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Polymorphism under Pressure of the Disilicates of the Heavier Lanthanoids $Ln_2Si_2O_7$ (Ln = Tm, Yb, Lu)

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A study of the phase diagram of thulium, ytterbium, and lutecium disilicates $Ln_2Si_2O_7$ in the ranges 0–70 kbar and 20–1600°C shows the extended polymorphism under high pressure of these compounds of which only one form was previously known at ambient pressure. The monoclinic D form appears at temperatures much lower than for the neighboring members of the series and its stability field is restricted to a rather narrow pressure interval around 20 kbar. The triclinic B form appears at pressures which increase from 20 to 40 kbar from Tm to Lu. A new tetragonal X form so far unknown in the disilicate series and isostructural with $Er_2Ge_2O_7$ is obtained for the three compounds. Compared to the B form it is a low temperature, low pressure form. The crystal data of the nine high pressure phases are given.

Introduction

The rare earth disilicates $Ln_2Si_2O_7$ offer a typical example of polymorphism in connection with the increasing ionic radius of the Ln^{3+} cations along the lanthanoid series. Systematic investigations of the structure of these compounds carried out by many authors under normal pressure and particularly by Felsche (*1*, *2*), Bondar (*3*, *4*), and Smolin (*5*, *6*), lead to the existence of seven different types (Figs. 1 and 2). Each compound exists in two or more forms according to the temperature, except the disilicates of the last three elements of the series, the small ones (thulium, ytterbium, lutecium) which have only been observed in the C monoclinic form isostructural with thortveitite (scandium disilicate). However, as can be seen in Fig. 1, this C form appears as a high-temperature form and it seems likely that other phases (such as the B phase) are

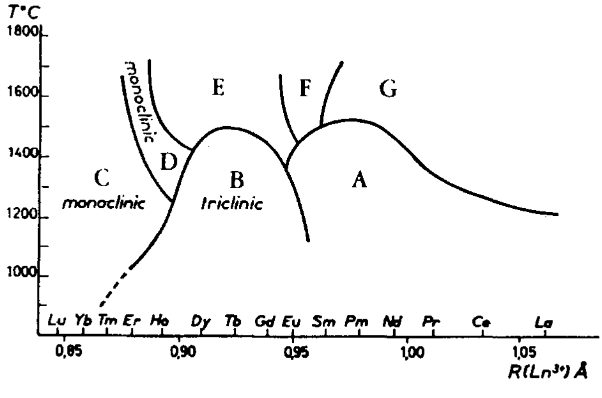

FIG. 1. Polymorphism of the rare earth disilicates $Ln_2Si_2O_7$ at atmospheric pressure according to Felsche (*1*).

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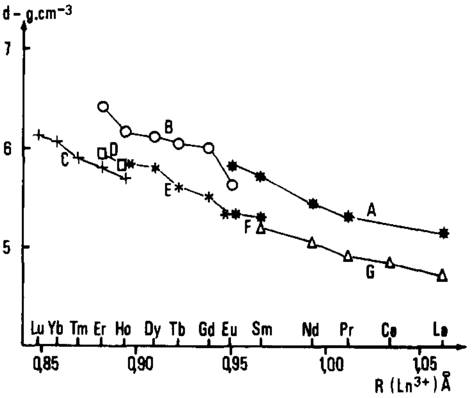

FIG. 2. Density of the various forms of the rate earth disilicates $Ln_2Si_2O_7$ according to Felsche (*1*).

thermodynamically stable in the low-temperature range. Examination of the densities of the various phases in the series which are plotted in Fig. 2 shows that for erbium and holmium disilicates, the *C* form is less dense than the *D* and *B* forms from which it can be inferred that the $C \rightarrow D$ and $C \rightarrow B$ transformations should be induced by thermal treatment under pressure. To check this prediction, experiments have been performed on $Tm_2Si_2O_7$, $Yb_2Si_2O_7$, and $Lu_2Si_2O_7$. The *B* and *D* forms of these three compounds were in fact obtained under proper pressure and temperature conditions; in addition, a new phase *X*, so far unknown in the series, was discovered (Fig. 3) (*7–9*).

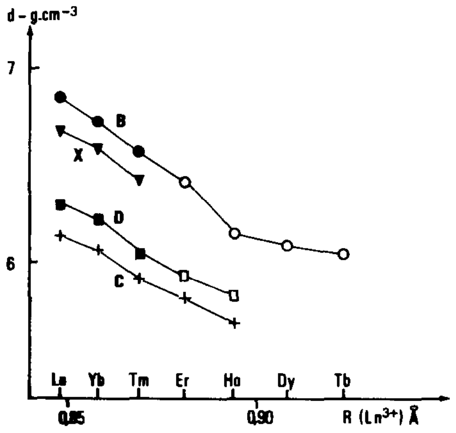

FIG. 3. Density of the high-pressure forms of lutecium, ytterbium, and thulium disilicates (full signs).

Experimental

The compounds were prepared from gels obtained by precipitation of a solution of lanthanoid chloride by silicic acid or from mixed oxides taken in stoichiometric proportions ($Ln_2O_3 + 2SiO_2$). The formation of the disilicate was obtained by heating the starting products in a platinum crucible in air. Complete reaction was achieved in a few hours at 1200°C for the gels, and at 1400°C for the oxides.

The treatments under pressure were performed in a belt apparatus in the ranges 0–70 kbar and 20–1600°C. The precompacted powders of pure *C* phase disilicates were inserted in a boron nitride container. Compression and decompression were made at ambient temperature and the duration of the thermal treatments was generally 1 hr.

The pressure during the runs is known from a calibration carried out at room temperature in a separate experiment, using the transitions of bismuth and barium at 25.4 and 55 kbar, respectively. Neglecting the pressure variation in the cell during heating, the accuracy is estimated to be ±3 kbar (*12*). During each experiment the temperature is measured by a Pt–Pt 10% Rh thermocouple with an accuracy of 3%. The pressure effect on the thermocouple emf has not been taken into account.

The crystalline form of the disilicates was determined before and after the pressure treatment by X-ray diffraction. Identification of the phases was accomplished by comparison of the powder diagrams with results previously published for other members of the series (*1*, *10*, *11*). When the new *X* phase was obtained the X-ray index was compiled using single-crystal electron microdiffraction.

Results

The pressure–temperature phase diagrams of the three disilicates are shown in Figs. 4–6. As expected, forms *B* and *D* were formed under pressure. Furthermore, a new form *X* was obtained in a particular P–T range for each compound. Considering that the starting products were in all cases the *C* form and that

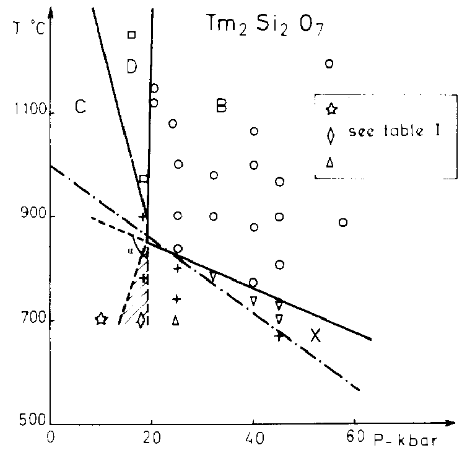

FIG. 4. P–T phase diagram of $Tm_2Si_2O_7$

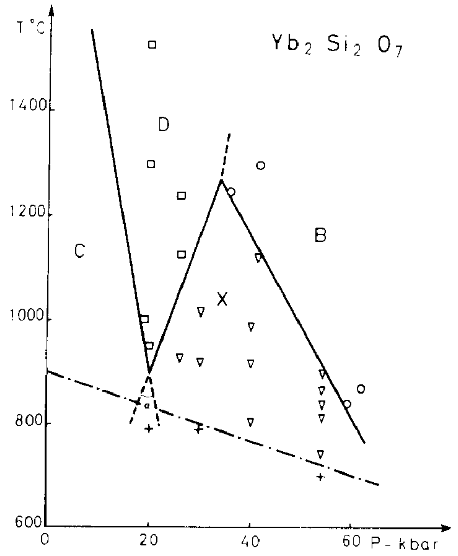

FIG. 5. P–T phase diagram of $Yb_2Si_2O_7$.

the treatments were limited in time, the boundaries between the various phases should not be considered as equilibrium lines [a discussion of this point is given in Ref. (*8*)]. The $C \rightarrow D$ boundaries were drawn taking into account the fact that at atmospheric pressure the C forms are stable up to the melting points (not shown on the figures). The interrupted lines represent the minimum temperature for a detectable transformation of the C form after 1-hr treatments. As it could easily be foreseen this temperature decreases with increasing pressure. The parts of the diagrams lying under these lines could not be determined from runs made in the above-mentioned experimental conditions. However, if one assumes that the phase boundaries in the diagram are not too distant from the equilibrium lines, one can assign limits to the position for the missing C–X boundaries and predict that these are located inside the α angles (Figs. 4–6). This leads to very steep C–X lines for $Yb_2Si_2O_7$ and $Lu_2Si_2O_7$ with the consequence that for these compounds the C form is most probably the one that is stable at ambient conditions. The case of $Tm_2Si_2O_7$ appears more interesting since the prediction is that the stable phase in these conditions might well be the new X phase. In order to get more precise information on this point we carried out additional experiments on this compound in which the starting product was obtained from an incomplete reaction between the oxides and in which the thermal treatments under pressure lasted 6 hr instead of 1 hr. The conditions and results of these experiments are summarized in Table I and are represented with special symbols in

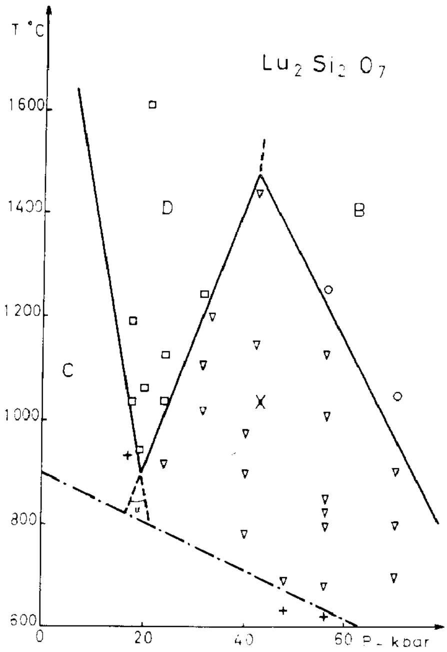

FIG. 6. P–T phase diagram of $Lu_2Si_2O_7$.

TABLE I

THULIUM DISILICATE REACTION PRODUCTS AT HIGH TEMPERATURES AND PRESSURES

Starting materials	Pressure (kbar)	Temperature (°C)	Final product[a]
$C-Tm_2Si_2O_7+Tm_2SiO_5+SiO_2$	10	700	$C-Tm_2Si_2O_7$
$C-Tm_2Si_2O_7+Tm_2SiO_5+SiO_2$	18	700	$C-Tm_2Si_2O_7+Tm_2SiO_5+SiO_2$
$C-Tm_2Si_2O_7+Tm_2SiO_5+SiO_2$	25	700	$X-Tm_2Si_2O_7$

[a] After reaction with 18 kbar of pressure at 700°C, there was no apparent change in the proportions of the phases.

Fig. 4. The new data appreciably reduce the possible range of the *C*–*X* line (shown by a shadowed angle) but still do not enable one to know which phase is stable under normal conditions.

General remarks can be made concerning the three diagrams. First, if one compares them with Fig. 1, one sees that, except for the appearance of the new form *X* under pressure, the stability fields of the different phases are located roughly in the same way with respect to each other. So, pressure seems to act in the same manner as the replacement of a rare earth by a lighter one, i.e., by one of larger ionic radius. This behavior is in line with the general observation that for oxides the cations are less compressible than the larger anions leading to an increase of the r(cation)/r(anion) ratio under pressure (*13*). Thus, the order of increasing densities or entropies is maintained throughout the series for forms *C*, *B*, and *D* (Fig. 3). Concerning the *D* form, it is interesting to note that pressure allows it to be prepared at a much lower temperature than is necessary for the neighboring disilicates at atmospheric pressure (900 instead of 1300 and 1350°C for holmium and erbium disilicates).

The most interesting feature of the diagrams is the appearance of the new *X* phase in the low temperature, medium pressure range. The unexpected consequence is that for the three compounds the stable phase at ambient conditions is not the *B* phase, as could be inferred by extrapolation of the $B \rightleftarrows C$ line of Fig. 1, but either the *C* or the *X* form. Moreover, it is possible that the *X* phase also exists for the neighboring disilicates and that it normally cannot be prepared at atmospheric pressure because of insufficient thermal activation in its temperature range.

Concerning the range of metastability of the high-pressure phases at ordinary pressure, it was found that the *X* and *B* forms convert back to *C* form between 900 and 1000°C for the three disilicates. *D* form is still not completely transformed to *C* form at 1300°C. This extended stability is probably related to the fact that *D* form is the highest temperature form.

Table II gives the X-ray powder diffraction patterns of the *D*, *X*, and *B* high-pressure phases of $Tm_2Si_2O_7$. These patterns were obtained on a diffractometer with the following conditions: Cu$K\alpha$ radiation; Ni filter; speed, 0.05° θ/mn; and Si as internal standard. Table II also shows the X-ray powder diffraction for B-$Lu_2Si_2O_7$ obtained by Reid (*14*) at 110 kbar and 1000°C.

Table III gives the crystal data of the nine high-pressure phases calculated by a least-squares refinement of the X-ray powder diffraction patterns.

In Tables II and III one can notice small differences between our results and Reid's. The same observation has already been made for *C* phases prepared at atmospheric pressure by various authors: Felsche (*1*), Smolin (*11*), Shannon (*10*) [a review on the subject is given in Ref. (*12*)]. It is possible that the discrepancies result from the purity of the products and also from differences in the method of preparation. This is almost certain for the *B* phases which were obtained at substantially different pressures. This may also come from a difference in the environment of the sample during heat treatments under pressure with possible defects resulting, such as oxygen vacancies in the samples.

Great similarities are found between the powder X-ray diffraction patterns of X-$Ln_2Si_2O_7$ (Ln = Tm, Yb, Lu) and of $Y_2Ge_2O_7$ or $Er_2Ge_2O_7$. The cell parameters of the *X*

TABLE II

X-RAY POWDER DIFFRACTION PATTERNS FOR HIGH-PRESSURE PHASES

$Tm_2Si_2O_7$-*D*		
$h\,k\,l$	I/I_0	d_{obs}
0 2 0	15	5.39
1 1 0	25	4.92
0 0 1	35	4.66
0 1 1	20	4.27
1 2 0	10	3.86
0 2 1	10	3.52
1 1 1	70	3.23
$\bar{1}$ 2 1	100	3.08
2 0 0	10	2.758
0 4 0	40	2.690
2 1 0	35	2.671
$\bar{1}$ 3 1	5	2.599
1 3 1	25	2.461
$\bar{2}$ 1 1	20	2.427
1 4 0	5	2.419
0 4 1 0 0 2	15	2.328
0 1 2 2 0 1	50	2.269
2 1 1	5	2.220
$\bar{1}$ 4 1	35	2.188
2 2 1	10	2.090
$\bar{1}$ 2 2	20	2.060

$Tm_2Si_2O_7$-*X*		
$h\,k\,l$	I/I_0	d_{obs}
0 1 1	50	5.79
1 1 0	15	4.66
1 1 1	20	4.35
0 1 3	10	3.41
0 2 1	50	3.18
1 1 3	15	3.035
0 0 4	60	2.997
1 2 0	10	2.949
0 2 2	20	2.889
1 2 1	30	2.864
1 2 2	100	2.646
0 2 3	25	2.543
1 1 4	5	2.524
1 2 3	10	2.375
0 1 5	25	2.255
0 3 1	15	2.163
1 1 5	5	2.132
1 3 0	20	2.086
1 3 1	10	2.054

$Tm_2Si_2O_7$-*B*			$Lu_2Si_2O_7$-*B* (*14*)		
$h\,k\,l$	I/I_0	d_{obs}	$h\,k\,l$	I/I_0	d_{obs}
0 1 0 1 0 0	10	6.56	0 1 0 1 0 0	10	6.478
0 1 1 0 0 2	3	5.95			
$\bar{1}$ 0 1	3	5.80			
$\bar{1}$ 0 2 1 1 1	15	4.45	1 1 1	10	4.422
$\bar{1}$ 1 1 1 0 2 $\bar{1}$ $\bar{1}$ 1	60	4.35 4.33	$\bar{1}$ $\bar{1}$ 1 $\bar{1}$ 1 1	65	4.297
1 $\bar{1}$ 1	15	4.16	1 $\bar{1}$ 1	20	4.093
			0 1 3	3	3.481
			1 0 3	3	3.360
0 $\bar{1}$ 3 0 2 0 2 0 0	25	3.282	0 $\bar{1}$ 3 0 2 0 2 0 0	35	3.242
1 1 3	20	3.094	1 1 3	9	3.074
0 0 4 0 2 2 1 2 0 2 1 0	100	2.969	0 0 4 0 2 2 $\bar{1}$ $\bar{1}$ 3	100	2.941
$\bar{1}$ 2 0 1 $\bar{1}$ 3 2 $\bar{1}$ 0	50	2.891	2 1 1	35	2.880
$\bar{1}$ $\bar{2}$ 1 2 0 2	20	2.840	$\bar{1}$ 2 1 2 0 2	13	2.815
0 $\bar{2}$ 2 2 $\bar{1}$ 1	40	2.782 2.772	0 $\bar{2}$ 2	85	2.743
$\bar{1}$ 0 4	10	2.733			
1 0 4	20	2.683	1 0 4 2 1 2	35	2.657
0 2 3	3	2.623			
1 $\bar{2}$ 2	10	2.525	1 $\bar{2}$ 2	13	2.487
$\bar{2}$ 1 3	3	2.395	1 $\bar{1}$ 4	3	2.388
$\bar{2}$ $\bar{1}$ 3	5	2.359	2 2 0	10	2.345
$\bar{2}$ $\bar{2}$ 1 0 1 5	3	2.293			
0 $\bar{1}$ 5 3 0 0	15	2.181	2 0 4 0 3 0	25	2.162
0 $\bar{2}$ 4	10	2.122			
3 1 0 $\bar{1}$ $\bar{1}$ 5	20	2.089	3 1 0 1 3 0	35	2.075
$\bar{1}$ 3 1 1 $\bar{1}$ 5 $\bar{3}$ 1 0	15	2.049	1 $\bar{1}$ 5	17	2.027

TABLE III

CRYSTAL DATA

Structure type *D* (monoclinic, Z = 2)

		$Tm_2Si_2O_7$	$Yb_2Si_2O_7$	$Lu_2Si_2O_7$	$Lu_2Si_2O_7$ (*14*)
a	Å	5.543 ± 0.005	5.516 ± 0.005	5.494 ± 0.005	
b		10.78 ± 0.01	10.70 ± 0.01	10.66 ± 0.01	
c		4.680 ± 0.005	4.678 ± 0.005	4.688 ± 0.005	
β	degrees	96.10 ± 0.10	96.17 ± 0.10	96.19 ± 0.10	
V	$Å^3$	278 ± 1	275 ± 1	273 ± 1	
ρ_{calc}	$g \times cm^{-3}$	6.04 ± 0.03	6.22 ± 0.03	6.30 ± 0.03	
Structure type *B* (triclinic, Z = 4)					
a	Å	6.548 ± 0.01	5.532 ± 0.01	6.514 ± 0.01	6.479
b		6.576 ± 0.01	6.555 ± 0.01	6.539 ± 0.01	6.508
c		11.92 ± 0.02	11.89 ± 0.02	11.84 ± 0.02	11.795
α	degrees	85.61 ± 0.20	85.72 ± 0.20	85.60 ± 0.20	85.54
β		91.19 ± 0.20	91.15 ± 0.20	91.47 ± 0.20	90.61
γ		88.19 ± 0.20	88.21 ± 0.20	88.16 ± 0.20	87.42
V	$Å^3$	512 ± 5	507 ± 5	502 ± 5	493.2
ρ_{calc}	$g \times cm^{-3}$	6.57 ± 0.06	6.73 ± 0.06	6.85 ± 0.06	
Structure type *X* (tetragonal, Z = 4)					
a	Å	6.594 ± 0.005	6.574 ± 0.005	6.565 ± 0.005	
c		12.00 ± 0.01	11.99 ± 0.01	11.95 ± 0.01	
V	$Å^3$	522 ± 1	518 ± 1	515 ± 1	
ρ_{calc}	$g \times cm^{-3}$	6.44 ± 0.01	6.59 ± 0.01	6.68 ± 0.01	

phase of the disilicates (obtained from single crystal electron diffraction) are also very close to those of the mentioned digermanates. It thus appears that, although the structure of phase *X* was not determined, it is most probably identical with the known structure of $Er_2Ge_2O_7$ (*15*).

From the preceding, it follows that the coordination number of the cation (rare earth) in the three disilicates increases with pressure from 6 in the *C* form (*1*) to 7 in the *X* form [$Er_2Ge_2O_7$ (*15*)] and finally, 8 in the *B* form (*2*), thereby exhibiting behavior in agreement with what is observed for most oxides (*13*). In the present case, the fact that 6 is a normal coordination number for the last lanthanoids explains why the "high-temperature" form *C* of the corresponding disilicates is stable at "low-temperature" and why it has been the only known form of these compounds for a long time.

Acknowledgment

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