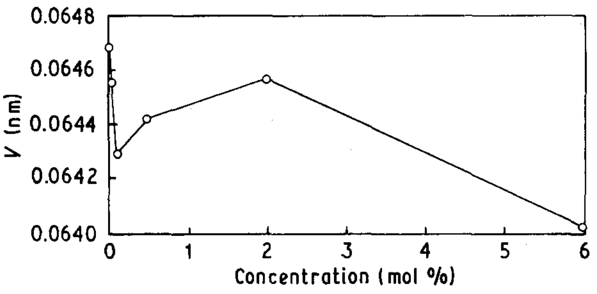

Figure 6 Effect of Ho$_2$O$_3$ additions on the unit cell volume of BaTiO$_3$ ceramics.

should lead to a shrinkage in the unit cell volume of BaTiO$_3$.

(ii) The substitution of a Dy^{3+} or Ho^{3+} ion instead of the Ti^{4+} ion (ionic radius 0.068 nm) can increase the unit cell volume.

(iii) The vacancy population in the Ba^{2+} site caused by the dopants, results in a shrinkage of the unit cell volume, where, for two Dy^{2+} or Ho^{3+} ions, one vacancy is needed to preserve electroneutrality [12].

A sharp decrease in the values of c/a and V of samples doped with 6 mol % is observed (Figs. 3–6). This may be explained as a phase transformation from the tetragonal to the cubic form at room temperature. This result is in agreement with work reported by Hanafi *et al.* [9] for BaTiO$_3$ doped with La$_2$O$_3$ and Yb$_2$O$_3$.

3.2. Infrared absorption spectra

The infrared absorption curves for undoped BaTiO$_3$ and for BaTiO$_3$ doped with Dy$_2$O$_3$ or Ho$_2$O$_3$ are shown in Figs. 7 and 8. All the spectra have one feature in common: they exhibit two main absorption bands at 375 cm^{-1} and 530 cm^{-1}. According to Last [13], the bands at 375 (ν_1) and 530 (ν_2) are due to bending of O$_{II}$–Ti–O$_I$ and stretching of T$_i$–O$_I$ vibrations in the BaTiO$_3$ lattice, respectively. The band appearing at 1670 cm^{-1} in the investigated samples corresponds to the hydroxyl (OH) impurities [14].

The effect of doping on the infrared absorption spectra is to produce a slight shift in the peak positions of ν_1 and ν_2. An increase in the line half-width of the absorption band (ν_1) with increased dopant concentration is observed and it changes to a plateau for the samples doped with 6 mol % of Dy$_2$O$_3$ or Ho$_2$O$_3$. X-ray studies show a sharp decrease in the unit cell volume of BaTiO$_3$ (Figs. 5 and 6) for these heavily doped specimens.

This high broadening of the band ν_1 is most probably due to a combination of factors:

(i) high degeneracy of the vibration state of the molecule which is related to symmetry changes;

(ii) thermal broadening of the lattice dispension band;

(iii) geometrical scattering by the powder samples [15]. The last factor, however, is neglected since

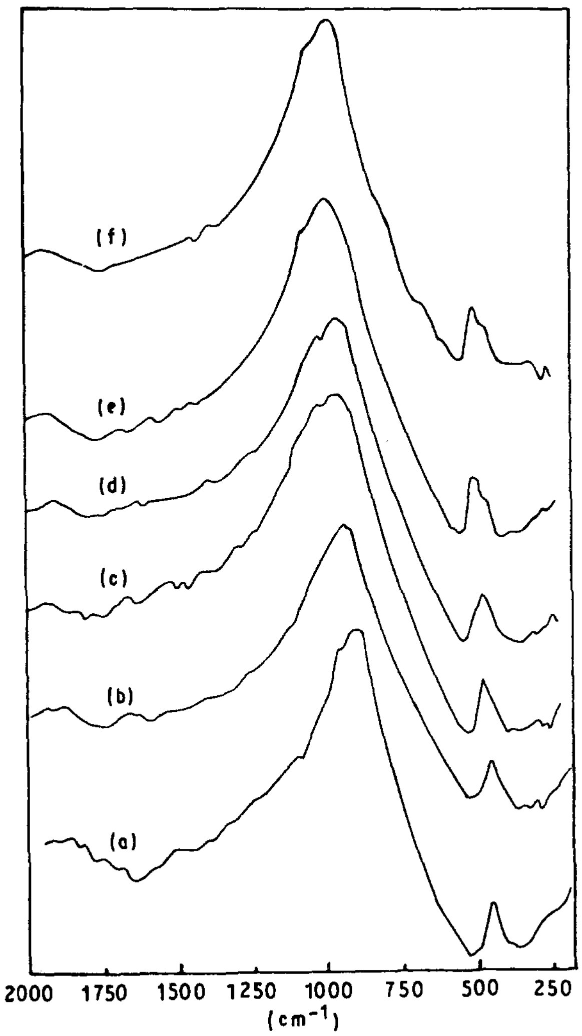

Figure 7 Infrared absorption of $BaTiO_3$ samples with different additives of Dy_2O_3 (a) undoped $BaTiO_3$, (b) + 0.01 mol %, (c) + 0.1 mol %, (d) + 0.5 mol %, (e) + 2 mol %, (f) + 6 mol %.

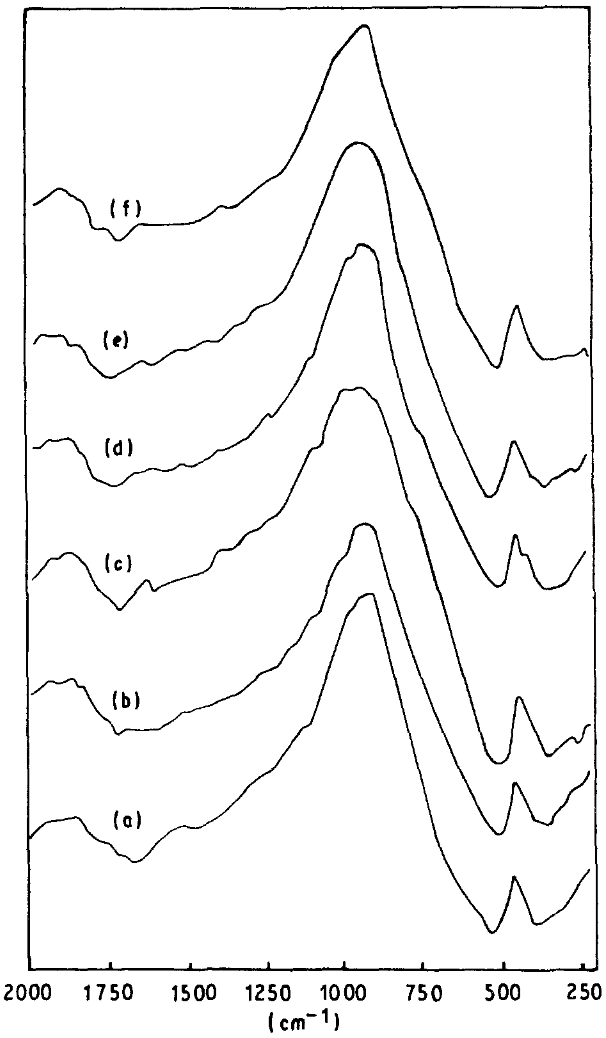

Figure 8 Infrared absorption of $BaTiO_3$ samples with different additives of Ho_2O_3. (See Fig. 7 for key.)

the same conditions of measurement were used [14].

X-ray analysis indicated that a solid solution is formed between $BaTiO_3$ and Dy_2O_3 or Ho_2O_3 in which Dy^{3+} or Ho^{3+} may occupy Ba^{2+} and/or Ti^{4+} sites in $BaTiO_3$. In the perovskite structure of $BaTiO_3$ the nearest distance at room temperature between Ti^{4+} and O^{2-} along the *c*-axis is 0.187 nm, and between Ba^{2+} and O^{2-} is 2.79 Å. Thus, in $BaTiO_3$ the interaction between Ti^{4+} and O^{2-} is stronger than that between Ba^{2+} and O^{2-} as the nearest distance is smaller and the titanium ion has four positive charges while barium has two [16]. For the sample doped with Dy_2O_3 or Ho_2O_3, the existance of Dy^{3+} (ionic radius 0.098 nm) or Ho^{3+} (ionic radius 0.097 nm) at the Ti^{4+} sites (ionic radius 0.068 nm), increases the nearest distance between Dy^{3+} and O^{2-}. Also the forces between O^{2-} and the trivalent cations Dy^{3+} or Ho^{3+} are less than the forces between O^{2-} and the tetravalent cations Ti^{4+}. Thus, it is reasonable to expect that the difference in broadening of the band ν_1 is due to changes in the forces between O^{2-} ions and different doped cations in $BaTiO_3$, in addition to the differences in the distance between the doped cations and O^{2-} ions. A similar treatment is reported by Last [13] on the perovskites $MgTiO_3$ and $CdTiO_3$.

A gradual increase in the concentration of dopants Dy_2O_3 or Ho_2O_3 (at 6 mol %) in $BaTiO_3$ is accompanied by a change in the crystal structure of $BaTiO_3$ from tetragonal to cubic at room temperature (see Figs. 3 and 4). This can lead to a slight distortion of octahedral symmetry which plays the major role in the high broadening for heavily doped specimens. Baraclough *et al.* [17] considered that any slight distortion from tetrahedral symmetry can lead to broad bands in the infrared spectra, as is actually observed.

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