

Studies of X-rays and electrical properties of SrMoO₄

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Received 7 November 1997, accepted 20 March 1998

Abstract : A polycrystalline sample of SrMoO₄ was synthesized by high-temperature solid-state reaction technique. Preliminary X-ray study has been carried out to check the formation of compound and to determine its preliminary crystal data. The variation of ac conductivity and dc resistivity with temperature has also been studied. Measurements of dielectric constant (ϵ) and loss tangent ($\tan \delta$) as a function of frequency (400 Hz–10 kHz) and temperature (–180° to 300°C) show that the compound is a linear dielectrics

Keywords : Solid state reaction, X-ray diffraction, dielectric constant and dc resistivity

PACS Nos. : 77.22 Gm, 61.10.Nz, 77 80.Bh

1. Introduction

Since the discovery of ferroelectricity in BaTiO₃ in 1945 [1], a large number of oxides of different structural families have been examined [2,3] in search of new materials for device applications. It has been found that each member of an oxide family has some interesting structural and physical properties in spite of some similarities in their chemical formula or compositions [4–7]. Among all the oxides studied so far, some molybdates and tungstates, such as Gd₂(MoO₄)₃ [8], PbMoO₄ [9], PbWO₄ [10] *etc.*, have interesting ferroelectric and related properties. Some molybdates and tungstates of the general formula ABO₄ (A = alkali ions; B = W, Mo) have very unusual successive phase (*i.e.* commensurate-incommensurate) transitions [11] in wide temperature range, with high electrical conductivity and dielectric loss [12] and low dielectric constant [13]. This has attracted us to synthesize and study structural, electrical and spectroscopic properties of different structural families of tungstates/molybdates, such as perovskite, tungstan bronze (TB) [14], spinel [15] and scheelite [16]. SrMoO₄, suitable for laser applications [17],

belongs to the scheelite structural family with the space group $I4_1/a$ [16]. Detailed literature survey on this compound suggests that except a few studies [18–20], not much work have been done on it. Therefore, we have carried out systematic studies on structural and electrical properties of the compound for the better understanding of its structural and physical properties and to check the existence of ferroelectric properties in it.

2. Experimental

The SrMoO_4 sample was prepared from strontium carbonate SrCO_3 (99% pure, M/s. Bugoyne Ltd.) and molybdenum oxide MoO_3 (999.5% pure, M/s. BDH Ltd.) in desired stoichiometry by solid state reaction technique. These component compounds were mixed in a agate-mortar for 2 h and calcined at 725°C in a platinum crucible for 20 h. The calcined powder was ground and recalined at 800°C for 18 h. The calcined powder was ground again to make fine and homogeneous powder which was uniaxially cold pressed into pellets (diameter = 10 mm and thickness = 1–2 mm) at a pressure of $4.5 \times 10^7 \text{ kg/m}^2$ using a hydraulic press. The pellets were then sintered at 825°C for 14 h. The quality and the formation of the compound were checked with an X-ray diffraction (XRD) technique.

For preliminary structural studies, an X-ray diffractogram was recorded at room temperature by a Rigaku X-ray powder diffractometer (Miniflex, Japan) with $\text{CuK}\alpha_1$ radiation ($\lambda = 0.15418 \text{ nm}$) for a wide range of Bragg angle 2θ , ($15^\circ \leq 2\theta \leq 90^\circ$) at the scanning rate of $2^\circ/\text{min}$. To measure the dielectric constant, the flat surfaces of the pellet sample were electroded with high purity and ultrafine silver particle paste. Measurements of dielectric constant (ϵ) and loss tangent ($\tan \delta$) of the sample were carried out both as a function of frequency (400 Hz to 10 kHz) and temperature (-180°C to 300°C) by GR 1620 AP capacitance measuring assembly in small temperature interval ($\sim 8^\circ\text{C}$). Measurement of dc resistivity was done both as a function of temperature (room temperature to 325°C) and biasing electric field (1.5–8 kV/m) by Keithley 617 programmable electrometer. Existence of spontaneous polarisation in the compound was checked using laboratory made Sawyer-Tower circuit.

3. Results and discussion

The sharp and single diffraction peaks (Figure 1) in the X-ray spectra (XRD) suggest that the compound was formed in a single phase. Lattice parameters and d -values of the compound were calculated for different crystal systems and unit cell configurations with observed d -values of strong, medium and low-intensity reflections using a standard computer program "powdin". Finally, lattice parameters and crystal system were selected on the basis of minimum $\sum \Delta d$ ($= d_{\text{obs}} - d_{\text{cal}}$) which was consistent and very much comparable with those of the calculated values obtained here and

values reported in JCPDS [21]. The refined lattice parameters are : $a = 11.4377 (10) \text{ \AA}$ and $c = 12.0316 (10) \text{ \AA}$ (estimated error in the parenthesis). A very good agreement

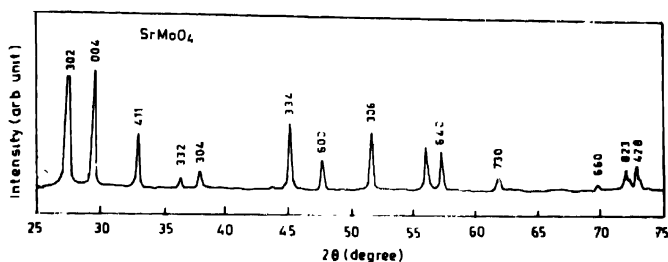


Figure 1. Room temperature X-ray diffractogram of SrMoO₄

between observed and calculated d -values (Table 1) suggests the correctness of the selected cell and structure.

Table 1. Comparison of some observed and calculated d -values (in \AA) of some reflections of SrMoO₄ at room temperature

hkl	d_{obs} (\AA)	d_{cal} (\AA)	I/I_0
302	3.2203	3.2203	100
004	3.0079	3.0071	67
411	2.7023	2.7031	28
332	2.4616	2.4601	6
304	2.3636	2.3615	9
334	2.0081	2.0076	34
600	1.9013	1.9063	15
306	1.7712	1.7748	29
640	1.5883	1.5861	20
730	1.5011	1.5018	6
660	1.3474	1.3479	3
823	1.3107	1.3108	10
428	1.2960	1.2964	13
902	1.2424	1.2434	4
664	1.2296	1.2301	21
419	1.2043	1.2043	15
717	1.1780	1.1779	7
1000	1.1438	1.1438	8
1012	1.1179	1.1183	4

Though it is not possible to determine the space group from the limited powder data, the reported space group $I4_1/a$ has been confirmed with some systematically absent reflections and physical properties. The particle size of the compound calculated using Scherrer's equation [22], was found to be 363 \AA , which was consistent with those observed from the particle size analyser.

The dielectric constant (ϵ) and loss ($\tan \delta$) decrease with increase in frequency at room temperature (Figure 2). At low frequencies, all the polarizations exist but with

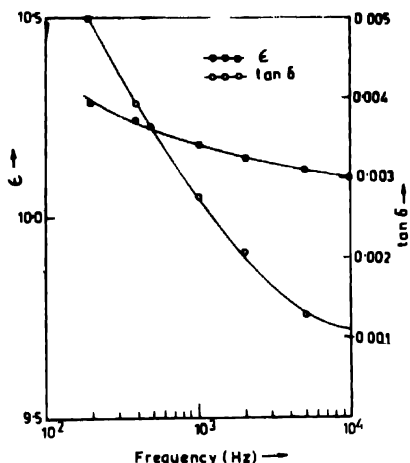


Figure 2. Variation of dielectric constant (ϵ) and loss ($\tan \delta$) of SrMoO_4 with frequency at room temperature.

increase in frequency some of the polarizations vanish. Therefore, the dielectric constant and loss decrease with increase in frequency. This suggests the normal behaviour of a dielectric. Variation of ϵ of the compound with temperature (-180°C to 300°C) at 10 kHz shows the linear dielectric behaviour of the compound. Below room temperature (upto -180°C), the values of ϵ and $\tan \delta$ were found to be about 10 and 0.005 respectively,

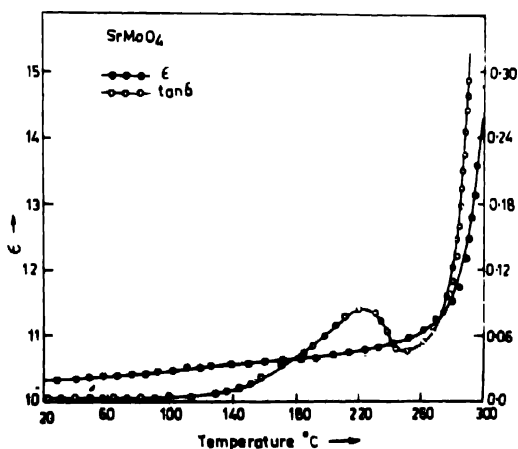


Figure 3. Variation of dielectric constant (ϵ) and loss ($\tan \delta$) of SrMoO_4 with temperature at 10 kHz.

(therefore, not shown in Figure 3) which are almost constant and linear. Variation of dielectric loss with temperature at a frequency 10 kHz shows a almost constant value

(in $\tan \delta$) with a small anomaly at 230°C. The slow increase at low temperature is due to lattice ionic polarizability and the faster increase in high temperature region is due to space charge polarization. Similar behaviour in ϵ and $\tan \delta$ has been observed in many molybdates and tungstates studied recently by us [23,24]. The electrical conductivity σ of the sample was calculated from the dielectric data using formula $\sigma = \omega \epsilon_0 \epsilon \tan \delta$, where ϵ_0 = dielectric constant in vacuum and ω = angular frequency. An activation energy E_A , calculated from the formula $\sigma = \sigma_0 \exp(-E_A/K_B T)$ (K_B = Boltzmann constant) was found to be 0.03 eV (Figure 4).

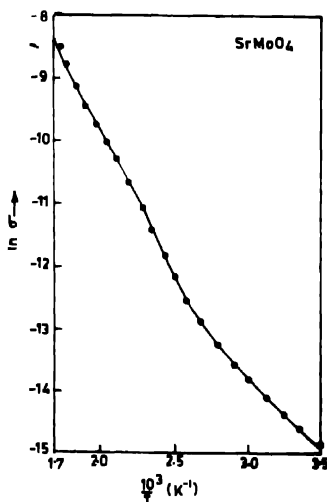


Figure 4. Variation of ac conductivity ($\ln \sigma$) of SrMoO₄ with inverse of temperature ($10^3/T$) at 10 kHz

Study of field dependence of dc resistivity (Figure 5) shows that the resistivity decreases with increase of electric field. This may be due to ionisation of gases and

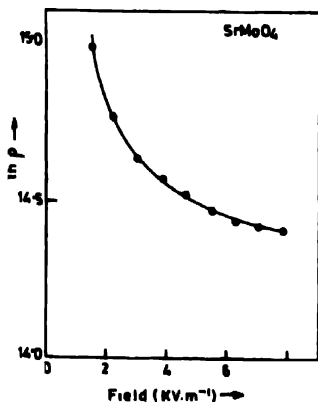


Figure 5. Variation of dc resistivity of SrMoO₄ with applied electric field at room temperature.

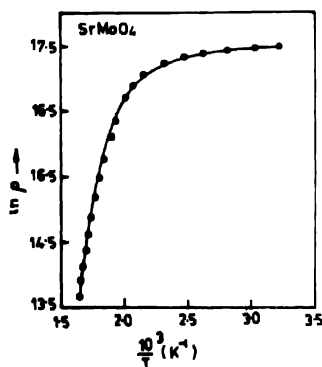


Figure 6. Variation of dc resistivity ($\ln \sigma$) of SrMoO₄ with inverse of absolute temperature ($1/T$).

moisture present in the pores/cracks of the compounds, thus increasing the conductivity of the ceramic samples in general [25]. Variation of $\ln \sigma$ with inverse of absolute temperature at constant electric field (7.87 kv/m^{-1}) is shown in Figure 6. The decrease of resistivity with increasing temperature can be explained on the basis that the insulators have no free carriers, but due to thermal energy, electrons can be set free from oxygen ions. Hence, conductivity of SrMoO_4 increases due to generation of electrons [25]. However, the compound shows a negative temperature coefficient of resistance (NTCR) similar to an extrinsic semiconductors above 100°C . As no D-E hysteresis loop in wide temperature range (liquid nitrogen temperature to 300°C) was observed, we concluded that the compound is non ferroelectric, which is very much consistent to our other studies. It is finally concluded that unlike many molybdates, this compound does not show any ferroelectric behaviour.

Acknowledgment

The authors wish to thank Sri S Bera and Ms. T Kar for their kind help in some experimental work.

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