

Phase transition in Na_2MoO_4 ceramics

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Abstract : Polycrystalline sample of Na_2MoO_4 compound was synthesized by high-temperature solid-state reaction technique. X-ray studies revealed that the compound has orthorhombic structure at room temperature. Measurements of dielectric constant (ϵ) and loss tangent ($\tan \delta$) were carried out from -190°C to 400°C . These studies show that the compound undergoes a ferroelectric phase transition at 14°C . Studies of dielectric hysteresis of the compound showed no hysteresis loop at room temperature (*i.e.* 29°C) suggesting normal (paraelectric) phase of the material.

Keywords : Solid-state reaction, dielectric constant, commensurate-incommensurate phase transition.

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1. Introduction

Phase transitions in halogenide crystals of a general formula A_2BX_4 , where A = monovalent alkali ions, $B = \text{Mn, Co, Cu, Zn, Cd, Hg}$, $X = \text{F, Cl, I, Br}$ have widely been investigated in last decades [1]. It has been found that, in general, they have $\beta\text{-K}_2\text{SO}_4$ -type orthorhombic structure with multiple or successive phase transitions from the high-temperature normal (*i.e.* paraelectric phase) to the low temperature ferroelectric commensurate phase *via* a modulated incommensurate phase [2–4]. Though a considerable amount of work has been done on the above crystals, there are no reports on the compound with $X = \text{Te, W, Mo}$. Therefore, to examine the successive, normal-incommensurate-commensurate phase transition, in polycrystalline samples of A_2BO_4 ($A = \text{alkali ions, } B = \text{W, Mo and Te}$) family, we have studied their preliminary structural and detailed dielectric and electrical conductivity properties. In the present paper, we report our above work on the Na_2MoO_4 compound.

2. Experimental details

The polycrystalline samples of Na_2MoO_4 was prepared by solid-state reaction technique using the raw materials : Na_2CO_3 (ultrapure, M/s Loba Chemical Co.) and MoO_3 (M/s John Baker Inc. USA) in a stoichiometry. These materials were mixed thoroughly in an agate mortar for 2 h. The mixed powder was calcined at 550°C for 5 h. The calcined powder was grounded and recalcined at 550°C for 6 h. Recalcined fine powder was then used to make pellets of 10 mm diameter and 1–2 mm thick under a pressure of $5 \times 10^7 \text{ kg/m}^2$. These pellets were then sintered at 600°C for 4 h. in an alumina crucible to reduce their porosity. The formation of the single phase compound was checked by X-ray diffraction (XRD) technique.

For preliminary structural studies, X-ray diffractogram of the material was recorded at room temperature with a miniflex Rikagu X-ray powder diffractometer with CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$) in a wide range of 2θ ($20^\circ \leq 2\theta \leq 100^\circ$) at scanning rate of $2^\circ/\text{min}$. The dielectric constant (ϵ) and loss tangent ($\tan \delta$) of Na_2MoO_4 were obtained as a function of frequency (400 to 10^4 Hz) at room temperature and of temperature (-190 to 400°C) at fixed frequency of 10 kHz over a small temperature interval (*i.e.* 2°C) using a GR 1620 AP capacitance measuring assembly in conjunction with a laboratory-made three-terminal sample holder which compensated the unwanted or stray capacitance. The temperature was measured using a chromel-alumel thermocouple.

The dc volume resistivity of the pellet sample was measured as a function of electric field (10 – 80 V/cm) at room temperature, and as a function of temperature of a constant electric field (10 V/cm) using a Keithley 617 programmable electrometer. The dielectric hysteresis of the sample was examined with the help of modified Sawyer-Tower circuit with dual trace oscilloscope at a field of 6 kV/cm.

3. Results and discussion

The sharp and single peaks of XRD pattern which was different from those of ingradient compounds, confirmed the formation of the single phase of the Na_2MoO_4 compound. All the XRD peaks (high, medium and low intensity) were indexed in different unit cell configurations and crystal systems with the help of a standard computer program package, POWDIN. Finally, a suitable unit cell was selected on the basis of the best agreement in observed and calculated d -values. The cell parameters were refined by least-squares method. They are : $a = 7.5140 \text{ \AA}$, $b = 8.3080 \text{ \AA}$ and $c = 6.022 \text{ \AA}$. A good agreement between observed and calculated d -values (Table 1) suggests the correctness of selected cell parameters of the orthorhombic crystal system at room temperature. Due to a limited number of reflection data it was not possible to uniquely determine the space group of the material.

The particle size (P) of the sample was calculated using Scherrer's equation, $P = K\lambda/(\beta_{1/2} \cos \Theta) 2\theta$ [5] ($K = \text{constant} = 0.89$, $\beta_{1/2} = \text{half peak width}$). The average particle size of the sample was found to be 270 \AA .

Table 1. Comparison of observed and calculated d -values (in Å) of some reflections of Na_2MoO_4 at room temperature. The estimated error in d is ± 0.0010 Å.

hkl	d_{obs} (Å)	d_{cal} (Å)
1 2 0	4.0046	4.0046
0 0 3	3.5072	3.5072
4 1 1	3.2554	3.2554
1 1 3	3.1646	3.1590
4 0 2	3.0585	3.0574
2 1 3	2.9689	2.9684
5 1 0	2.8227	2.8224
0 0 4	2.6301	2.6304
1 1 4	2.4684	2.4736
4 0 4	2.1550	2.1548
7 0 2	1.9894	1.9877
2 4 2	1.8697	1.8692
2 3 4	1.8484	1.8487
0 0 6	1.7554	1.7550
8 2 1	1.6894	1.6895
8 0 3	1.6557	1.6559
0 2 6	1.6156	1.6156

The variation of dielectric constant (ϵ') and tangent ($\tan \delta$) with frequency for the compound is shown in Figure 1. The variation of these parameters show that both the

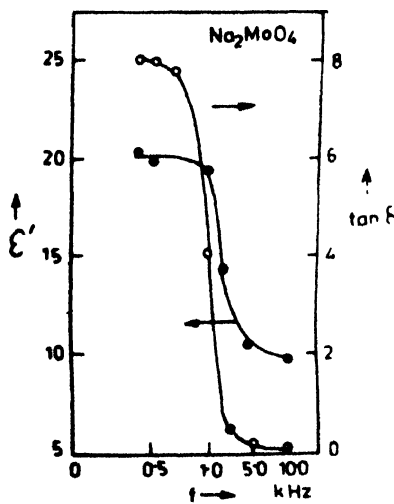


Figure 1. Variation of dielectric constant (ϵ') and dielectric loss ($\tan \delta$) of Na_2MoO_4 with frequency (f) at room temperature.

dielectric parameters decrease with the increase of frequency, which is an usual behaviour of a dielectric. The higher value of ϵ' at low frequency is due to the presence of all the different types of polarisation (*viz.* electronic, dipolar, interfacial, orientational, electronic *etc.*) in the compound at room temperature (29°C) and at low frequency. Similar dielectric behaviour with respect to frequency was found in some other ferro-electric ceramics [6–8].

The variation of ϵ' and $\tan \delta$ with temperature (–50°C to 400°C) at a fixed frequency of 10 kHz is shown in Figures 2 and 3. Though the dielectric investigations were

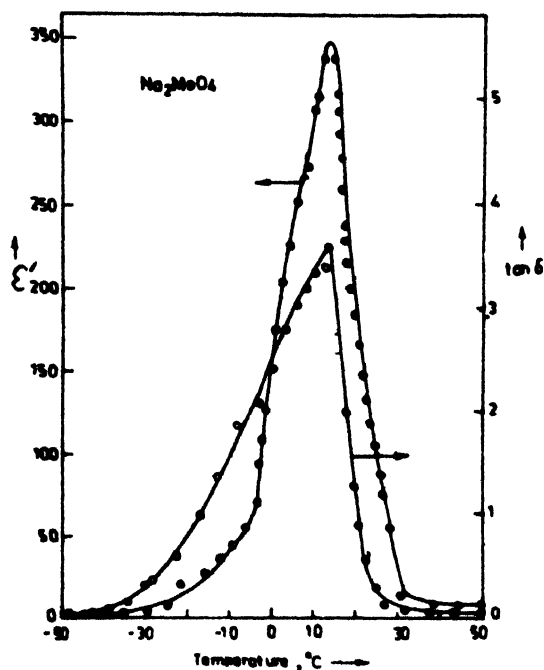


Figure 2. Variation of dielectric constant (ϵ') and loss tangent ($\tan \delta$) of Na_2MoO_4 with temperature (–50°C to 50°C) at 10 kHz.

carried out from liquid nitrogen temperature (*i.e.* –190°C), it has not been shown in the Figure 2 because there was no significant variation of dielectric constant within temperature range (–196 to –50°C). A sharp dielectric anomaly was observed at 14°C with $\epsilon'_{\text{max}} = 347$. Figure 3 shows variation of the dielectric constant and dielectric loss as a function of temperature (50°C to 400°C) at a frequency of 10 kHz. It can be seen that the dielectric constant increases very sharply beyond 300°C. It appears that this may be due to the presence of space charge polarisation at high temperature and low frequency.

The calculations of ac dielectric conductivity (at 10 kHz) at different temperatures have been done using the relation $\sigma = \omega \epsilon_0 \epsilon' \tan \delta$, where ω is the angular frequency,

ϵ_0 = dielectric permittivity in free space. Figure 4 and Figure 5 show the variation of $\ln \sigma$ with inverse of absolute temperature in the low (-30°C to 30°C) and high (250°C to 400°C)

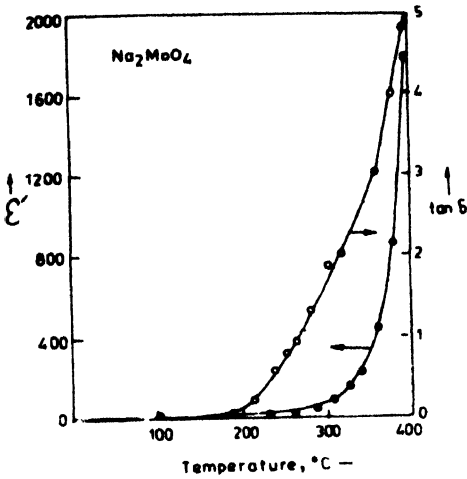


Figure 3. Variation of dielectric constant (ϵ') and dielectric loss ($\tan \delta$) of Na_2MoO_4 with temperature (50°C to 400°C) at 10 kHz.

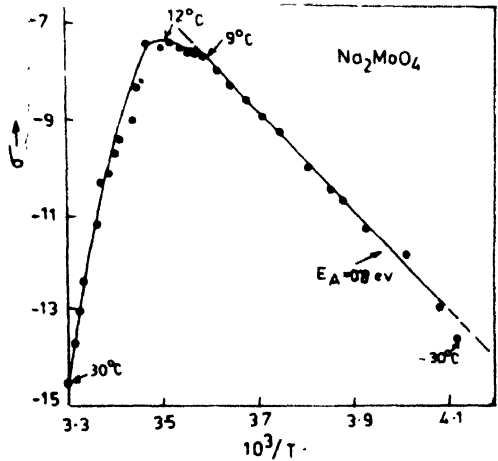


Figure 4. Variation of ac conductivity ($\ln \sigma$) of Na_2MoO_4 with inverse of absolute temperature from (-30°C to 30°C) at 10 kHz.

temperature regions, respectively. The activation energy, E_A calculated from Figure 4 (between -30°C to 10°C) is 0.7 eV is observed. In the high-temperature region, the

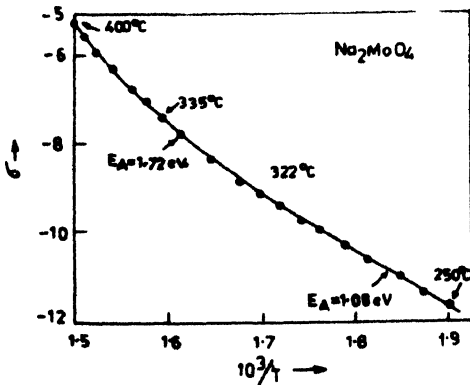


Figure 5. Variation of ac conductivity ($\ln \sigma$) of Na_2MoO_4 with inverse of absolute temperature from (250°C to 400°C) at 10 kHz.

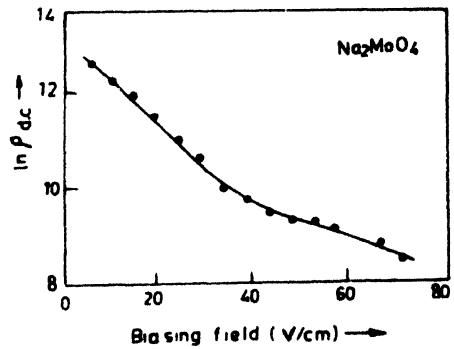


Figure 6. Variation of dc resistivity ($\ln \rho_{dc}$) of Na_2MoO_4 with biasing electric field at room temperature.

activation energy increases from 1.08 to 1.72 eV as temperature increases. From the room temperature (29°C) to 200°C , the value of $\ln \sigma$ ranges from -1.43 to -1.46 , which shows that over a wide range of temperature the material shows an ac conductivity whose variation with temperature is not very significant.

Figure 6 shows the variation of dc resistivity ($\ln \rho_{dc}$) with the biasing electric field at room temperature. It is observed that the dc resistivity of this compound decreases with increase in biasing electric field. This effect was observed by others for a number of compounds [9–11].

The variation of dc volume resistivity ($\ln \rho_{dc}$) with the inverse of absolute temperature is shown in Figure 7. Decrease of the dc resistivity of the compound with increase in temperature is due to the progressive increase of thermal energy inside the material which gives rise to more and more free electrons, and hence ρ_{dc} decreases. Below 68°C, ρ_{dc} is observed to decrease with the decrease in temperature. Similar anomaly has

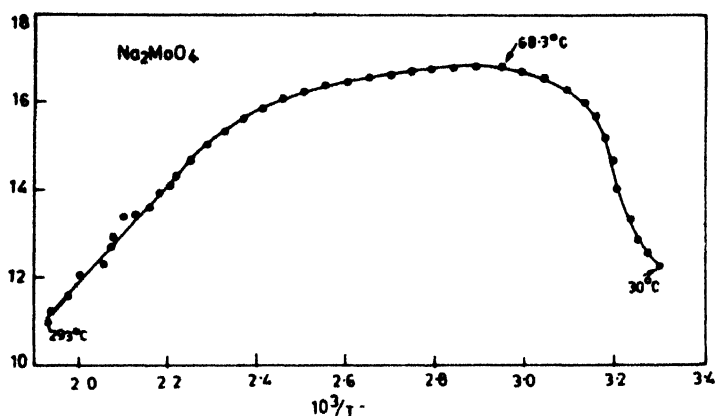


Figure 7. Variation of dc resistivity ($\ln \rho_{dc}$) of Na_2MoO_4 with inverse of absolute temperature.

been observed in the case of Rb_2TeO_4 , Tl_2TeO_4 and Na_2WO_4 compounds [12–14]. At low temperatures, decreasing trend of ρ_{dc} with decrease in temperature has been found in many superconductor ceramics.

No hysteresis loop (E vs P) for Na_2MoO_4 compound at room temperature was found.

4. Conclusions

It is concluded that Na_2MoO_4 has an orthorhombic structure at room temperature and exhibits a phase transition at 14°C. Although it was observed that in many compounds of the A_2BO_4 -type, there exists successive phase transition [ferroelectric commensurate phase-incommensurate phase-paraelectric normal phase] within the temperature range of investigation in Na_2MoO_4 . Unlike many other compounds of the family, only one phase transition is observed. Similar behaviour in Na_2WO_4 and Tl_2MoO_4 of the A_2BO_4 family [14,15] was also found.

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