Phase transitions in Na_2TeO_4 ceramics

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Abstract. Polycrystalline samples of NaTeO_4 were prepared by conventional solid-state reaction technique at low temperature (600°C). X-ray powder diffraction (XRD) technique was used to check the formation of single phase NaTeO_4 compound with cell parameters $a = 10.602(1) \text{ \AA}$; $b = 70.622(1) \text{ \AA}$ and $c = 8.506(1) \text{ \AA}$ in orthorhombic crystal system. Detailed studies of dielectric constant (ϵ) (and loss tangent ($\tan \delta$)) as a function of frequency (400 Hz–10 kHz) and temperature (-120°C – 260°C) show that the compound has two phase transitions in the ferroelectric phase.

Keywords. Polycrystalline; phase transition; ceramics; dielectric constant.

1. Introduction

Since the discovery of ferroelectricity and its related properties in BaTiO_3 (Wul and Goldman 1945), a large number of oxides in different forms have been studied using various experimental techniques in search of new materials for device applications such as transducers, computer memory and displays, electro-optic modulators, hydrophones, IR detectors, etc (Okada and Ossaka 1980; Deb 1988; Pilgrim *et al* 1990; Okuyama and Hamakawa 1991; Tondon *et al* 1992). Tireless efforts are still going on either in search of new ferroelectrics or new compositions of known compounds. The compounds with a general formula A_2XY_4 (A = alkali metal ions or equivalent monovalent complex ions and XY_4 = divalent tetravalent complex) are typical materials exhibiting commensurate-incommensurate phase (Yamaguchi *et al* 1987) and orthorhombic β - K_2SO_4 type structure with space group $Pm\bar{c}n$ in their high-temperature phase. Amongst all of them, K_2ZnCl_4 is ferroelectric at room temperature and undergoes an incommensurate-commensurate phase transition at 130°C (Zanbergen *et al* 1979). The incommensurate phase of the compound transforms to the normal phase with orthorhombic structure (space group $Pm\bar{c}n$) at 280°C (Gesi 1984). Further, some crystals of a general formula A_2XY_4 (A = Rb; X = Zn, Co and Y = Cl, Br) have similar type of successive phase transitions (Haga *et al* 1993; Shimizu *et al* 1995). From an extensive literature survey it has been found that except few works (Sharma *et al* 1999; Singh *et al* 1999), not much is known about A_2TeO_4 (A = alkali ions). Therefore we have carried out preliminary X-ray and detailed dielectric, polarization and electrical conductivity studies of the compounds. The present

report on Na_2TeO_4 is part of our systematic study of A_2TeO_4 family.

2. Experimental

The polycrystalline samples of Na_2TeO_4 were prepared by conventional high-temperature solid-state reaction technique in an air atmosphere with raw materials Na_2CO_3 (AR grade 99.9% M/s S.D. Fine Chem, India) and TeO_2 (99% M/s Aldrich Chemical Co. Inc, USA) in a suitable stoichiometry. The compounds were thoroughly mixed in an agate-mortar for 2 h. The mixed powders were calcined at 600°C for 6 h in alumina crucible. The process of grinding and calcination was repeated several times till the formation of the compound was confirmed. Finally calcination was completed at 600°C . Fine homogeneous powder of the resulting materials was then used to make cylindrical pellets of diameter 10 mm and thickness 1–2 mm under an isostatic pressure of about $5.5 \times 10^7 \text{ kg/m}^2$. Polyvinyl alcohol (PVA) was used as binder which was burnt off during the sintering of the pellets. X-ray diffraction technique was used to check the formation of Na_2TeO_4 compound prepared with reaction $\text{Na}_2\text{CO}_3 + \text{TeO}_2 + \text{O}$ (obtained from air). X-ray diffractogram of the Na_2TeO_4 was recorded at room temperature using X-ray diffractometer (Philips) with $\text{CoK}\alpha$ radiation ($\lambda = 1.789 \text{ \AA}$) in a wide range of Bragg angles ($10^\circ \leq 2\theta \leq 65^\circ$) at a scanning speed $2^\circ/\text{min}$. The sintered pellets were polished to make both their surfaces flat and parallel and were electroded with high purity silver paste for electrical measurements.

The dielectric constant (ϵ) and loss tangent ($\tan \delta$) of the pellet samples were obtained as a function of frequencies (400– 10^4 Hz) at room temperature, and as a function of temperature (-120 – 260°C) at fixed frequency (10 kHz)

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over a small temperature interval using a GR 1620 AP capacitance measuring assembly in conjunction with laboratory-made three-terminal sample holder. Measurement of dc resistivity (ρ) was carried out as a function of electric field and temperature (30–300°C) using a Keithley programmable electrometer.

3. Results and discussion

The sharp and single peak of XRD pattern of Na_2TeO_4 which was different (in position) from those of the components carbonate/oxides, suggested the formation of single-phase new compound. All the peaks of the XRD pattern were indexed and cell parameters were determined in various crystal systems with a standard computer program 'powdin'. Finally, a particular unit cell of orthorhombic system was selected for which sum of differences in observed and calculated d -values (i.e. $\Sigma\Delta d = \Sigma(d_{\text{obs}} - d_{\text{cal}})$) was found to be minimum. Table 1 shows a good agreement between observed and calculated d -values, which suggests the correctness of selection of crystal system and cell parameters. The finally selected cell parameters, refined by least-squares method are: $a = 10.602(1)$ Å; $b = 10.622(1)$ Å and $c = 8.506(1)$ Å. The linear particle size (L) of the sample, calculated from X-ray diffraction profiles using Scherrer (1918) equation,

$$L = (0.89)\lambda/(\beta_{1/2} \cos\theta),$$

where $\beta_{1/2}$ is the full width at half maximum and θ gives the peak position of diffraction line, was found to be 250 Å.

Figure 1 shows the variation of dielectric constant (ϵ) and loss factor ($\tan \delta$) as a function of frequency (400 Hz–10 kHz). The nature of variation of these parameters shows that ϵ and $\tan \delta$ decrease with the increase of frequency which is the normal behaviour of a dielectric. This is due to the presence of all different types of polarizations (viz. electric, dipolar, interfacial, orientational, etc)

Table 1. Comparison of d_{obs} and d_{cal} (in Å) of some reflections of Na_2TeO_4 at room temperature.

h	k	l	d_{obs}	d_{cal}	I/I_0
1	1	0	5.1385	5.1533	100
0	1	1	5.0759	5.0699	19
2	0	3	4.9317	4.9330	15
2	0	4	3.9172	3.9139	22
4	1	0	3.6464	3.6409	18
3	0	5	3.4062	3.4025	14
2	0	5	3.2207	3.2212	13
4	1	3	3.0638	3.0638	16
3	1	4	2.9665	2.9709	25
6	0	3	2.8792	2.8740	24
7	0	0	2.8563	2.8577	18
5	1	3	2.7792	2.7820	51

in the compound at room temperature (30°C) and low frequency. Similar dielectric behaviour was found in some ferroelectric ceramics (Bera and Choudhary 1995; Misra *et al* 1995).

Figure 2 shows the temperature dependence of ϵ and $\tan \delta$ at 10 kHz which shows two anomalies. The a.c.

Figure 1. Variation of dielectric constant (ϵ) and loss tangent ($\tan \delta$) of Na_2TeO_4 as a function of frequency at room temperature.

Figure 2. Variation of dielectric constant (ϵ) and loss tangent ($\tan \delta$) of Na_2TeO_4 with temperature (–120°C–260°C) at 10 kHz.

Figure 3. Variation of $\ln \rho_{dc}$ as a function of inverse of absolute temperature ($1/T$) of Na_2TeO_4 at 10 kHz and at constant and varying fields.

electrical conductivity (σ) and activation energy of Na_2TeO_4 were calculated using the formula

$$\sigma = \omega \epsilon \epsilon_0 \tan \delta \text{ and } \sigma = \sigma_0 \exp(-E_a/K_B T),$$

where ω is the angular frequency, ϵ_0 the vacuum permittivity, E_a the activation energy and K_B the Boltzmann constant. At 10 kHz, E_a has been calculated from the slope of the $\ln \sigma$ vs $1/T$ graph and was found to be 0.66×10^{-1} eV in the high-temperature region. Such a low value of activation energy is due to high ionic conductivity of Na_2TeO_4 supporting the superionic nature of it in high temperature region (Anderson 1964; Robert and Newnham 1975). No proper hysteresis loop has been observed in the unpoled Na_2TeO_4 compound. The variation of d.c. resistivity as a function of electric field at room temperature is shown in figure 3. It can be seen that the d.c. resistivity of Na_2TeO_4 decreases with increasing biasing field. Resistivity comes down with increasing biasing field.

The variation of d.c. resistivity ($\ln \rho$) with inverse of absolute temperature ($1/T$), at a constant electric field (10 V/cm) is also seen in figure 3. It is found that resistivity decreases as temperature increases.

Finally, it is concluded that Na_2TeO_4 has an orthorhombic structure at room temperature and successive phase transitions at $-96 \pm 2^\circ\text{C}$ and $88 \pm 2^\circ\text{C}$.

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