

X-ray and dielectric studies of $\text{Sm}_2(\text{MoO}_4)_3$

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MS received 11 May 1987

Abstract. The polycrystalline samples of $\text{Sm}_2(\text{MoO}_4)_3$ have been prepared by heating appropriate quantities of oxides. The X-ray powder diffraction technique has been used to provide information about lattice parameter, space group and basic structure. The dielectric constant has been measured as a function of frequency (560 Hz–13 MHz) and temperature (30–220°C) to know the ferroelectric transition temperature.

Keywords. Ferroelectrics; ferroelastics; orthorhombic phase; dielectric constant.

PACS No. 77-80

1. Introduction

$\text{Sm}_2(\text{MoO}_4)_3$ is a member of rare-earth molybdate family with a general formula $R_2(\text{MoO}_4)_3$ where R = trivalent rare earth ions. Since the discovery of ferroelectricity in $\text{Gd}_2(\text{MoO}_4)_3$ (GMO), $\text{Sm}_2(\text{MoO}_4)_3$ (hereafter SMO) and other members of the family (Borchardt and Bierstedt 1967), a considerable amount of work has been done particularly on GMO. It has been found that the family possesses many interesting and fundamental properties such as ferroelectric, ferroelastic and piezoelectric etc at room temperature ($T_c \sim 150\text{--}200^\circ\text{C}$) which make them very useful for wide industrial applications. It is interesting to note that rare earth molybdates are found in many structural modifications under the varying physical conditions (Nassau *et al* 1971). Ferroelectric properties are found in orthorhombic β' modification obtained from high temperature β phase on rapid cooling (Borchardt and Bierstedt 1966). It has been observed that despite some structural similarities, physical properties of all the members are not the same. To get a better understanding of SMO, which is one of the less studied compounds of the family, its structural and dielectric properties have been studied. As the large single crystal of optically good quality of SMO is difficult to grow due to the complex morphology, we have used polycrystalline samples here.

2. Experimental

The SMO samples were prepared by solid state reaction of stoichiometric mixture of samarium oxide, Sm_2O_3 (Indian Rare Earth Ltd., 99.99% pure) and molybdenum oxide, MoO_3 (BDH, 99.5% pure). The oxides were mixed in agate mortar with ethanol for about 2 hr. The powder was heated at 800°C for 14 hr in a platinum crucible. The process of firing and mixing was repeated for a number of cycles. Finally cylindrical pellets were prepared from fine powder of the compound by applying a pressure of

4 tones/cm². The pellets were then sintered in a platinum crucible at 1100°C for about 10 hr. To obtain the orthorhombic phase the specimen were rapidly quenched to room temperature in going through the ferroelectric phase transition at $T_c = 197^\circ\text{C}$ (Brixner *et al* 1971). The quality and the formation of the compound, (i.e. β' modification) were checked with X-ray technique.

X-ray diffractogram of SMO was taken using a Jeol (JXR-Japan) diffractometer with $\text{FeK}\alpha$ radiation (i.e. $\lambda = 1.9373 \text{ \AA}$). The width of the powder profiles was monitored carefully and compared with the instrumental slit width and also with the results obtained from standard sample KCl.

To measure the dielectric constant, the flat surfaces of the specimen was coated with silver paste to work as electrodes. The dielectric constant (K) and loss ($\tan \delta$) were measured at room temperature in the wide frequency range 560 Hz to 13 MHz using a high frequency impedance analyser with $\pm 2\%$ accuracy. The temperature dependence of the dielectric constant and loss was measured by an universal bridge (Wayne Kerr, B-224) at 1592 Hz in the temperature region 30–220°C. The dielectric loss was not found significant and therefore is not given here. The room temperature dc conductivity was measured with GR-dc conductance bridge and was found to be $3.414 \times 10^{-10} \text{ ohm}^{-1}\text{cm}^{-1}$.

3. Results and discussion

The lattice constant of SMO was obtained from the least-squares refinement method using 20 (widely spread in θ) reflections of the powder diagram. These are; $a = 10.4320$

Table 1. Comparison of some calculated and observed d values of SMO in the ferroelectric phase.

hkl	d_{obs}	d_{cal}	I/I_0
111	6.0940	6.0933	22
002	5.3878	5.3830	55
201	4.6950	4.6941	60
202	3.7500	3.7459	100
220	3.6950	3.6955	75
003	3.5930	3.5887	53
221	3.4950	3.4953	100
310	3.3020	3.3002	80
113	3.2330	3.2282	11
222	3.0500	3.0466	67
023	2.9597	2.9602	60
132	2.8204	2.8199	35
004	2.6913	2.6915	15
400	2.6096	2.6080	12
331	2.4022	2.4015	15
420	2.3354	2.3345	30
333	2.0333	2.0311	35
025	1.9914	1.9914	42
423	1.9571	1.9569	22
350	1.7937	1.7942	25

± 0.0079 , $b = 10.4730 \pm 0.0079$, $c = 10.7660 \pm 0.0045$ Å. The observed (obtained from powder diagram) and calculated (based on refined lattice constants) d values have been compared in table 1. A good agreement between d_{obs} and d_{cal} was found. Even with limited observed reflections the space group was found to be Pba2 which is consistent with the reported ferroelectric phase. The density calculated from the experimental X-ray data is in good agreement (about 90%) with the theoretical value. The average apparent particle size calculated from the powder profile was 605 Å.

Figure 1 shows the frequency dependence of dielectric constant measured at room temperature. It is found that unlike many normal ferroelectrics, the dielectric constant of SMO does not decrease significantly with increase in frequency. This suggests the existence of ferroelasticity in the compound. Because of the prominent ferroelastic nature of the material the spontaneous polarization is not a primary order parameter. In figure 2, variation of dielectric constant with temperature at 1592 Hz has been shown in the temperature region 30–220°C. As expected, the dielectric constant of SMO at room temperature was low (9.5). The K value was almost constant with temperature. However a small anomaly was observed at $193 \pm 1^\circ\text{C}$. This behaviour has been observed in GMO (Aizu *et al* 1969) and some other compounds of rare-earth molybdate family (Keve *et al* 1970; Voronkova *et al* 1978). A small variation in dielectric constant with temperature has been explained (Voronkova *et al* 1978; Aizu 1970) due to its ferroelastic behaviour. On cooling from the paraelectric phase the

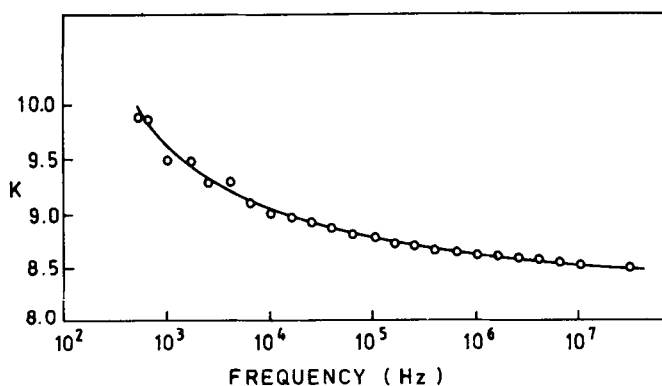


Figure 1. Variation of K with frequency (560 Hz–13 MHz) in SMO.

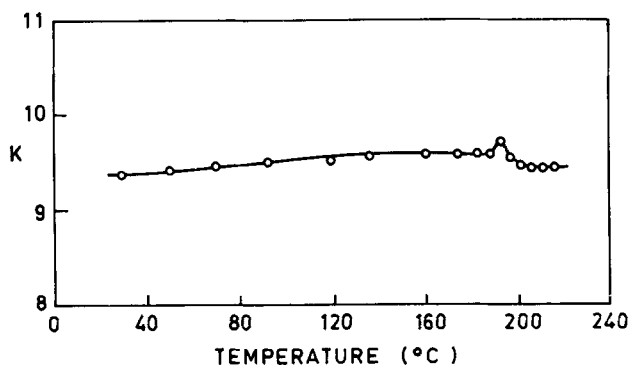


Figure 2. Variation of K with temperature (30–220°C) in SMO.

material becomes elastically unstable at T_c which gives rise to spontaneous strain and hence the acoustic phonon becomes unstable (Aizu 1969). Therefore a small dielectric anomaly is observed in this compound. Finally, the dielectric and structural studies lead us to the conclusion that SMO is a ferroelectric-ferroelastic material. The results of SMO mixed with other rare-earth ions in different proportions will be reported later.

Acknowledgements

The authors wish to thank Dr H S Maity and Mr R N Basu for their kind help in some experimental work. One of us (MR) gratefully acknowledges the fellowship from DST, Government of India.

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