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An X-ray diffraction and DTA study of the ferroelectric transition in barium sodium niobate

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The structural behaviour of barium sodium niobate has been studied in the region of the ferroelectric Curie point (~ 580°C) by means of high-temperature X-ray diffraction and DTA. No significant changes in the diffraction pattern are observed until temperatures in the vicinity of T_c are reached; the patterns are then consistent with the structure retaining tetragonal symmetry through the transition but assuming a significantly lower c/a ratio. The results are compared with thermal expansion measurements made on single crystals. The thermal effect associated with the transition has been used to determine the order of the transition and the results suggest that the reaction is first order.

1. Introduction

Ferroelectric barium sodium niobate (stoichiometric formula $Ba_2NaNb_5O_{15}$ and hereafter referred to as B-S-N) is a useful opto-electronic material and has been of particular interest in the second harmonic generation of visible 0.53 μ radiation within a 1.06 μ (infra-red) laser cavity [1]. Considerable effort has been directed towards understanding the constitution [2-4] and structural properties [5, 6] of this mixed oxide and, as a result, crystals of suitable quality for such device applications can now be grown.

The room temperature ferroelectric phase has an orthorhombic tungsten bronze type structure with subcell dimensions $a_0 \approx 17.59$Å, $b_0 \approx 17.62$Å, and $c_0 \approx 4.0$Å, the precise values depending on composition [7]. The c-axis of the true unit cell is in fact double that of the subcell [3, 8] but the structure is more frequently referred to the subcell used here. The crystals are pseudo-tetragonal and only by optical [9], dilatometric [10], and lattice constant measurements [7] can the orthorhombic symmetry be identified and the correct axes assigned. A transformation to a truly tetragonal structure with $a_T \approx 12.5$Å and $c_T \approx 4.0$Å occurs at ~ 260°C and the crystallographic changes associated with this transition have been studied in detail [5, 10]. This structure is stable up to the Curie point (T_c) of ~ 580°C where the material becomes paraelectric. The crystal structure above T_c is at present unknown. The present paper reports the results of a high-temperature X-ray diffraction and DTA investigation into the nature of the ferroelectric-paraelectric phase transition in this material.

2. Experimental techniques

The X-ray diffraction pattern has been studied in the temperature range 25 to 1000°C using a Materials Research Corporation high-temperature attachment for a Philips vertical diffractometer. The MRC furnace is a filament heating type of furnace. The powdered sample is placed directly onto a tantalum strip which acts as the current-carrying element. Thermal gradients across the specimen can be reduced with an auxiliary radiant heater adjacent to the sample. The specimen temperature, monitored by a Pt/Pt 13% Rh thermocouple spot-welded to the underside of the filament, was calibrated against a standard silver sample. Specimens of B-S-N were prepared by grinding single crystal material of the invariant composition [2] since this was found to give better-defined patterns than material taken from the melt. Diffraction patterns

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were recorded with Co$K\alpha$ radiation *in vacua* better than 1×10^{-5} torr. DTA measurements were taken on Netzsch equipment fitted with Pt/Pt 13% Rh thermocouples. Heating and cooling rates of 5° min^{-1} were employed and the experiments were performed in air.

3. Results and discussion

The room-temperature powder patterns revealed a structure in good agreement with previous observations even though some of the reflections were rather indistinct, especially at high angle. In Table I, low-angle interplanar spacings and intensities measured at two elevated temperatures, one above the orthorhombic–tetragonal transition and the other above T_c, are compared with those recorded at room temperature for a typical B-S-N sample having the invariant composition. The reflections have been indexed to a tetragonal cell by assuming $a = b =$ (average

TABLE I Interplanar spacings and relative intensities of a B-S-N sample at three temperatures. The intensities have been normalized to the strongest line on the 425° C pattern. The lines marked with an asterisk are composite reflections where one or more of the components have not been identified.

hkl	*d*(Å)	I	*d*(Å)	I	*d*(Å)	I
	25° C		425° C		900° C	
130	5.646	10	5.662	9	5.693	10
001	4.023	23	4.029	16	4.008	25
240	3.964	9	3.981	10		
150	3.484	20	3.496	17	3.503	27
221	3.390	9	3.399	12	3.383	7
131	3.266	76	3.277	48	3.264	43
440	3.134	2	3.153	4	3.157	2
350	3.038	76	3.050	100	3.061	47
041	2.976	12	2.986	12	2.976	52
060	2.953	37	2.970	25		
241	2.822	67	2.833	59	2.823	54
260	2.807	38	2.811	37		
151	2.628	12	2.634	12	2.631	11
441	2.468	9	2.476	4	2.476	4
351	2.416	4	2.424	2		
061	2.377	4	2.385	2		
370	2.325	6	2.333	5	2.341	4
280	2.145	10	2.155	9	2.163	14
002	2.006	47	2.009	30	2.000	43
480	1.978	10	1.981	10		
390	1.862	18	1.869	27	1.881	16
661	1.850	6	1.857	10	1.858	7
481, 680	1.772	37	1.775	38	1.783	58
191	1.755	25	1.762	17	1.766	16
152	1.736	6	1.741	6	1.734	9
391, 442	1.690	15	1.695	12	1.702	7
352	1.673	31	1.679	27	1.672	42*
062	1.658	7	1.663	7	1.657	2
262	1.630	7	1.635	9		
0.10.1, 681	1.617	21	1.622	18	1.627	16
591	1.580	4	1.583	2	1.588	2
880	1.562	4	1.568	2	1.578	17*
3.11.0, 790	1.550	4	1.556	2	1.564	5
6.10.0	1.517	12	1.522	11	1.527	2
282, 5.11.0	1.463	9	1.468	6	1.475	5
482	1.408	2	1.411	2	1.410	4
5.11.1	1.375	7	1.379	6	1.384	2
392	1.365	7	1.370	9	1.368	7
13.3.0	1.325	18	1.330	31	1.330	14

of true *a* and *b*). The difference between the true orthorhombic and assumed tetragonal patterns is negligible at low angles and the reflections can all be indexed in terms of this tetragonal phase. This low angle indexing is in good agreement with that given by Barns [7].

Although identification of differences in the *d*-spacing of the R.T. pattern and that recorded above the O-T transition is impossible at low angles (apart from their overall increase at the higher temperature) a few anomalous intensity changes are apparent, particularly in some $\{hk0\}$ reflections. The importance of this observation cannot be assessed on the available evidence. Since the orthorhombic distortion of B-S-N is extremely small, $b_0 - a_0 \approx 0.03$Å at room temperature, and becomes smaller with increasing temperature [10], the difference in the patterns of the two phases below and above the transition is correspondingly difficult to detect. Distinction between $\{hk0\}$ and $\{kh0\}$ types on a powder pattern is thus virtually impossible at low angles, and at high angles, where such differences would be more readily observable, the poor definition of many of the reflections impedes accurate measurement. A further demonstration of this lack of resolution is provided by the fact that the R.T. pattern can also be readily indexed in terms of a tetragonal cell with $a = 12.5$Å which is known to be the stable structure above ~ 260°C.

Significant differences are revealed, however, when the pattern recorded above T_c is compared with those recorded at lower temperatures. Several reflections are apparently absent and many others exhibit pronounced changes in *d*-spacing and intensity which cannot be readily accounted for solely by the temperature increase. All these changes are reversible on cooling and no further anomalies were detected between T_c and 1000°C.

An examination of the *d*-spacings of the 900°C pattern (see Table I) showed that it could be satisfactorily indexed on a Bunn chart to the same tetragonal indices as deduced for the room temperature pattern, but with a significantly reduced c/a ratio; most of the apparent absent reflections are then explained in terms of overlapping lines. Thus, for example, the *d*-spacings of the (240) and (001) reflections increase and decrease respectively on the Bunn Chart with lowering of the c/a ratio, and at a value corresponding to the satisfactory fit of all the lines of the 900°C pattern, these two reflections overlap at an intermediate *d*-spacing as observed on the pattern. A similar argument applies to other apparently absent reflections indicated in Table I. In most cases, the resultant increased intensity of the single observed line is consistent with a composite reflection. The absence of two low-angle reflections, (351) and (061), cannot be explained on this argument. However, their intensities at 25°C are very low and become progressively weaker with increasing temperature and are presumably too diffuse to be detected at 900°C. If this assumption of a reduced c/a in the region of T_c is correct, then we can infer that not only does *c* decrease significantly in this region, as shown by the $\{00l\}$ behaviour, but that *a* also increases, since shifts are also detected in $\{hk0\}$ type reflections whose interplanar spacings are independent of the *c*-axis behaviour.

These results are in very good agreement with previous thermal expansion measurements made on this material. Dilatometric measurements [10] along the three principal crystallographic directions of the room temperature orthorhombic phase have shown that expansion anomalies do occur in the region of T_c, particularly in the *c*-axis where, prior to the transition, a large contraction is observed; this is accompanied by much smaller expansions in the original *a* and *b* axes. A plot of c/a versus temperature derived from those dilatometric curves is presented in Fig. 1 for the two crystals tested. c/a values have been referred to the room temperature pseudo-tetragonal phase and the curves have been

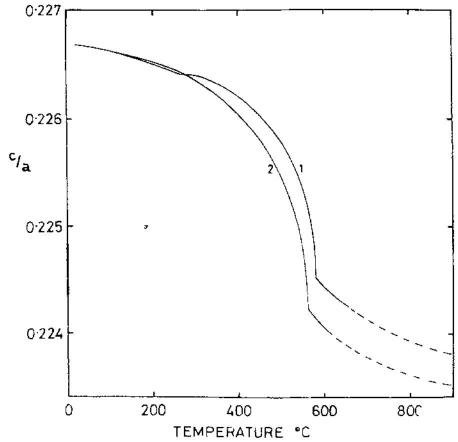

Figure 1 Variation of c/a with temperature derived from dilatometric measurements on two single crystals of B-S-N [10].

TABLE II Comparison of c/a values of the ferroelectric and paraelectric phases derived from X-ray and dilatometric measurements.

	c/a			
Temperature (°C)	(002) − (060) Reflections ± 0.001	Bunn Chart ± 0.001	Dilatometer Crystal 1	Crystal 2
			± 0.0001	
25	0.226	0.227	0.2267	0.2267
900	0.224	0.224	0.2237	0.2235

normalized to coincide at 20° C. The decrease in c/a occurs over the whole temperature range (660° C being the upper limit of the dilatometric measurements) but is particularly marked in the region of T_c. The magnitude of the total c/a change depends on the initial parameters of the room temperature material which vary with composition. The kink in the curve for crystal 1 at 260° C corresponds to the O-T transition; the magnitude of this effect is directly related to the parameter changes at the transition and to the inherent twin density of the material produced as a result of cooling through this transition [10]. Thus, crystal 2 having the invariant composition [10] with an associated reduction in twin density, shows very little effect at this transition. The temperature at which the break in the curve occurs, which corresponds to the Curie point, is also composition dependent, in agreement with previous observations [11]. In Table II, c/a values for the present X-ray work derived both from the Bunn Chart and directly from the (002) and (060) reflections are compared at 25 and 900° C with values extrapolated from the dilatometric work in Fig. 1. It can be seen that satisfactory agreement exists among the values derived for the c/a ratio of the high temperature tetragonal form.

Further confirmation of the unusual expansion behaviour of this material is provided in Fig. 2 where the interplanar spacing of the (001) and (002) reflections have been measured between 25 and 1000°C. Both curves have the same general form exhibited by the c-axis of the single crystal of B-S-N measured dilatometrically [10-12]. An initial increase in d-spacing with temperature up to 400°C is followed by a marked contraction in the region of T_c, which then becomes essentially temperature invariant above T_c. The temperature gradients inherent in the filament type of specimen stage used in these experiments make temperature measurement less accurate than in the dilatometer and probably account for the slight differences in the c-axis temperature dependence as derived from the two reflections. The X-ray beam irradiates a greater sample area at low angles and the behaviour of the (001) reflection thus corresponds to a greater range of sample temperature resulting in a less well-defined curve. Comparison of $\Delta c/c$ values deduced from these curves with those measured dilatometrically shows good overall agreement despite these instrumental difficulties and these curves thus provide striking confirmation of the anomalous c-axis expansion behaviour in the region of T_c.

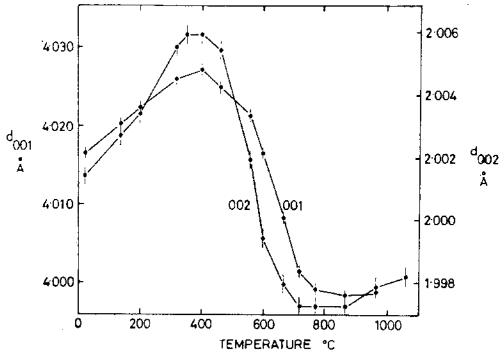

Figure 2 Interplanar spacing as a function of temperature for the (001) and (002) reflections.

Although the break in the expansion curves at T_c is well-defined [10] the volume change associated with the ferroelectric-paraelectric transition occurs over a fairly wide temperature range as indicated in Fig. 1. Thus it is not clear from this evidence whether the transition is of first or second order. In ascribing the appropriate order to the analagous expansion anomaly in KH_2PO_4, Cook [13] has used a test of temperature hysteresis which can exist at first order transitions but not at ones of second order. A similar test has been applied to DTA measurements of the Curie point in KH_2PO_4 and some of its homologues [14], and this technique has been

TABLE III Curie temperatures measured by DTA on various compositions within the B-S-N phase field.

	Composition (mol %)			Curie temperature T_c (°C) Heating		Cooling	
	Na_2O	BaO	Nb_2O_5	Deviation	Peak	Deviation	Peak
1	7.3	41.6	51.1	552	562	566	562
2	7.8	40.5	51.7	552	560	568	560
3	8.0	41.0	51.0	560	568	575	570
4	8.2	40.7	51.1	572	580	585	580
5	8.3	40.1	51.6	575	580	583	578
6	8.3	38.7	53.0	565	575	582	575

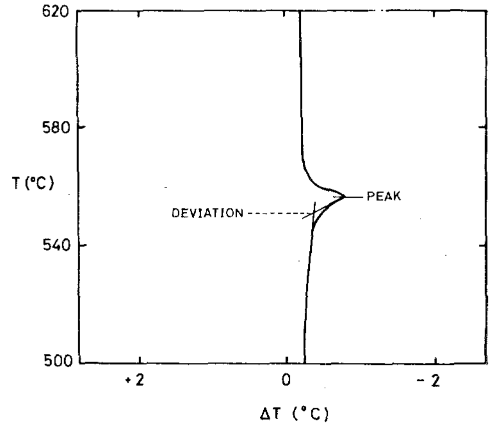

Figure 3 Typical DTA trace in the vicinity of the Curie point of B-S-N. The construction shows how one measurement of T_c was taken; the other was taken as the peak temperature.

used on B-S-N in an attempt to determine the order of this reaction.

A typical DTA curve in the vicinity of T_c is shown in Fig. 3 which was recorded on crystal grown from the invariant composition. The value of T_c has been obtained from such traces in two ways; firstly the temperature at the point of deviation from the base line as derived from the construction shown in the figure, and secondly the peak temperature. Measured values of T_c thus obtained on heating and cooling cycles on material of varying composition within the B-S-N phase field are shown in Table III. There exists very good agreement in the peak values on heating and cooling but a large hysteresis is found when the other deviation values are compared. The accuracy of the temperature measurement in these experiments was ± 2° so that this hysteresis can be regarded as significant.

Consideration of heat flow calculations has shown [15] that the peak in a DTA curve can be taken as the transition temperature only if the temperature at the centre of the sample has been recorded; measurement of the surface temperature of the sample requires the point of departure from the base line to be taken as the transition temperature. In the present equipment the thermocouple is in thermal contact with the bottom of a platinum crucible containing the sample and so the second procedure appears relevant. On this basis, the results on B-S-N imply a hysteresis associated with the Curie point suggesting that the transition is of first order. It should be noted, however, that Cook [13] found it necessary to use a heating/cooling rate less than 1 ° $\min^{-1}$ for a reliable result; since a faster rate has been used in the present work this conclusion must be regarded as tentative. Indeed, the available evidence from the dilatometric measurements, where a rate of 2° $\min^{-1}$ was employed, shows very little hysteresis through T_c [10]. Incidentally, considerable hysteresis existed at the O-T transition in the expansion work where the volume change was very much smaller [10]. No thermal effect has so far been detected at this transition and so a comparison is not possible.

The value of T_c measured by DTA varies from 550 to 585° C with changing composition. No systematic investigation of the composition dependence has been performed but these values fall well within the range given previously [11]. It has also been shown that the thermal history of the sample can markedly influence the transition temperature [16] and this observation may account for the discrepancy between T_c values obtained by dilatometry and DTA on material of composition 3 (crystal 1 in Fig. 1). The dilatometer sample was cut from a slowly-cooled Czochralski-grown single crystal whereas the DTA sample was taken from a rapidly cooled melt. Quenching reduces T_c [16] and this is reflected in the lower value observed for the melt in Table III.

Both the dilatometric and X-ray expansion results indicate that tetragonal symmetry is retained above T_c but with a reduced c/a ratio. During a study of the atomic configuration of B-S-N [17] it was pointed out that a completely ordered arrangement of the NbO_6 octahedra in the tungsten bronze type structure, which align themselves with some distortion along the polar c-axis, leads to a doubling of the c-axis of the unit cell. Such a doubling has been observed by X-ray techniques [3, 8]. The reduced c/a of the high temperature phase probably corresponds to a collapse of this alignment as the material passes through the ferroelectric-paraelectric transition. In the ferroelectric form all the metal atoms are displaced from their nearest mean plane of oxygen atoms [17]. It is this displacement that determines the macroscopic polarity in the ferroelectric phase. In the paraelectric phase, the metal atoms most probably lie in these oxygen planes and the macroscopic effects observed in the region of the Curie point in the present experiments are probably associated with the relaxation of these displaced metallic atoms.

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