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Synthesis, structure and characterization of ceramic $Ca_4Bi_2Ti_4Nb_6O_{30}$

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Abstract. The polycrystalline samples of $Ca_4Bi_2Ti_4Nb_6O_{30}$ (herein designated CBTN) were synthesized by the conventional ceramic method. Preliminary X-ray structural study of the compound showed the formation of a single phase solid solution having orthorhombic structure in the paraelectric phase. Measurements of the dielectric constant (ε') and dielectric loss (tan δ) as a function of temperature (– 180–200°C) at 1 kHz and 10 kHz and also as a function of frequency (10^2 Hz to 10^4 Hz) at five different temperatures [– 180°C, – 40°C, – 10°C, 26°C (room temperature) and 75°C] have shown a dielectric anomaly and a phase transition at – 13 ± 1°C in CBTN.

Keywords. Tungsten bronze (TB) structure; X-ray diffraction; dielectric constant; phase transition.

1. Introduction

The studies of a wide variety and range of materials of tungsten bronze (TB) type structure have been undertaken till date. Some niobates with TB structure such as barium sodium niobate (BNN) and potassium lanthanum niobate (PLN) (Van Uitert *et al* 1967) continue to be a cynosure of all eyes owing to their numerous industrial applications. The dielectric constant, electrical conductivity, specific heat and pyroelectric coefficients of ferroelectric $Sr_{1-x}Ba_xNb_2O_6$ (SBN) are investigated as a function of temperature and as a function of the Sr/Ba composition (Glass 1969). The several possible causes of diffuse phase transition (DPT) in respect of compounds like potassium strontium niobates (PSN) (Clarke and Burfoot 1974) have been reported. Studies of the structural and electrical characteristics of some ferroelectric oxides of TB structure (Choudhary and Choudhary 1990) have been published. Of late, studies on the structural and dielectric properties of $Ba_2Na_3RNb_{10}O_{30}$ (R = Nd and Cd) have been carried out for better understanding of their phase transition mechanisms (Choudhary *et al* 1993), besides a series of other similar studies concerning the various characterization aspects of different TB niobate materials (Kumari *et al* 1995; Sharma *et al* 1996, 1997, 1999a,b).

From the detailed literature survey on the TB structure based niobate materials, it can be seen that not much work on the structural and ferroelectric properties of $Ca_4Bi_2Ti_4Nb_6O_{30}$ (CBTN) ceramics has been done. In view of this, it is, therefore, worthwhile to synthesize it and carry out its characterization to understand this material which basically possesses $A_xB_2O_6$ type structure (Jaffe *et al* 1971). It has, indeed, a disordered TB structure since five out of the six sites are only occupied here. The trivalent ions available at the A site of structure compensate the charge imbalance resulting from the tetravalent Ti^{4+} ions at the B site.

2. Experimental

The polycrystalline sample of $Ca_4Bi_2Ti_4Nb_6O_{30}$ was prepared from stoichiometric mixtures of constituent high purity (A R grade) oxides (M/s Sarabhai Chemics) and carbonates (M/s Loba) by a high-temperature solid-state reaction technique. These materials were mixed thoroughly in an agate mortar and calcined at 1000°C for 12 h in a platinum crucible. The calcined powders were reground to make fine and homogeneous powders which were uniaxially cold pressed into pellets at a pressure of 5×10^6 kg wt/m^2. The pellets were then sintered at 1200°C for about 18 h. These pellets were electroded by silver paint for measurement of the dielectric parameters (ε' and tan δ). To check the formation of the single phase compound, an X-ray diffractogram of the pellet sample was taken by Rigaku MINIFLEX (Japan) X-ray powder diffractometer using CuK_α radiation ($\lambda = 0{\cdot}15418$ mm) for a wide range of Bragg angle, 2θ ($15° \leq 2\theta \leq 80°$).

Measurements of the capacitance and dissipation factor of the sample were carried out by G R 1620 capacitance measuring assembly, USA, both as a function of frequency (10^2 to 10^4 Hz) and temperature from low temperature (liquid nitrogen) to 200°C. A chromel alumel

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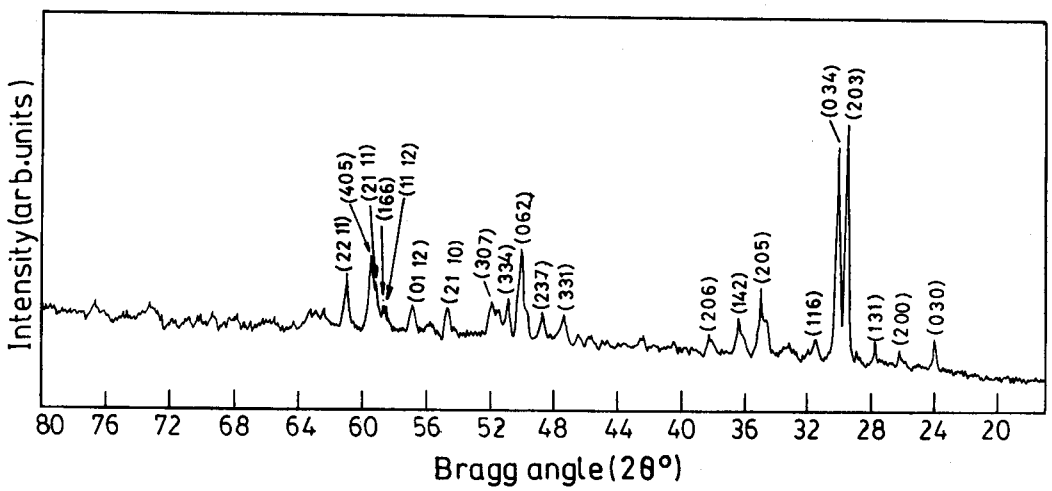

Figure 1. Room temperature XRD pattern of $Ca_4Bi_2Ti_4Nb_6O_{30}$ (CBTN).

thermocouple was used as a temperature sensor. From capacitance measurements, the dielectric permittivity was determined whereas the dissipation factor was used in the calculation of dielectric loss at different frequencies. Measurements were repeated in cooling and heating modes to check the validity and reliability of the dielectric parameters.

3. Results and discussion

Using the d-values of 21 strong and moderate reflections of CBTN material depicted in figure 1, the lattice parameters were calculated with the help of a standard software. The cell parameters $a = 6{\cdot}771(1)$ Å, $b = 11{\cdot}124(1)$ Å and $c = 19{\cdot}623(1)$ Å can account for all the observed reflections. The calculated d-values are compared with observed d-values in table 1. The good agreement between the calculated and observed d-values suggests the correctness of preliminary crystal system and cell configuration. With limited powder data, it has not been possible to determine the space group of the material.

Figures 2 and 3 display variation of the dielectric constant (ε') and dielectric loss (tan δ) of the material as a function of temperature at two different frequencies viz. 1 kHz and 10 kHz. The measurements were carried out during heating from liquid N_2 temperature. It is evident from figure 2 that the dielectric constant remains almost constant up to about – 60°C. Thereafter, there is an abrupt rise in its value which finally peaks at – 13°C. The peak value of higher frequency data (i.e. 10 kHz) is, however, found to be less than the corresponding value for 1 kHz. This may be attributed to intrinsic dielectric response of the material for different frequencies. The peak in tan δ vs temperature graph also occurs at – 13°C. This, therefore, suggests that the dielectric anomaly observed is due to a thermodynamic phase transition as expected in accordance with Kramer–Kronig relationship (Lines and Glass 1977). The rising trend in figure 3 beyond 80°C at both frequencies may, however, be attributed to an increase in the conductivity of the material possibly due to thermally activated processes. Although the variation of dielectric constant (ε') and dielectric loss (tan δ) with temperature at two different frequencies (1 kHz and 10 kHz) appears to be sharp, it is, however, not of the type usually reported for ordered relaxors (Shrout and Halliyal 1987). In any relaxors, the temperature at which tan δ peaks is invariably lower than the temperature corresponding to the peak of dielectric constant (Cross 1987).

Table 1. Comparison of observed and calculated d-values (Å) of some reflections in CBTN at room temperature.

h	k	l	d_{obs}	d_{cal}	I/I_0
0	3	0	3·7078	3·7078	14
2	0	0	3·3885	3·3885	9
1	3	1	3·2090	3·2091	13
2	0	3	3·0179	3·0088	100
0	3	4	2·9545	2·9581	90
1	1	6	2·8356	2·8474	13
2	0	5	2·5672	2·5648	34
1	4	2	2·4882	2·4887	21
2	0	6	2·3530	2·3532	21
3	3	1	1·9198	1·9199	23
2	3	7	1·8670	1·8664	16
0	6	2	1·8207	1·8218	25
3	3	4	1·7939	1·7954	21
3	0	7	1·7585	1·7590	19
2	1	10	1·6794	1·6794	19
0	1	12	1·6183	1·6183	18
1	1	12	1·5740	1·5737	18
1	6	6	1·5704	1·5691	19
2	1	11	1·5619	1·5629	19
4	0	5	1·5547	1·5547	62
2	2	11	1·5189	1·5186	38

Figure 4 depicts the frequency dependence of ε' and tan δ of ceramic CBTN at five different temperatures, – 180°C, – 40°C, – 10°C, 26°C and 75°C. The dashed lines in the figure indicate the variation in tan δ while the solid lines stand for the same in ε'. It is apparent from the figure that at temperature relatively far away from the phase transition temperature i.e. – 180°C, 26°C and 75°C, there is practically no variation both in ε' and tan δ values. As one, however, approaches the transition temperature (– 13°C) both ε' and tan δ are seen to rise sharply at the low frequency side. This trend is more evident for data at 10°C. This simply implies that the system responds more sensitively at this frequency because each of different domain sizes transforms into the paraelectric phase above – 13°C. Figure 5 shows the variation of $1/\varepsilon'$ vs temperature above the peak temperature. The good quality of straight line fit which has been obtained by the least squares method to the observed data points justified the validity of Curie–Weiss

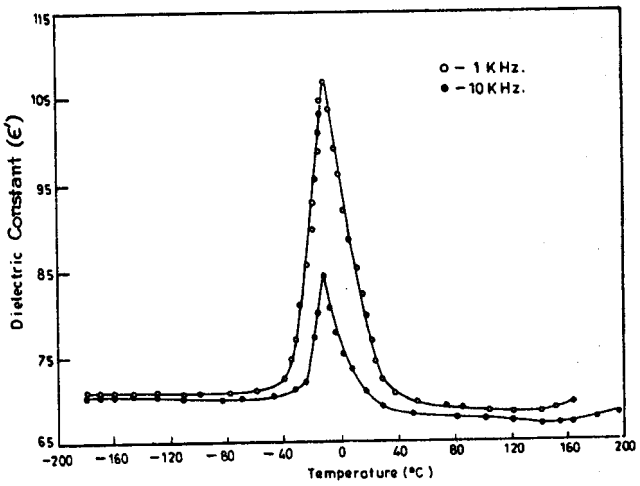

Figure 2. Variation of dielectric constant (ε') of CBTN as a function of temperature at two frequencies (1 kHz and 10 kHz).

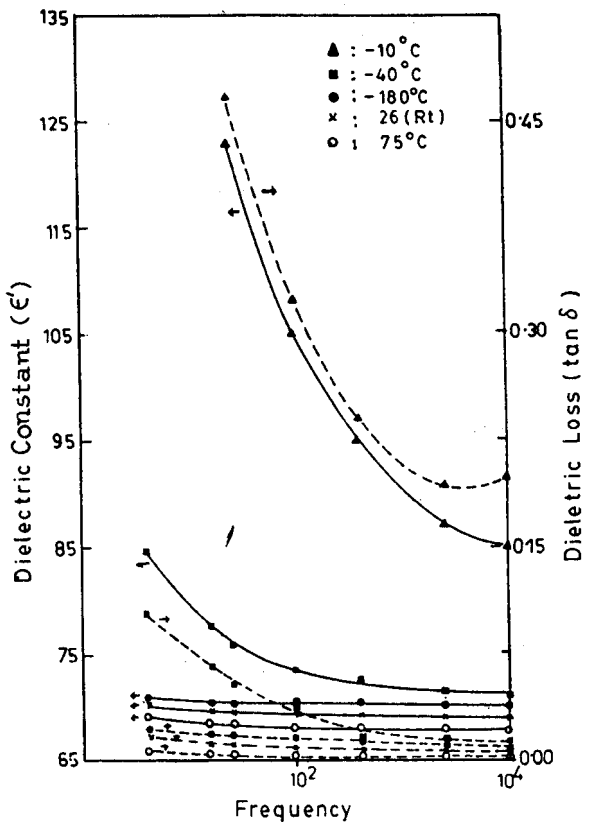

Figure 4. Frequency dependence of both ε' and tan δ of CBTN at five different temperatures.

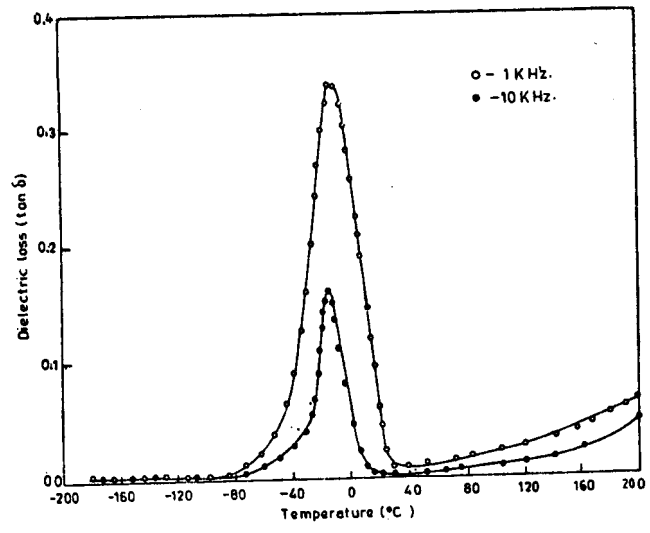

Figure 3. Variation of dielectric loss (tan δ) of CBTN as a function of temperature at two different frequencies (1 kHz and 10 kHz).

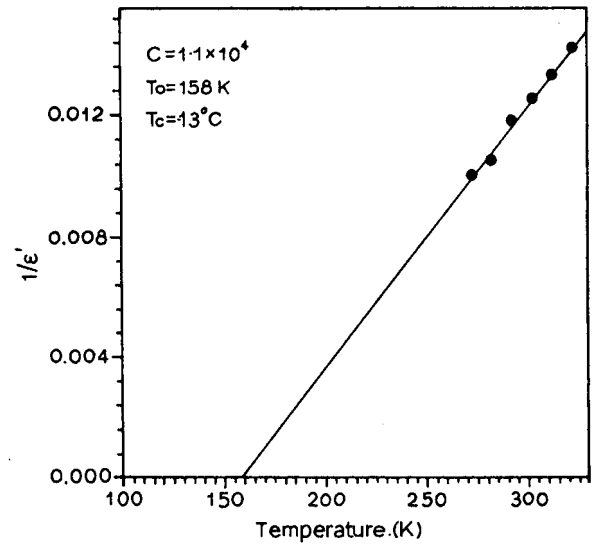

Figure 5. Variation of $1/\varepsilon'$ vs temperature (T) of CBTN above its peak temperature.

law in the paraelectric region. The Curie–Weiss temperature (T_0) is found to be – 115°C which seems to be well below the phase transition temperature. This, in turn, enables us to infer that phase transition in the CBTN material is of a first order nature (Lines and Glass 1977). The value of Curie constant, C (= 1·1 × 10^4) is also in the expected range of ferroelectric materials.

To summarize, it may be said that the single phase compound (CBTN) has been synthesized and characterized for its structure and dielectric characteristics. The compound has orthorhombic lattice structure in the paraelectric phase at room temperature having lattice parameters a = 6·771(1) Å, b = 11·124(1) Å and c = 19·623(1) Å. A dielectric anomaly in the ε' vs T plot, characteristic of ferroelectric phase transition, has been observed.

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