DSC and X-Ray Study on $Gd_2(MoO_4)_3$

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Lattice parameters and thermal expansion of the three crystallographic modifications (α, β and β') of gadolinium molybdate have been determined.

The α-β and β'-β transitions have also been investigated by means of DSC and DTA measurements.

For the first one a transition enthalpy of 7.5 ± 0.5 kcal/mol was evaluated, while it was observed that factors such as the thermal history, the particle size and the heating/cooling rate affect the peak areas of the second one.

The results can be explained on the basis of the model proposed by Jeitschko for the β'-β transition provided that the necessary kinetic aspects are taken into account.

Gadolinium molybdate ($Gd_2(MoO_4)_3$) can exist in three crystallographic modifications [1]: a monoclinic α phase, thermodynamically stable up to 862 °C, a tetragonal β phase, thermodynamically stable from 862 °C to the melting point* and a metastable orthorhombic β' phase. In spite of lacking thermodynamic stability, the β' phase is the only one that can be obtained at room temperature if crystals of gadolinium molybdate are grown from the melt, since no transition from the β to the α phase occurs at 862 °C and the (metastable) β phase transforms into the metastable β' phase at 160 °C. In addition, thechnological interest in gadolinium molybdate is mostly connected to the β' phase which simultaneously presents ferroelectricity and ferroelasticity [3–5]. Scientific interest too has till now been confined to the β' and β phases, so that their lattice parameters have been studied by several authors [6–10], whereas little is known about those of the α phase and their temperature dependence [11]. A similar situation exists for what concerns the β'-β and β-α transitions: while the former transition has been widely studied [4, 5, 9, 10, 12] (although different ideas still exist on its nature), no information can be found on the latter except that a single crystal of gadolinium molybdate requires about three days at 800 °C to transform completely into the α phase [13].

In order to draw a more general picture of gadolinium molybdate, a better knowledge of the ferroelectric-paraelectric transition is needed besides information on the kinetics of the β-α conversion and on the lattice parameters of both phases.

Consequently, the purposes of this paper are: (i) the determination of the lattice parameters of the β and α phases in the entire temperature range of their metastable (β) or stable existence, and (ii) the calorimetric characterization of the β'-β transition.

Experimental

a) Apparatus

Thermal measurements have been performed by means of a DuPont 1090 Thermal Analysis System equipped with the "910 Differential Scanning Calorimeter". High temperature DTA cells (1200 °C and 1600 °C) have been used to record the α-β transition and the melting of gadolinium molybdate, the temperature of both processes being too high for the DSC cell to be used.

A powder diffractometer Philips PW 1011 has been used for the X-ray measurements. A homemade polythermal attachment [14] which allows one to operate in the temperature range -150 °C $\div$ 950 °C was employed for determinations at superambient temperatures. Lattice constants refinement has been obtained by a standard least squares procedure. According to Wilson [15] the observed

* For the sake of completeness, it must also be mentioned that some DTA evidence of a non disruptive transition to a γ phase just before the melting point has been found by Nassau et al. [2]; this phase, however, is not discussed in the present paper.

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values were corrected for specimen displacement and thin sample aberration.

Single crystal growth was accomplished by means of a Metal Research LTD BCG 265 apparatus. RF heating was used, and the temperature control of the solid-liquid interface has been obtained by a feed-back circuit using a radiation pyrometer as the temperature detecting device.

b) Procedures

α-$Gd_2(MoO_4)_3$ was prepared by solid state reaction (in sealed quartz tubes, at 700 °C) of stoichiometric amounts of the constituent oxides (Gd_2O_3 Fluka puriss. and MoO_3 Alfa Inorganics 99.9%).

Owing to the high vapour pressure of MoO_3 the reaction temperature of 700 °C has always been approached slowly, allowing prereaction to occur at lower temperatures, in order to avoid explosion of the quartz tube. About one week was required to obtain the complete conversion of the oxides into α-$Gd_2(MoO_4)_3$, as confirmed by X-ray and DTA analyses.

Single crystals have been prepared by the Czochralski melt-pulling technique (pulling rate 5 mm/h). Rotationless pulling was used, which was proved [16] to produce better quality crystals. A slight excess of MoO_3 (0.2 wt%) was added to the α-$Gd_2(MoO_4)_3$ used as starting material to compensate for MoO_3 volatilization due to the slow decomposition of the melt [16]. Platinum crucibles of 20 cm^3 volume have been used, and crystals of 10 mm diameter and 20–30 mm length were grown. Microcrystals for the X-ray and DSC measurements were obtained by grinding these crystals and sieving to the desired sieve fraction. DTA on these samples did not show any evidence of the α-β transition.

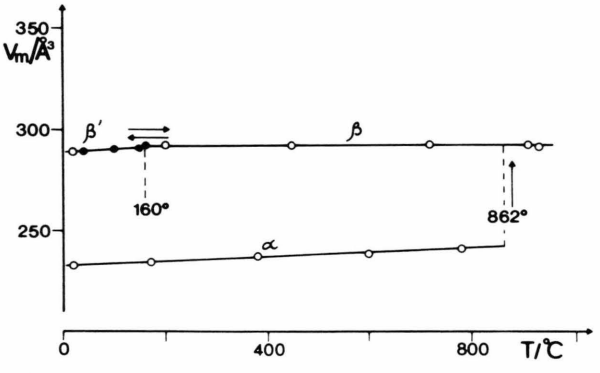

Fig. 1. Molecular volumes as a function of temperature for β', β and α phases of gadolinium molybdate; full circles: data from [9].

Results and Discussion

Table 1 reports the lattice parameters obtained for the α, β' and β phases. For the last two phases good agreement with the literature data [6–10] is found. Concerning the α phase it is to be noted that no standard error for the relevant lattice parameters is reported in [11], so that any direct comparison is not possible.

Thermal expansion studies were performed both on powders obtained by solid state reaction (α phase), and on those obtained by single crystal (β' and β phases). The results are reported in Figure 1. It can be noted that when α-$Gd_2(MoO_4)_3$ is heated, only this form is present up to 862 °C, at which temperature transformation occurs into the β form. On cooling the latter form, no reversal transition to the α phase can be observed, while a "reversible" transition to an orthorhombic β' phase occurs at 160 °C. On the other hand, if β'-$Gd_2(MoO_4)_3$ is investigated, the "reversible" transition to the β phase can again be observed at 160 °C while no evidence of the α phase can be found in the entire temperature range. The different degree of reversibility of the β-β' and β-α transitions might be due to the large difference in the molecular volumes of the β and α phases (about 50 $Å^3$), in comparison with that of the β and β' phases (about 0.40 $Å^3$ as can be deduced from [9]).

Table 1. Lattice parameters for the three crystallographic modifications of gadolinium molybdate.

T/°C	Phase	System	*a*/Å	*b*/Å	*c*/Å	β angle
20	α	Monoclinic	7.555 (3)	11.448 (4)	11.453 (4)	109.33 (1)
20	β'	Orthorhombic	10.392 (5)	10.416 (5)	10.696 (5)	–
200	β	Tetragonal	7.395 (4)		10.676 (6)	–

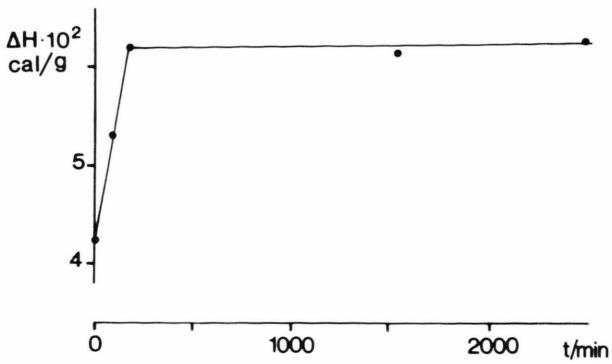

Fig. 2. Enthalpy per unit mass for the β' to β transition as a function of the annealing time at 500 °C. All the results have been obtained by DSC measurements performed under identical experimental conditions.

Thermal analysis measurements have been performed to confirm the X-ray results with respect to the general behaviour of the different phases and to determine the temperature ranges of their stable or metastable existence. While different heating traces are recorded for the α and β' phases (showing an endothermic peak at 862 °C and 160 °C, respectively), substantially similar traces are recorded on cooling (both showing the exothermic peak due to the β-β' transition). A transition enthalpy of 7.5 ± 0.5 kcal/mol has been evaluated for the α-β transition on the basis of repeated measurements with a high temperature DTA cell. The thermal effect of the β'-β transition will be discussed later: both for the latter transition and the kinetics of the β-α conversion DSC is necessary since DTA has not the accuracy and precision required to obtain quantitative information on these processes. Owing to the intrinsic temperature limits of DSC (commercial apparatuses can be used up to 700–750 °C), measurements on the β-α conversion could only be performed in an indirect way: if samples of β-$Gd_2(MoO_4)_3$ are annealed for different times at a desired temperature (below 862 °C) at which the β-α transition can take place, and subsequently analyzed by DSC, then the greater is the degree of β-α conversion, the smaller will be the area of the β'-β transition peak.

Figure 2 reports as an example the enthalpies per unit mass measured for the β'-β transition as a function of the annealing time at 500 °C. After annealing, samples were allowed to cool to room temperature and then analyzed.

While it seems that no β-α transition occurs at this temperature in nearly two days, the increase of the energy per unit mass clearly shows that the thermal history of the sample affects the β'-β transition. This makes an accurate analysis of this transition not only interesting on its own but necessary before the kinetics of the β to α conversion can be studied. Similar results have been obtained on samples annealed at 600 °C.

Figure 3 reports the DSC curves obtained under identical experimental conditions for samples of different grain size after an "in situ" annealing of three hours at 120 °C. It can be seen that the peak shapes are very different: by progressively decreasing the particle size, less intense and much broader

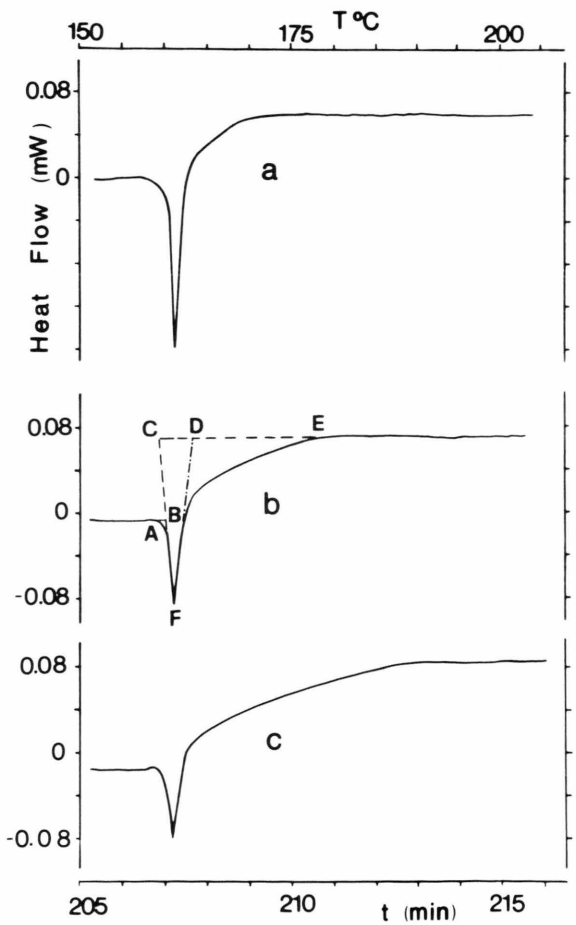

Fig. 3. DSC curves (heating rate 5 °C/min) for the β' to β transition on samples of different grain size (l/μm) after an annealing of 3 h at 120 °C; a) $125 < l < 180$; b) $l < 45$ μm; c) $l < 25$ μm.

Table 2. β'-β transition enthalpies (10^2 cal/g) for samples of different particle size (l) and annealing condition.

annealing / l/μm	< 25	< 45	125–180
T/°C / t/h			
120 / 3	25.1	13.5	7.0
100 / 1.5	17.2	10.6	6.9

peaks are obtained. The reaction enthalpies (expressed as energy per unit mass) reported in Table 2 are obtained in the usual way on the basis of the peak areas (e.g., the area ABCEFA in Figure 3b). The Table reports also the results for the three samples after an annealing of 1.5 h at 100 °C. It can be noted that the sample formed with the largest particles seems to be practically unaffected by the change of the annealing conditions, while sensibly smaller values of the reaction enthalpy are obtained for the other two samples. If for the latter samples the partial areas (DEFD in the same Figure) are taken into account, the values 0.076, 0.151 cal/g (at 120 °C), and 0.050, 0.103 cal/g (at 100 °C) are obtained in the case of the larger and smaller particle size, respectively. It is interesting to note that for both pairs the above values are in the ratio 1:2, that is close to the particles surface-to-volume ratios for the two grain sizes, which may be estimated as 1:1.8.

Measurements under identical experimental conditions were performed on samples of identical grain size but without any annealing. The results can be summarized as follows:

a) practically identical peaks are obtained for the largest particle size independently from annealing;

b) once again, the largest particles correspond to the narrowest peak, but the peak broadening with decreasing particle size is now remarkably smaller than after annealing, so that larger peak areas are now obtained with increasing particles size;

c) as a consequence, while nearly equal reaction enthalpies are obtained for the 125–180 μm sample before and after annealing, values several times smaller are obtained for the sample with the smallest particle size.

From the comparison of these data the conclusion can be drawn that annealing undoubtedly affects the ferro-paraelectric transition of gadolinium molybdate, but its influence is linked to the sample grain size.

Figure 4 reports the DSC cooling curves on the same samples whose heating curves after annealing are reported in Figure 3. Here the following remarks can be made. First, the peak areas increase with particle size: this is just the opposite of what was found with the corresponding heating curves. Comparison shows that the 125–180 μm sample presents similar peak areas either on heating after annealing or on cooling, while for the other two samples the smaller are the peak areas on cooling the larger are those on heating. The second observation concerns the base-line. It is horizontal and has a high background noise before the peak, while it becomes a straight line with a large exothermal slope and a very small background noise after the peak. It is noticeable that the exothermal slope

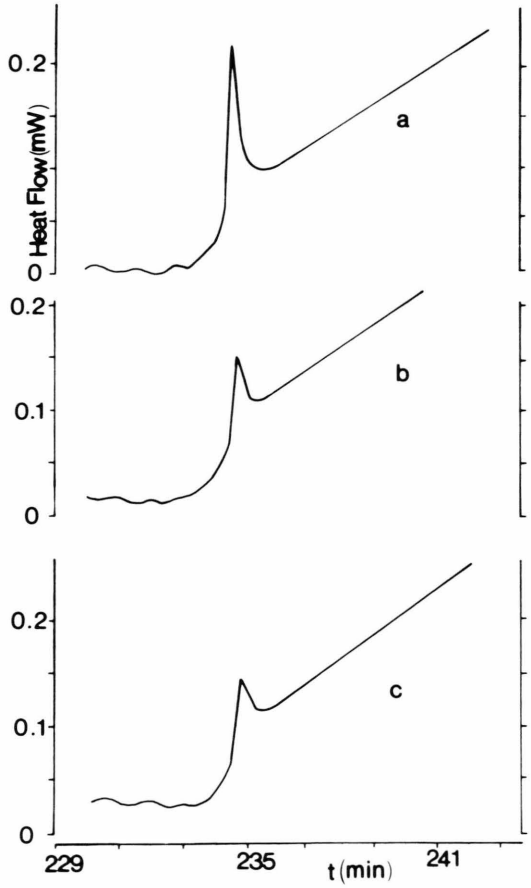

Fig. 4. DSC cooling curves for the β to β' transition (cooling rate 5 °C/min) on the same samples whose heating curves are reported in Fig. 3.

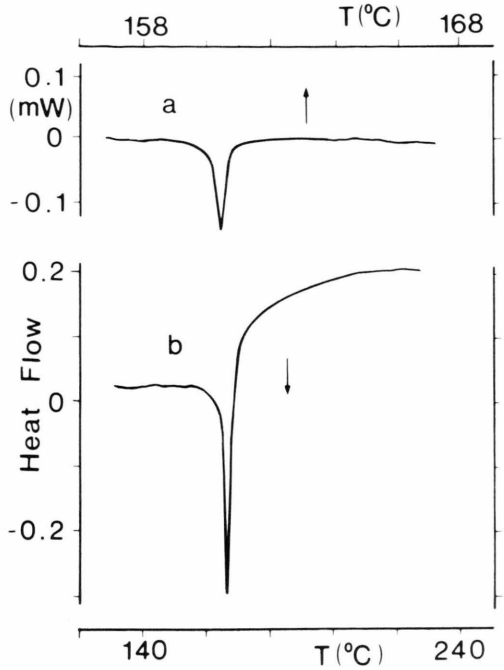

Fig. 5. Effect of the heating rate on the β' to β transition peak area (sample grain size: $125 < l < 180$) a) heating rate 1 °C/min; b) heating rate 10 °C/min.

Table 3. Some representative results obtained for the β'-β transition enthalpy under different experimental conditions (grain size, thermal treatment, scanning rate).

Size	Annealing	T incr./ decr.	Rate °C/min	Enthalpy (10^2 cal/g)
crystal	3 h at 120 °C	incr.	5	7.6
crystal	–	decr.	5	6.0
crystal	–	decr.	2	4.7
125–180	–	incr.	1	3.4
125–180	–	incr.	2	4.9
125–180	3 h at 120 °C	incr.	5	7.0
125–180	–	incr.	10	10.0
125–180	–	decr.	2	4.9
125–180	3 h at 120 °C	decr.	5	5.2
45	–	incr.	2	2.9
45	3 h at 120 °C	incr.	5	13.5
45	3 h at 120 °C	decr.	5	3.3
25	3 h at 120 °C	incr.	5	25.1
25	–	incr.	5	4.0
25	–	decr.	5	3.6

looks as independent of the particle size. This suggests that a frozen-in energy (proportional to the cooling rate) is released after the peak. This hypothesis is confirmed by measurements on both annealed and non annealed samples: if the cooling rate is decreased, the exothermal base-line slope decreases. Moreover, smaller peak areas are obtained with decreasing cooling rate.

The dependence of the peak area on the scanning rate is obviously observable also on heating. Figure 5 reports as an example the heating curves obtained at 1 °C/min and 10 °C/min on a 125–180 μm sample: the larger area is nearly three times the smaller one.

Table 3 summarizes part of the results obtained for the β'-β transition enthalpy under different experimental conditions. The dependence of the enthalpy values on grain size, annealing treatment and heating rate is evident.

No explanation of our data can be given if the possibility of gradual changes between the low (β') and high (β) temperature phases of gadolinium molybdate is not taken into account. This hypothesis was first made by Jeitschko [10] and allowed him to account for temperature dependent physical properties of the ferroelectric phase. In his opinion, small regions of the low temperature structure can still be present above the transition temperature; moreover, the structural change below the transition temperature is of the displacive type, while no unambiguous decision between the two models of positional order-disorder transition and displacive transition can be taken for the final step of the β'-β transition.

What is implicit in this idea, and clearly explicitated by our results, is that, owing to the slowness of these structural changes, very different results can be obtained through the same experimental procedure on samples of different history or, in other words, the history of the sample acts as a variable that must be fixed if the actual state of the system has to be defined. Moreover, it is likely that higher strain energies have to be overcome in large particles than in small ones. As a consequence, atom displacements below the transition temperature can be dependent not only on the thermal treatment of the sample but also on its particle size.

If the hypothesis is made that, due to the strain energy, shorter atom displacements take place as a consequence of an identical thermal treatment in larger than in smaller microcrystals, and that regions where no displacement occurs can remain in the first ones, our results can all be explained. Thus it may be understood why annealing exerts an effect and why this effect is larger on small particles. The results, conflicting at first sight, of higher intensity

and smaller area observed on the larger particle peaks after annealing, can also be explained: the shorter atom displacements below the transition temperature require larger displacements at the transition temperature, which can justify the peak height. On the other hand, shorter atom displacements are associated with the presence of regions that do not undergo transition, and this can explain the smaller areas.

One more remark has to be made about the dependence of the peak area on the heating rate (see Table 2, and Figure 5). The fact that larger areas are obtained with increasing heating rate indicates that the role of power supply at the transition temperature can affect the mass fraction that undergoes transition: this is just what one would expect on the basis of the behaviour proposed for the β'-β transition. Thus the same kinetic consideration accounts for both the exothermal base-line slopes of Fig. 4 and their decrease with decreasing cooling rate. If a too high cooling rate is used (that does not allow "equilibrium" atom positions to be reached at each temperature), more or less large amounts of the high temperature structure are frozen-in (depending on the cooling rate), and a strain energy release is observed below the transition temperature which is substantially dependent on the cooling rate.

Thus the complex thermal behaviour of the β'-β transition can be totally understood if the Jeitschko model for this transition is supplemented by some kinetic aspects.

The knowledge gained by DSC analysis would then make possible the indirect study of the kinetics of the β-α conversion, provided the required care be devoted to fix the sample manipulation procedure and experimental conditions. This point seems to be confirmed by measurements in progress. This research was partially supported by M.P.I. (40% funds).

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