

Amorphization of rare-earth molybdates under high pressure

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(Submitted 29 December 1994)

Pis'ma Zh. Éksp. Teor. Fiz. **61**, No. 3, 217–221 (10 February 1995)

Subjecting the β' modification of the compounds $\text{Gd}_2(\text{MoO}_4)_3$, $\text{Tb}_2(\text{MoO}_4)_3$, $\text{Sm}_2(\text{MoO}_4)_3$, and $\text{TbGd}(\text{MoO}_4)_3$ to pressures up to ~ 7 GPa results in an amorphization. The temperature intervals of stability have been studied. The enthalpies of crystallization of the amorphous states of these compounds have been determined. © 1995 American Institute of Physics.

At atmospheric pressure, the compounds $\text{R}_2(\text{MoO}_4)_3$ (where $\text{R}=\text{Pr, Nd, Sm, Eu, Gd, Tb, Dy}$) form two thermodynamically stable, crystalline modifications: the high-temperature β phase (space group $P4_2/m$) and the low-temperature α phase ($C2/c$) (Ref. 1). Upon heating, an α - β phase transition is observed at $T\sim 1078$ – 1260 K (the transition temperature increases with decreasing atomic number of the rare earth). This transition is characterized by a significant increase ($\sim 25\%$) in specific volume.^{1,2} Such a large difference in specific volumes slows down the polymorphic conversion and makes it a simple matter to supercool the β phase to low temperatures. In the metastability region of the β phase, a transition is observed at 418 – 508 K (depending on the atomic number of the cation R) to another metastable phase, β' (space group $Pba2$). The β' phase is ferroelectric, and the β - β' transition itself is accompanied by small volume and thermal effects.^{1,3}

Working from the assumption that a high pressure would promote the conversion of a “porous” metastable β' phase into a denser metastable α phase, Brixner² subjected $\text{Gd}_2(\text{MoO}_4)_3$ to pressures up to 6.5 GPa at temperatures $T\leq 670$ K. However, the pressure resulted in an amorphization, rather than a β' - α conversion. When amorphous $\text{Gd}_2(\text{MoO}_4)_3$ was heated, an exothermic peak was observed in the temperature interval 816 – 863 K. Failing to achieve the desired result, Brixner abandoned this study; Ref. 2 remains the only publication on the solid-phase amorphization of the compound $\text{Gd}_2(\text{MoO}_4)_3$. We felt it worthwhile to study the effect of high pressure on the structural state of not only $\text{Gd}_2(\text{MoO}_4)_3$ but also several other isomorphous compounds of the $\text{R}_2(\text{MoO}_4)_3$ family. Specifically, we selected $\text{Gd}_2(\text{MoO}_4)_3$, $\text{Tb}_2(\text{MoO}_4)_3$, $\text{Sm}_2(\text{MoO}_4)_3$, and $\text{TbGd}(\text{MoO}_4)_3$ for study. It has been shown that all these compounds become amorphous when subjected to high pressure. We have determined the intervals over which the resulting amorphous modifications are stable, and we have measured the corresponding heats of crystallization.

We studied single crystals and powders of these compounds of rare-earth molybdates, which originally had a β' structure. The samples were treated in a “toroid” pressure chamber at pressures ~ 7 GPa at room temperature. The samples were held for times ranging from 2 h to 3 days under these conditions. Calorimetric measurements were

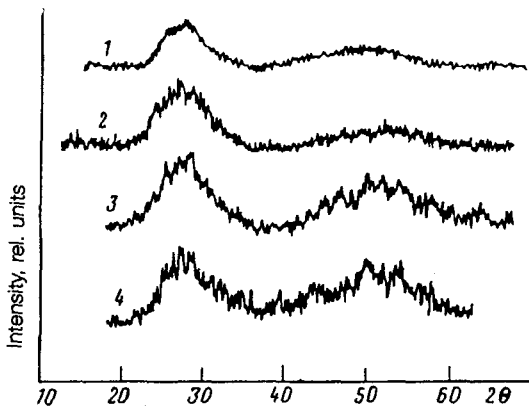


FIG. 1. Diffraction patterns of amorphous modifications of rare-earth molybdates. 1— $\text{Sm}_2(\text{MoO}_4)_3$; 2— $\text{Tb}_2(\text{MoO}_4)_3$; 3— $\text{TbGd}(\text{MoO}_4)_3$; 4— $\text{Gd}_2(\text{MoO}_4)_3$.

carried out on a Perkin Elmer DSC-7 microcalorimeter over the temperature range 300–1020 K at a scanning rate of 10 K/min. A Siemens D-500 apparatus was used for the x-ray diffraction. These recordings were made in $\text{Cu } K\alpha$ radiation at room temperature.

Figure 1 shows x-ray diffraction patterns of the compounds $\text{Gd}_2(\text{MoO}_4)_3$, $\text{Tb}_2(\text{MoO}_4)_3$, $\text{Sm}_2(\text{MoO}_4)_3$, and $\text{TbGd}(\text{MoO}_4)_3$ after pressure treatment as described above for times ranging from 2 to 4 h. All the diffraction patterns have two rounded peaks, which indicate amorphization of these compounds. The positions of the crests of these peaks are the same (within the experimental errors) for all compounds studied: 0.323 ± 0.002 nm for the first peak and 0.180 ± 0.001 nm for the second. Upon amorphization, the color of the $\text{Tb}_2(\text{MoO}_4)_3$ and $\text{TbGd}(\text{MoO}_4)_3$ samples changes, from colorless to yellow and pale yellow, respectively. No change in color occurs for the compounds $\text{Gd}_2(\text{MoO}_4)_3$ and $\text{Sm}_2(\text{MoO}_4)_3$, which remain in an amorphous state, colorless and yellow, respectively.

During the heating of the amorphous phase, the calorimetric results revealed a substantial heat evolution at $T \geq 770$ K (Fig. 2), due to crystallization of the samples. The

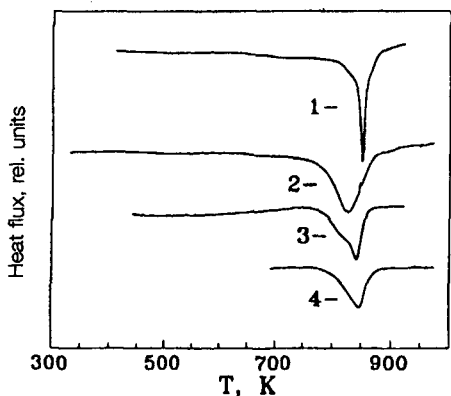


FIG. 2. Calorimetric curves of the crystallization process. 1— $\text{Sm}_2(\text{MoO}_4)_3$; 2— $\text{Gd}_2(\text{MoO}_4)_3$; 3— $\text{Tb}_2(\text{MoO}_4)_3$; 4— $\text{TbGd}(\text{MoO}_4)_3$.

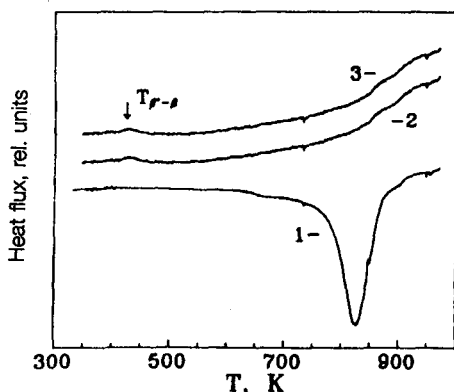


FIG. 3. Calorimetric curves of three successive heatings of amorphous $\text{Gd}_2(\text{MoO}_4)_3$. 1—First heating; 2—second; 3—third. Here $T_{\beta'-\beta}$ is the temperature of the ferroelectric transition.

heats of crystallization are 30.6, 28.3, 21.2, and 19.8 kJ/mole for $\text{Sm}_2(\text{MoO}_4)_3$, $\text{Gd}_2(\text{MoO}_4)_3$, $\text{TbGd}(\text{MoO}_4)_3$, and $\text{Tb}_2(\text{MoO}_4)_3$, respectively. During subsequent heating cycles (Fig. 3), the high-temperature exothermic peak is missing from the calorimetric curves, but a peak corresponding to the ferroelectric β' - β transition arises. If we work from the thermal effect of the β' - β transition, which is given in the literature,³ to calculate the mass of the β' phase undergoing conversion, we find that it constitutes ~50–60% of the mass of the sample in the calorimeter. This result indicates that the sample consists of more than one phase after the transition from the amorphous state to the crystalline state. Specifically, after the first heating of initially amorphous $\text{R}_2(\text{MoO}_4)_3$ samples to temperatures ~870 K, we can identify lines on their x-ray diffraction patterns which correspond to the α and β' phases. We can also see some other lines, which can be attributed to their oxides, R_2O_3 and MoO_3 . This heating was carried out to temperatures below the temperature of the polymorphic α - β transition. The β phase thus formed from the amorphous state in the region in which the β phase is metastable.

When the samples are held at ~7 GPa for more than 1 day, their diffraction patterns reveal, along with the rounded peaks, reflections from crystalline phases. Although it is difficult to completely identify these lines, because of their significant broadening, we can identify some of the most intense lines as reflections from the dense α phase and also from oxides of the rare earth and the molybdenum.

Nearly all substances which go into an amorphous state as (a) the pressure is raised (C and SiO_2 are examples⁴⁻⁶), (b) the pressure is lowered (Ge, Si, and GaSb are examples⁷⁻⁹), and (c) the pressure is either raised or lowered (H_2O is an example¹⁰⁻¹²) have a common feature: the presence of at least two crystalline modifications, which differ markedly in specific volume. The melting lines of the less dense phase are curves which have a maximum or a negative slope with respect to the pressure axis. The melting curves of the denser phase have a positive slope.

In accordance with this topology of the P - T phase diagrams, the amorphization process is usually linked with a loss of the stability of the crystal with respect to long-range order upon a crossing of the extrapolation of the melting curve into the metastable

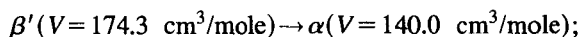
region.¹³ If the point at which the melting curve is intersected lies below the glass point (T_g) of the material, and if the polymorphic transition is retarded, the sample become amorphous. The process of solid-phase amorphization which occurs in this manner may thus be thought of as a "melting" of the crystalline phase below T_g , accompanied by a loss of long-range order, with no change in the chemical composition of the original crystalline phase.

There are, on the other hand, other causes of a solid-phase amorphization of substances under pressure, e.g., the decomposition of a chemical compound. If a compound becomes thermodynamically unstable with respect to its original chemical composition upon the application of pressure, there may exist a temperature interval in which the crystallization of the products of this decomposition is slowed down. The decomposition process would then come to a halt in its initial stage, leading to a loss of both long-range and short-range order. An effect of this sort apparently occurs¹⁴ in Nb_2O_5 . The thermodynamic stimulus for the amorphization process is the term $\Delta P \Delta V$ in the Gibbs potential, where ΔP is the extent to which the pressure exceeds the equilibrium value for the given compound, and ΔV is the difference between the specific volumes of this compound and of the end products of its decomposition.

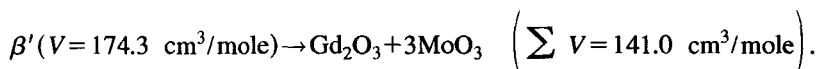
If the transition to an amorphous state in the cases described above is interpreted as a "congruent melting" of the substance below T_g , the amorphous state obtained in the first stage of the decomposition should be identified with a supercooled liquid corresponding to a mutual solution of the end products of a chemical decomposition reaction, and the amorphization process itself should be interpreted as an "incongruent melting." The basic distinction between these two amorphization processes can be established by arranging a further conversion of the amorphous modification, which is a metastable intermediate state of the substance, into the final crystalline state, by smoothly varying any of the following: the pressure, the duration of the pressure treatment, the temperature. In the first case, the system should go into a single-phase crystalline state, while in the second it should go into a state of crystalline decomposition products.

In the case of compounds of the $\text{R}_2(\text{MoO}_4)_3$ family, both the $\beta' - \alpha$ polymorphic transition and the decomposition of the original compound into oxides are accompanied by essentially the same decrease in volume, in a first approximation (if compressibility is ignored):

1. for the polymorphic conversion,



2. for decomposition,



Two possible mechanisms for solid-phase amorphization are thus competing in these compounds:

a) a loss of long-range order as the result of a "melting" of β' phase which has lost its stability;

b) a change in the short-range chemical order which exists in the original crystalline compound in the first stage of the decomposition and thus a loss of long-range atomic order.

The question of the mechanism for the amorphization of $R_2(\text{MoO}_4)_3$ is thus not as obvious, but some preliminary conclusions can be drawn from the results of this study.

The high-temperature part of the P - T phase diagram of rare-earth molybdates has yet to be studied, and we do not know the shape of the melting curves of the α and β modifications. On the one hand, the probability that the melting point of the β phase may be lowered to ~ 1100 K by a pressure of 6–7 GPa is low, especially since we observe the initial stages of the amorphization of molybdates at pressures of only ≈ 2 –3 GPa. On the other hand, we note a study by differential thermal analysis¹⁵ of the synthesis of $R_2(\text{MoO}_4)_3$ from mixture of $R_2\text{O}_3$ and MoO_3 . For $R = \text{Sm}$, Rode *et al.*,¹⁵ observed a significant heat evolution at ~ 823 –893 K. These temperatures correlate well with the temperature interval of the crystallization of amorphous $\text{Sm}_2(\text{MoO}_4)_3$ (Fig. 2). Also noting that reflections from the oxides $R_2\text{O}_3$ and MoO_3 appear on the x-ray diffraction patterns as the duration of the pressure treatment is raised, one might suggest that the most probable amorphization mechanism at temperatures near room temperature is decomposition. However, the question of the physical cause of the instability of the β' phase of these compounds with respect to a loss of long-range order can be reliably resolved only by a further detailed study of the amorphization process and of the physical properties of the resulting amorphous states, combined with a study of the P - T diagram in the melting region.

This study was financed by the Russian Fund for Fundamental Research (Projects 93-02-03661 and 93-02-03271). We wish to thank A. F. Gurov for assistance in carrying out some of the calorimetric measurements. We also thank B. K. Ponomarev for useful comments offered in a discussion of the results.

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Translated by D. Parsons