

Synthesis and dielectric properties of $Ba_3NaRNb_{10}O_{30}$ [R = La and Sm]

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Abstract. Polycrystalline samples of $Ba_3NaRNb_{10}O_{30}$ (R = La and Sm) have been prepared by high temperature solid-state reaction method. The X-ray powder diffraction technique has been used to test the formation of the compounds. Lattice parameters, space groups and basic structures of the compounds have been obtained from X-ray data. The dielectric constant has been measured as a function of frequency (100 Hz–10 kHz) and temperature (–180 to 200°C) to understand transition mechanism in these ferroelectric compounds.

Keywords. Ferroelectrics; tetragonal phase; dielectric constant.

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1. Introduction

Barium-sodium rare earth niobates, $Ba_3NaRNb_{10}O_{30}$ (R = La and Sm) are members of a niobate family which have tungsten-bronze type structures. Nowadays, a large number of ferroelectric oxides with tungsten-bronze (TB) structure have been studied which are useful for many industrial applications. It has been found that this niobate family possesses many interesting properties such as electro-optic (Nenzo *et al* (1967)), nonlinear (Abraham *et al* (1971)), elasto-optic, pyroelectric, (Glass (1969)), acousto-optic (Ventiurini *et al* (1969)) etc. It has also been observed that some members of this niobate family which contain rare-earth ions are found to be very important and useful because of the existence of diffuse phase transition in them. For the better understanding of the diffuse phase transition in $Ba_3NaRNb_{10}O_{30}$ (R = La and Sm), we have completed preliminary X-ray structure and detailed dielectric properties, which are reported here.

2. Experimental

The polycrystalline samples of $Ba_3NaRNb_{10}O_{30}$ (R = La and Sm) were prepared by high-temperature solid-state reaction of stoichiometric mixtures of oxides and carbonates at high temperature ($\sim 1000^\circ\text{C}$). The constituent oxides/carbonates were of high purity ($> 99.9\%$). The mixtures were thoroughly mixed in a agate-mortar for 2 h and kept in methanol for about 24 h. The dried powders of the compounds were then calcined at 1000°C in a platinum crucible for about 10 h. The process of mixing and calcination were repeated many times to get homogeneous fine powders. Finally,

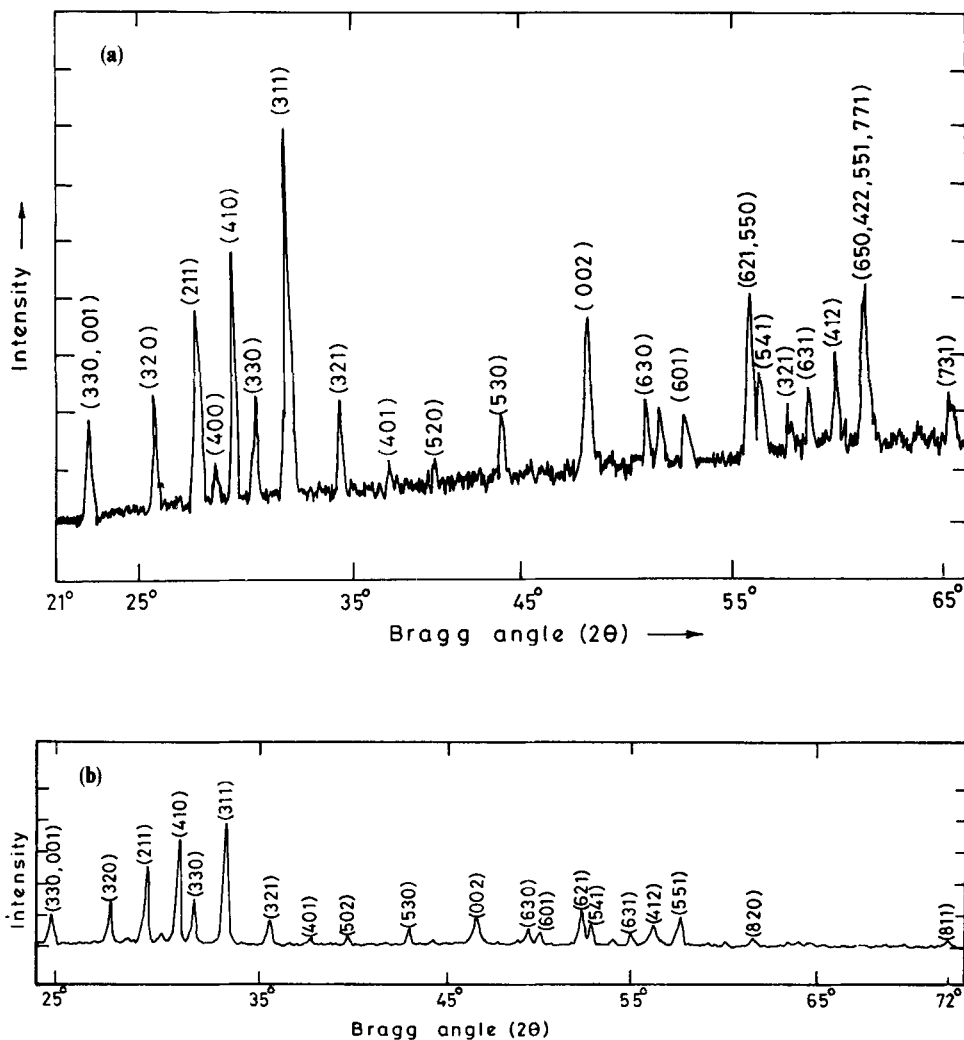


Figure 1. Comparison of room temperature X-ray profiles of $\text{Ba}_3\text{NaRNb}_{10}\text{O}_{30}$ (figure 1a, $R = \text{La}$ and figure 1b, $R = \text{Sm}$).

cylindrical pellets of diameter 1.12 cm and varying thicknesses were prepared from the powders at the pressure of $9 \times 10^6 \text{ kg/m}^2$ using a hydraulic press. The pellets were sintered in a platinum crucible at 1250°C for about 24 h to obtain high density ($\sim 95\%$ of the theoretical value) samples. The quality and formation of the compounds were checked with X-ray diffraction technique.

At room temperature ($\sim 30^\circ\text{C}$), X-ray diffractograms of the above compounds were taken using a Jeol (JXR Japan) (figure 1b) and Philips (figure 1a) diffractometers with CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$) in a wide range of 2θ ($15 \leq 2\theta \leq 75^\circ$).

To measure the dielectric constant of these compounds, air-drying silver paint was applied to both the faces of the samples to work as electrodes. The dielectric constant (K) of the compounds was measured as a function of frequency (100 Hz–10 kHz) and

temperature (liquid nitrogen temperature to 200°C for $Ba_3NaLaNb_{10}O_{30}$ and room temperature of 200°C for $Ba_3NaSmNb_{10}O_{30}$) using Gr 1620 capacitance bridge with oscillator and preamplifier detector.

3. Results and discussion

The lattice constants of these compounds were obtained from the least-squares refinement method using 20 (widely spread in θ) reflections of the powder diffraction profile. These are: $a = 12.475(5)$ Å and $c = 3.950(6)$ Å (space group P4bm) for $Ba_3NaLaNb_{10}O_{30}$; and $a \sim b = 12.342(4)$ Å and $c = 3.920(6)$ Å (space group Ccm2) for $Ba_3NaSmNb_{10}O_{30}$. Even with limited observed strong reflections, the space groups of the compounds were confirmed. Comparison of calculated (using the above lattice constants) and observed d -values of these compounds has been in tables 1 and 2. Single and sharp peaks of all the reflections (figure 1) of the above compounds clearly suggest the single phase nature of the compounds. At room temperature, the crystal structure of $Ba_3NaLaNb_{10}O_{30}$ was found to be tetragonal which is very close to the low-temperature (below -45°C) orthorhombic structure. Similarly at room temperature $Ba_3NaSmNb_{10}O_{30}$ has orthorhombic structure which is very close to tetragonal structure above T_c (i.e. 127°C). A good agreement between d_{obs} and d_{cal}

Table 1. Comparison of observed and calculated d values (in Å) of some reflections in $Ba_3NaLaNb_{10}O_{30}$ at room temperature. The estimated errors in d_{obs} is 10^{-3} Å.

hkl	d_{obs}	d_{cal}	I/I_0
731	1.5100	1.5122	13
650, 422	1.6050	1.6098	44
551, 711			
412	1.6480	1.6494	26
631	1.6800	1.6813	15
322	1.7080	1.7102	12
541	1.7435	1.7460	23
550	1.7580	1.7606	42
601	1.8380	1.8383	15
630	1.8580	1.8597	23
002	1.9676	1.9673	41
530	2.1389	2.1394	18
520	2.4090	2.4008	11
401	2.4420	2.4441	9
321	2.5920	2.5983	26
311	2.7890	2.7859	100
330	2.9370	2.9362	30
410	3.0270	3.0256	68
400	3.1179	3.1179	12
211	3.2133	3.2156	52
320	3.4596	3.4599	32
330			
001	3.9342	3.9350	30

Table 2. Comparison of observed and calculated d (in Å) values of some reflections in $Ba_3NaSmNb_{10}O_{30}$ at room temperature. The estimated errors in d_{obs} is 10^{-3} Å.

hkl	d_{obs}	d_{cal}	I/I_0
330	3.9281	3.9202	26
001			
320	3.4261	3.4238	38
211	3.1835	3.1964	65
410	2.9935	2.9941	68
330	2.9065	2.9097	39
311	2.7597	2.7604	100
321	2.575	2.5787	22
401	2.4250	2.4249	6
520	2.3008	2.2924	6
530	2.1291	2.1171	13
002	1.9601	1.9601	22
630	1.8548	1.8471	13
601	1.8317	1.8320	10
621	1.7580	1.7562	29
541	1.7310	1.7301	16
631	1.6691	1.6659	10
412	1.6453	1.6399	16
551	1.5952	1.5948	23
820	1.5029	1.4971	6
841	1.3019	1.3019	6

suggests that the structural parameters of these compounds reported above are correct. The linear particle size P calculated from many X-ray profiles using the Scherrer's equation

$$P = \frac{K\lambda}{\beta_{1/2} \cos \theta} \quad (K = 0.89, \beta_{1/2} = \text{half-width})$$

was found to be approximately 300 Å.

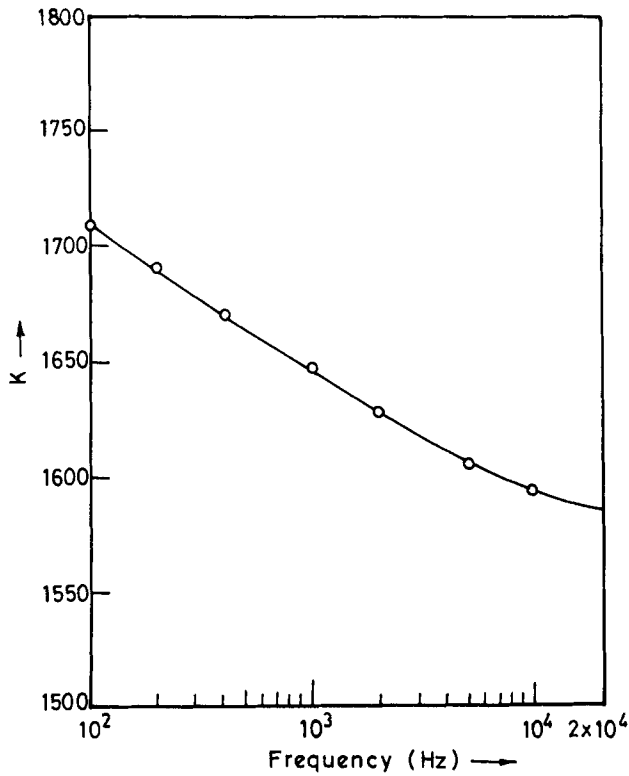


Figure 2. Room temperature (30°C) dielectric constant (K) of $\text{Ba}_3\text{NaLaNb}_{10}\text{O}_{30}$ as a function of frequency (10 Hz–10 kHz).

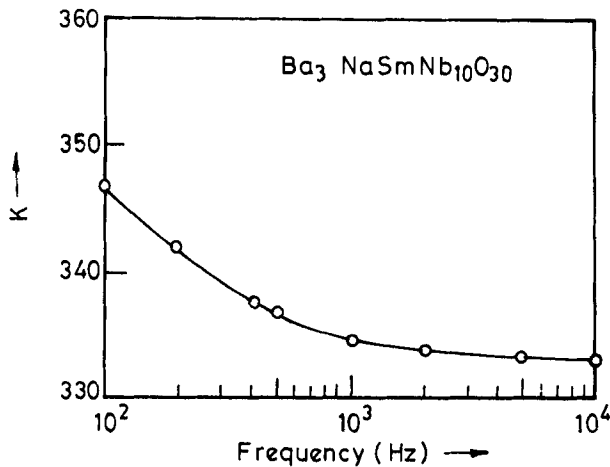


Figure 3. Variation of dielectric constant (K) of $\text{Ba}_3\text{NaSmNb}_{10}\text{O}_{30}$ as a function of frequency.

Figures 2 and 3 show the frequency dependence of dielectric constant (K) measured at room temperature. It has been observed that there is a small variation in the dielectric constant in high frequency. Figures 4 and 5 show the variation of dielectric constant of the above compounds with temperature (-180 to 220°C) at 1 kHz . It has been observed that transition temperatures of $Ba_3NaLaNb_{10}O_{30}$ and $Ba_3NaSmNb_{10}O_{30}$ are -45° and 127°C respectively. It has also been observed that these two compounds

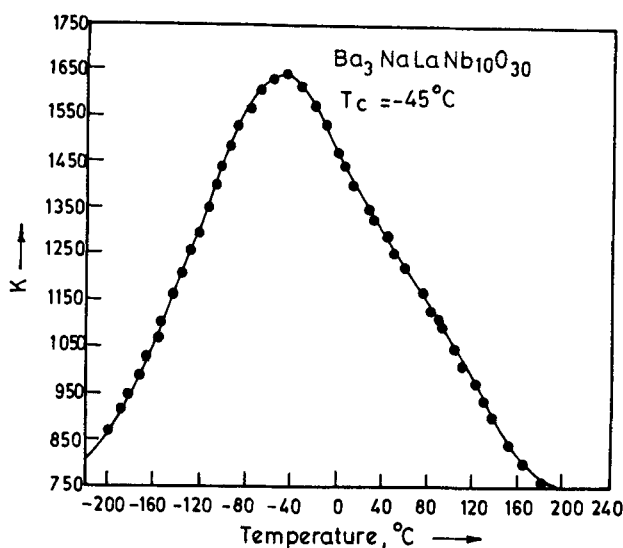


Figure 4. Variation of dielectric constant (K) of $Ba_3NaLaNb_{10}O_{30}$ at 1 kHz in the temperature range -196 and 200°C ; maximum K at $T_c(-45^\circ\text{C}) = 1650$.

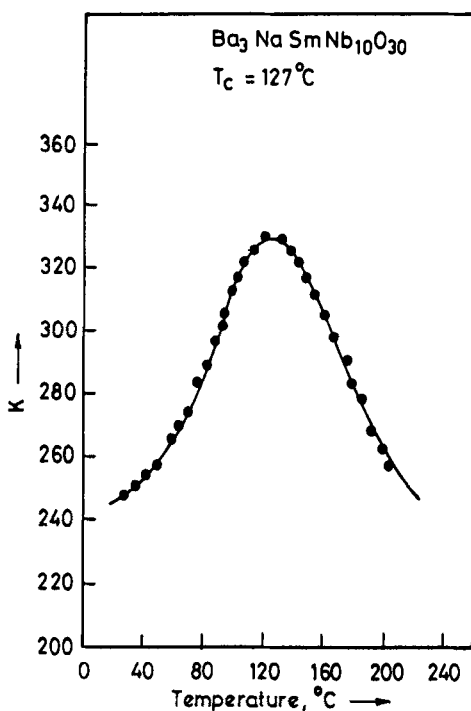


Figure 5. Variation of K of $Ba_3NaSmNb_{10}O_{30}$ at 1 kHz in the temperature range 30 – 220°C . Maximum K at $T_c(127^\circ\text{C}) = 335$.

have diffuse phase transition. The broadening (diffuse) phase transition may be observed due to the structural disorder created by the presence of void (which has been observed in SEM) and size of the rare earth ions which has been suggested by others (Lines and Glass 1977) also. It is interesting to note here that though there is some similarity in diffuse phase transition in both compounds, transition temperature is quite different in them.

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