X-RAY AND THERMAL STUDIES
OF FERROELECTRIC Dy$_2$(MoO$_4$)$_3$

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Dysprosium molybdate, Dy$_2$(MoO$_4$)$_3$, displays a ferroelectric phase transition at 145 °C. The X-ray and thermal (DTA, TG and DSC) properties of this compound have been studied. The X-ray study confirmed the ferroelectric phase in the orthorhombic space group Pba2. Thermal analysis demonstrated the existence of a ferroelectric and another phase transition in this compound.

Dysprosium molybdate, Dy$_2$(MoO$_4$)$_3$, is a member of the family of rare earth molybdates with general formula R$_2$(MoO$_4$)$_3$ (where R = trivalent rare earth ion). These materials have been found to be promising for many industrial applications, due to some of their special physical properties, such as ferroelectric-ferroelastic, etc. [1–3]. Ferroelectric properties have been reported for the orthorhombic modification of gadolinium molybdate [4]. The ferroelectric, ferroelastic and other related properties for some of the compounds of this family have made them attractive for device applications [5, 6]. Dy$_2$(MoO$_4$)$_3$ (hereafter DMO) is isostructural with gadolinium molybdate, GMO, and of interest by virtue of its ferroelectric properties [1]. Only two rare earth molybdates, GMO and TMO (terbium molybdate Tb$_2$(MoO$_4$)$_3$), have been thoroughly investigated [7], because of their relatively easy growth of good-quality single-crystals by the Czochralsky method [8]. However, little effort has been made to study the other isostructural molybdates, in part because of the specific difficulties involved in obtaining their single-crystals as a result of their complex morphology [9, 10]. The complex morphology is particularly a problem in the case of DMO, because of its reconstructive phase transition at about 1030°, accompanied by disintegration of the crystal itself [11]. It has been observed that its structural modification and physical properties are highly sensitive to the conditions of preparation. The ferroelectric β' phase in the compound can be obtained only by rapidly quenching the sample from the high-temperature (1000°) β phase to room temperature. As not much work has been done on DMO, we have studied its X-ray and thermal

properties (qualitative and quantitative) acquire more information for a better understanding of the practical application of the compound.

Experimental

Preparation of samples

All investigations were carried out on polycrystalline samples prepared from stoichiometric proportions of dysprosium oxide, Dy_2O_3 (Indian Rare-Earth Ltd., 99.99% pure) and molybdenum oxide, MoO_3 (BDH, England, 99.5% pure) by repeated grinding in an agate mortar, and firing at 800° in a platinum crucible for a few days. The final product was sintered at 1100° for 24 hours. As mentioned earlier, the ferroelectric β' phase was obtained by rapidly quenching the DMO powder from high temperature (1000°) to room temperature. As before [12], the formation of the desired β' phase (i.e. the ferroelectric phase) and the quality of the compound were checked with a conventional X-ray technique.

X-ray study

The X-ray powder diffractograms were recorded with a Philips X-ray diffractometer, using CuK_α radiation ($\lambda = 1.542$ Å), with a Ni filter, from $2\theta = 15°$ to $75°$, at a scanning rate of $2°/min$. The width of the powder profile was carefully monitored and compared with the instrumental slit width. The peak positions (diffraction angles) were carefully centred and determined for calculation of the interplanar spacings (d values) and lattice constants. The clean and sharp powder profile of DMO indicates the high level of purity of the compound. The agreement between the observed and calculated d values was found to be very good. The reported ferroelectric orthorhombic space group Pba2 [8, 11] was confirmed from the indexed powder lines. The calculated and observed d values are compared in Table 1.

Thermal studies

To establish the structural transformation in the material, we carried out qualitative and quantitative thermal analysis of DMO by means of differential thermal analysis (DTA), thermogravimetry (TG) and differential scanning calorimetry (DSC). DTA and TG curves were recorded simultaneously in static air atmosphere with a Stanton–Redcroft STA–780 thermal analyser at a heating rate of 10 deg/min from room temperature to 1100°. The sample, weighing approximately 15 mg, was heated in an alumina crucible, and Al_2O_3 was used as

Table 1 Comparison of the observed and calculated d (Å) values of ferroelectric DMO

hkl	$d_{obs.}$	$d_{cal.}$	I/I_0
020	5.1708	5.1752	44
201	4.6423	4.6432	55
202	3.6931	3.7006	82
220	3.6484	3.6553	63
003	3.5343	3.5375	60
221	3.4502	3.4561	86
130	3.2729	3.2723	92
222	3.0043	3.0102	100
023	2.9209	2.9204	76
132	2.7802	2.7853	55
400	2.5811	2.5818	38
313	2.4016	2.3998	13
331	2.3741	2.3751	14
240	2.3142	2.3134	27
224	2.1553	2.1471	13
403	2.0842	2.0854	38
150	2.0275	2.0297	10
333	2.0054	2.0068	50
025	1.9603	1.9637	71
423	1.9319	1.9343	40
350	1.7714	1.7740	27

reference material. A Pt–Pt–Rh 13% thermocouple was used as a temperature-sensing device. Differential scanning calorimetry was carried out on a powder sample of DMO in a DuPont 910 DSC cell in static air atmosphere from room temperature up to 600°, at a heating rate of 5˙deg/min. Non-hermetically crimped aluminium pans were used, with an empty pan as reference. A chromel–alumel thermocouple was used to measure temperature in this experiment. The change in enthalpy, ΔH (joule/gram), was calculated via the following formula [13]:

$$\Delta H = \frac{60\, E \cdot A \cdot B \cdot \Delta qs}{m}$$

where m = mass of the sample (mg)
    A = peak area (cm²)
    B = TIME-BASE setting (min/cm)
    Δqs = y-axis sensitivity (mv/cm), and
    E = cell calibration coefficient.

Results and discussion

The d values of the peaks of the powder profile were calculated via Bragg's equation and then indexed. The d values of these peaks were also calculated from the determined cell dimensions $a = 10.327(5)$, $b = 10.350(5)$, and $c = 10.612(5)$ Å, which are consistent with the reported values [14]. We found very good agreement between the calculated and experimental d values. The reported space group Pba2 [6] was confirmed by the systematic absence of some reflections in our limited data. The intensities of the peaks were estimated visually. The X-ray studies revealed that the d values and intensities of most of the peaks of DMO were similar to those of SMO [12] and GMO [6], which indicates the similarity in their structures in the ferroelectric phase.
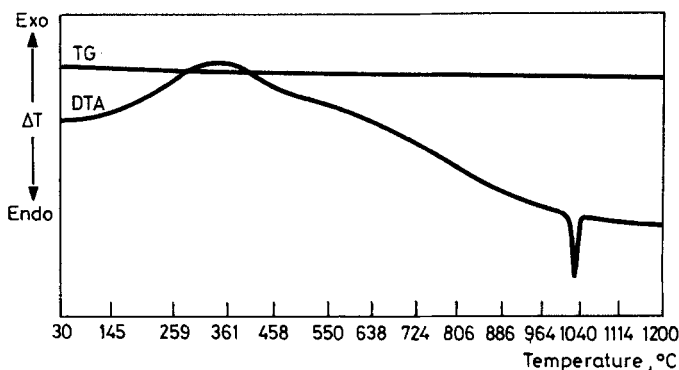

Fig. 1 DTA and TG curves of DMO

Figure 1 shows the DTA and TG traces of the compound. During heating, the DTA curve yields an endothermic peak at 1030°. The TG curve shows a negligibly small weight loss ($< 2\%$), which may be due to the loss of moisture. The occurrence of a polymorphic phase transition in the compound [10] is supported by our TG curve, which is almost constant. The low-temperature ferroelectric phase transition in DMO at 145°, observed in many experiments, was not detected in our DTA measurement. Similarly, no phase transitions was observed for Nd and Gd mixed SMO [15, 16] with the same DTA technique. As the compound has ferroelectric-ferroelastic properties, we may expect the absorption or evolution of a very small quantity of heat at the transition temperature. This was observed in our DSC experiment. Further, the expected small heat anomaly might have been suppressed by the insensitivity of the thermocouple used. No other peak except that at 1030° was observed in the high-temperature region. The negligible weight loss of this

compound reveals its better thermal stability and perfectness in the measured temperature region.

Determination and evaluation of the qualitative and quantitative thermal effect on the sample from the DSC curve recorded directly with the DuPont thermal analyser are highly sensitive to the experimental conditions. Here we observed the ferroelectric phase transition in DMO at 145°, as shown in Fig. 2. This was not
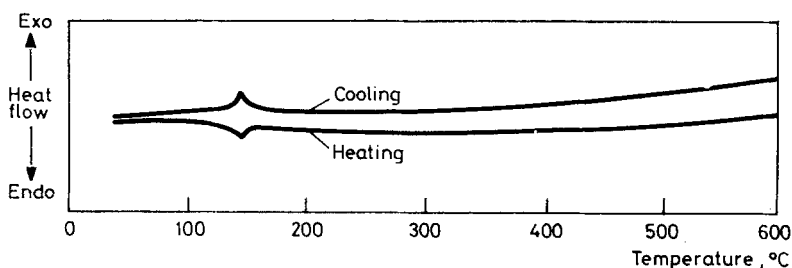

Fig. 2 DSC curve of DMO

detected in our DTA measurement. The DSC technique yields quantitative data from measurements of the peak area, which can be utilized for the calculation of ΔH. This yields $\Delta H = 6.42$ joule/gram at T_c (i.e. 145°) in both the heating and the cooling cycle of the experiments. Although a small variation in the indicated temperature was detected, the relationship between the indicated and the true temperature remains essentially linear over the region with which we are concerned.

Conclusions

With the use of the thermal analysis techniques, the ferroelectric phase transition associated with the other structural phase transition in DMO provided useful information about the single-phase character of the prepared compound, which was supported by the X-ray data.

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Zusammenfassung — Dysprosiummolybdat, $Dy_2(MoO_4)_3$ (Abk.: DMO), ein Vertreter der Seltenerdenmolybdatreihe zeigt bei 145 °C einen ferroelektrischen Phasenübergang. Röntgendiffraktion und thermische Eigenschaften (DTA, TG, DSC) der genannten Verbindung wurden untersucht. Auf Grund der Röntgendiffraktionsuntersuchung gehört die ferroelektrische Phase in die orthorhombische Raumgruppe Pba2. Mittels Thermoanalyse konnte bei dieser Verbindung die Existenz ferroelektrischer und anderer Phasenübergänge nachgewiesen werden.

Резюме — Молибдат диспрозия показывает ферроэлектрический переход при 145 °C. Проведены термический (ДТА, ТГ и ДСК) и рентгеноструктурные исследования данного соединения. Рентгенофазовый анализ подтвердил, что ферроэлектрическая фаза относится к орторомбической пространственной группе Pba2. Термический анализ показал наличие ферроэлектрического и другого фазового перехода.