JOURNAL OF SOLID STATE CHEMISTRY **30**, 203–208 (1979)

Garnet–Perovskite Transformations in the Sm_2O_3–Ga_2O_3 and Gd_2O_3–Ga_2O_3 Systems

M. A. DIGIUSEPPE AND S. SOLED

Corporate Research Center, Allied Chemical Corporation, Morristown, New Jersey 07960

Received September 5, 1978; in revised form December 12, 1978

The effect of heating garnet melts to various temperatures has been investigated. The previously reported decomposition of the garnet phase due to loss of Ga_2O_3 was corroborated. However, it was also observed that when gallium oxide loss is prevented and the maximum temperature of the melt exceeds a critical value, phase separation of garnet to perovskite and β-gallium oxide occurs:

$$RE_3Ga_5O_{12} \rightleftarrows 3REGaO_3 + Ga_2O_3.$$

The reverse reaction will occur by reheating the two-phase mixture to the garnet melting point.

Introduction

The use of rare earth aluminum and gallium garnets ($RE_3Al_5O_{12}$, $RE_3Ga_5O_{12}$) as solid state laser materials or as substrates for magnetic bubble memory devices requires the growth of large high-quality single crystals (*1–3*). Consequently, information about phase stabilities in these garnet systems is important. For example, dysprosium aluminum garnet ($Dy_3Al_5O_{12}$) decomposes at temperatures slightly above its melting point to dysprosium aluminum perovskite ($DyAlO_3$) and Al_2O_3 (*4*). Similar decompositions from a garnet structure to a distorted perovskite with the concurrent segregation of a second phase have been reported to occur for a number of rare earth gallium garnets in the presence of a flux (*5, 6*).

In this study we observed the reversible phase transformation of garnet to distorted perovskite and β-gallium oxide for $Sm_3Ga_5O_{12}$ and $Gd_3Ga_5O_{12}$. Differential thermal analysis (DTA) was used to investigate the effect of the variation of temperature on the phenomenon.

Experimental

Garnet samples used in all experiments were prepared initially as polycrystalline material by adding Sm_2O_3 or Gd_2O_3 (JMC, United Mineral Corp., 99.99%), freshly dried at 1200°C, to Ga_2O_3 (Alusuisse, 99.99%) and heating the mixture in a platinum crucible to 1450°C in air. Several successive heating and grinding cycles produced homogeneous samples. The $RE_3Ga_5O_{12}$ garnet formulation is used throughout this paper for simplicity; the actual nominal compositions used were $Sm_3Ga_5O_{12}$ + 0.25 mole% excess Ga_2O_3 (*1*) and $Gd_{3.05}Ga_{4.95}O_{12}$ + 0.25 mole% excess Ga_2O_3 (*1, 7, 8*). The excess Ga_2O_3 was used to compensate for losses during preparation.

Crystals of $Sm_3Ga_5O_{12}$ and $Gd_3Ga_5O_{12}$ were grown by the Czochralski technique (*9*)

0022-4596/79/110203-06$02.00/0

using a furnace design similar to that previously reported (*1*). An atmosphere of nitrogen with 0.9 vol% O_2 for $Sm_3Ga_5O_{12}$ and 1.5 vol% O_2 for $Gd_3Ga_5O_{12}$ was used during growth. A 30-kW, 310-kC Lepel RF generator was used to heat a 50.8 × 50.8-mm iridium crucible. Crystal diameter was controlled by sensing crystal weight during growth. Flat interface boules with diameters of 19.1 or 22.1 mm were grown at a pull speed of 1.37 mm/hr.

The effect of gallium oxide loss on garnet decomposition was studied at various temperatures above the melting point in the same atmosphere as used during crystal growth. All samples (≈ 100 mg) were held in open cylindrical iridium crucibles ($r = 2.5$ mm, $h = 21.0$ mm; Engelhard, 99+) at the designated temperature for 70 min followed by either slow cooling (100°C/hr) or rapid quenching to room temperature.

Simultaneous DTA and thermal gravimetric analysis (TGA) were performed on a Mettler TA-1 instrument. Several small randomly shaped single-crystal chips of $Sm_3Ga_5O_{12}$ or $Gd_3Ga_5O_{12}$, totaling approximately 200 mg, were placed into capped iridium crucibles similar to those used in the decomposition experiments. The sample-containing crucible together with an empty reference crucible and lid were heated in a water-cooled tungsten resistance furnace. A purging stream (50 cm^2/min) of zirconium-scrubbed He provided an inert atmosphere. For the linearly programmed temperature experiments, the heating rate was maintained at 25°C/min. Temperatures were sensed by a W/W (26%) Re thermocouple. Prior to some of these experiments, the iridium lids were electron-beam welded onto the crucibles.

Crystallized phases were identified by X-ray diffraction using a Norelco diffractometer with monochromatic radiation (AMR 3-202 focusing monochromator) and a medium-intensity copper source [$\lambda(CuK\alpha_1)$, 1.5405 Å]. A scan speed of 1° 2θ/min was used for all samples.

Results and Discussion

After the Czochralski crystal growth of $Sm_3Ga_5O_{12}$ or $Gd_3Ga_5O_{12}$, it was observed that in some instances the residual melt crystallized as a perovskite and β-gallium oxide mixture. When this mixture, which was stable at room temperature, was reheated to the respective garnet melting points (T_m of $Sm_3Ga_5O_{12} \simeq 1664°C$; T_m of $Gd_3Ga_5O_{12} \simeq 1735°C$), monophase garnet reformed on cooling. These garnet phases and perovskite–gallium oxide mixtures are shown in Fig. 1. This phase separation can be represented as:

$$RE_3Ga_5O_{12} \rightleftarrows 3REGaO_3 + Ga_2O_3.$$

It has been noted that $SmGaO_3$ was found in the residual melt if Ga_2O_3 was lost during the crystal growth of $Sm_3Ga_5O_{12}$ (*10*). Our initial studies focused on the effect of the loss of Ga_2O_3 from overheating $Sm_3Ga_5O_{12}$ and $Gd_3Ga_5O_{12}$ melts. These results are summarized in Table I. When the melts were heated to maximum temperatures of at least 100°C above the respective garnet melting points, perovskite was the principal phase upon cooling. In melts cooled from 100 to 200°C above the melting point, $RE_4Ga_2O_9$ was the major phase, while at even higher temperatures RE_2O_3 appeared. The loss of Ga_2O_3 proceeds via a Ga_2O intermediate (*11, 12*). The effect of the continuous loss of Ga_2O_3 can be represented by the following chemical equations:

$$RE_3Ga_5O_{12} \rightarrow 3REGaO_3 + Ga_2O_3,$$

$$4REGaO_3 \rightarrow RE_4Ga_2O_9 + Ga_2O_3,$$

$$RE_4Ga_2O_9 \rightarrow 2RE_2O_3 + Ga_2O_3.$$

Perovskite formation occurred as a result of the loss of Ga_2O_3 from the garnet melt; however, this loss is irreversible and could not account for the observed reverse trans-

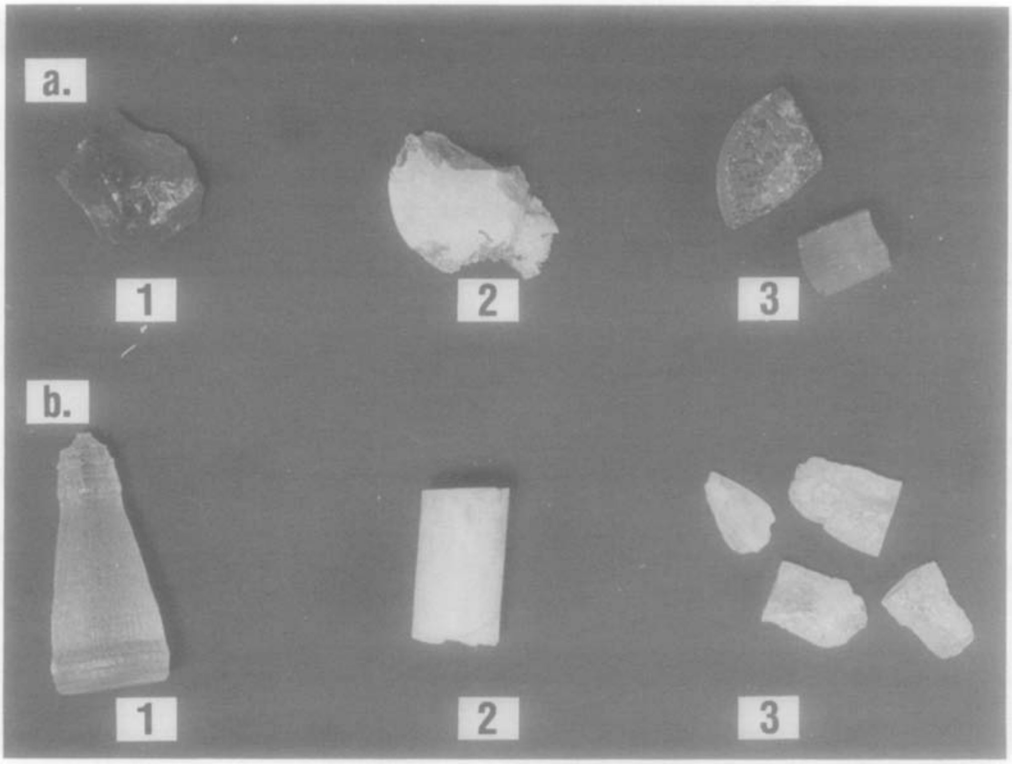


FIG. 1. (a) 1, $Sm_3Ga_5O_{12}$; 2, after phase separation $Sm_3Ga_5O_{12} \rightarrow 3SmGaO_3 + Ga_2O_3$; 3, after reverse reaction $3SmGaO_3 + Ga_2O_3 \rightarrow Sm_3Ga_5O_{12}$, when perovskite–gallium oxide mixture is heated to the garnet melting point. (b) 1, $Gd_3Ga_5O_{12}$; 2, after phase separation $Gd_3Ga_5O_{12} \rightarrow 3GdGaO_3 + Ga_2O_3$; 3, after reverse reaction $3GdGaO_3 + Ga_2O_3 \rightarrow Gd_3Ga_5O_{12}$, when perovskite–gallium oxide mixture is heated to the garnet metling point.

TABLE I

PHASES FORMED BY THE LOSS OF Ga_2O_3 FROM $Sm_3Ga_5O_{12}$ AND $Gd_3Ga_5O_{12}$ GARNET MELTS

Garnet	Temperature (°C, held 70 min)	Cooling rate (°C/hr)	Principal phases present after cooling to room temperature
$Sm_3Ga_5O_{12}$	1870	Quenched	$SmGaO_3 + Sm_4Ga_2O_9$
$Sm_3Ga_5O_{12}$	>1870	100	$Sm_4Ga_2O_9$
$Gd_3Ga_5O_{12}$	1842	100	$GdGaO_3 + Ga_2O_3$
$Gd_3Ga_5O_{12}$	1916 to 1930	100	$Gd_4Ga_2O_9$
$Gd_3Ga_5O_{12}$	>1950	100 or quenched	$Gd_4Ga_2O_9$ + monoclinic Gd_2O_3

formation of perovskite and Ga_2O_3 back to garnet. In order to further investigate the temperature dependence and reversible nature of this process DTA and TGA studies were performed in capped iridium crucibles to prevent the loss of Ga_2O_3. The samples were again heated to and cooled from different temperatures above the respective garnet melting points. During cooling from 25°C above the melting point, single exotherms appeared. The crystallized phase was identified as garnet. When maximum heating temperatures exceeded the melting point by more than 70°C, two exothermic transitions occurred on cooling, corresponding to the crystallization of both *RE*GaO_3 and Ga_2O_3. This phase separation is independent of the cooling rate. After repeated cycling of the perovskite and gallium oxide mixture to 25°C above the garnet melting point, reversion to the garnet phase occurred. During the heating cycles preceding the reversion, a complex pattern of multiple endotherms were usually observed. In most instances, at least two cycles were necessary to achieve this transformation. These results are shown in Table II and Figs. 2 and 3.

During these experiments, total weight losses varied between 0.0 and 0.3%. Therefore, several experiments were repeated in crucibles which were welded shut. Identical results were obtained, which indicated that these small weight losses were inconsequential to the garnet phase separation.

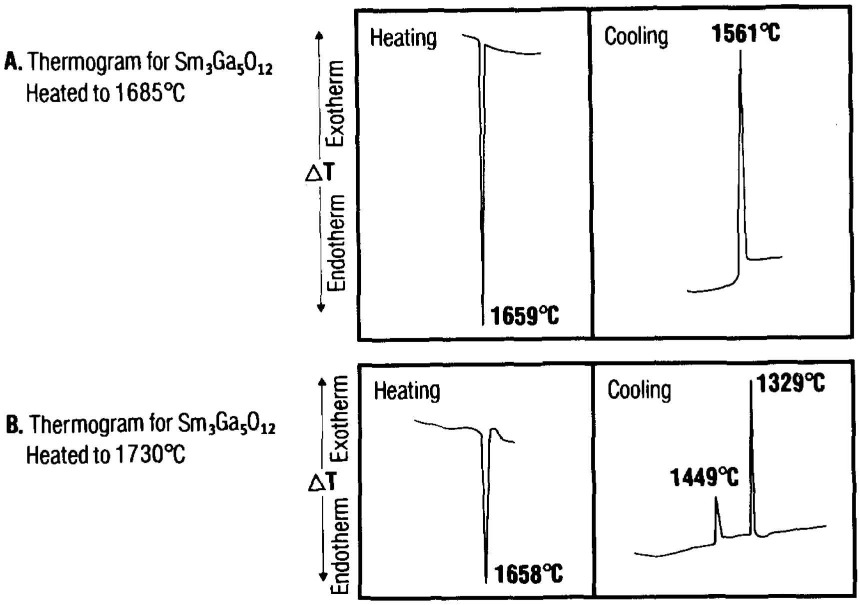
The garnet phase appears to be thermodynamically more stable than the perovskite phase in the solid state. Garnet can be prepared by direct solid state reaction of rare earth and gallium sesquioxides; however, attempts to prepare perovskite in an analogous manner during this work and also by other investigators (*10*) were unsuccessful, with the resulting products consisting of garnet plus $RE_4Ga_2O_9$. This behavior could be related to the stabilizing influence the tetrahedral site provides for gallium in the garnet structure. The perovskite, however, can be prepared by cooling molten samples of equimolar mixtures of the sesquioxides. Consequently, the crystallization process has an important influence on the formation of the perovskite phase.

The crystallization patterns of both garnet and perovskite were examined in more

TABLE II

DTA DATA ILLUSTRATING THE EFFECT OF HEATING GARNET MELTS WITHOUT THE LOSS OF Ga_2O_3

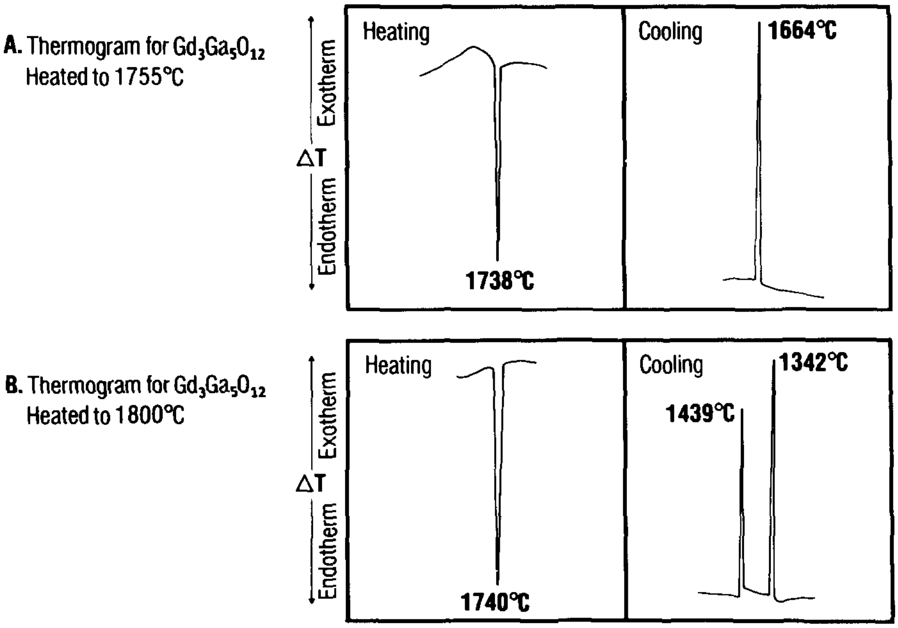
Sample	Maximum heating temperature (°C)	Endotherm temperature (s) (°C)	Exotherm temperature (s) (°C)
$Sm_3Ga_5O_{12}$ 9-2986	1685	1661	1622
$Sm_3Ga_5O_{12}$ 9-2987	1685	1664	1627
$Sm_3Ga_5O_{12}$ 9-2988	1685	1655	1628
$Sm_3Ga_5O_{12}$ 9-2987	1730	1669	1466, 1335
$Sm_3Ga_5O_{12}$ 9-2988	1730	1664	1463, 1336
$Sm_3Ga_5O_{12}$ 9-2985	1790	1664	1458, 1332
$Sm_3Ga_5O_{12}$ 9-2640	1790	1669	1443, 1334
$Sm_3Ga_5O_{12}$ 9-2655	1905	1653	1419, 1318
$Gd_3Ga_5O_{12}$ 9-3109	1755	1738	1664
$Gd_3Ga_5O_{12}$ 9-3110	1755	1736	1615
$Gd_3Ga_5O_{12}$ 9-3109	1800	1740	1439, 1342
$Gd_3Ga_5O_{12}$ 9-3110	1800	1748	1438, 1337
$Sm_3Ga_5O_{12}$ 9-3148	1685	1645	1603
(cycled)	1730	1646	1450, 1390
	1685	1521, 1641	1615
	1685	1643	1618
$Sm_3Ga_5O_{12}$ 9-3146	1685	1640	1449
(cycled)	1730	1645	1448, 1312
	1685	1338, 1385, 1435	1459, 1316
	1685	1336, 1384, 1477	1455, 1320
	1685	1421, 1565, 1642	1576



A. Thermogram for $Sm_3Ga_5O_{12}$
Heated to 1685°C

B. Thermogram for $Sm_3Ga_5O_{12}$
Heated to 1730°C

FIG. 2.



A. Thermogram for $Gd_3Ga_5O_{12}$
Heated to 1755°C

B. Thermogram for $Gd_3Ga_5O_{12}$
Heated to 1800°C

FIG. 3.

detail. A qualitative estimation of the crystallization activation energies can be obtained from the variation in shape of the crystallization exotherms (*13*). For example, at a 25°C/min cooling rate, the width at half-height of both the garnet and perovskite exotherms are similar (≃30 sec). At a 1°C/min cooling rate, however, the perovskite exotherm broadens (width ≃70 sec) while the garnet exotherm remains unchanged. This broadening indicates that perovskite has a lower crystallization activation energy than garnet and is kinetically favored over garnet in the crystallization process.

Our results are consistent with the idea that near the melting temperature, the "structure" of the liquid is similar to that of the solid. As the temperature of the melt is raised, changes in the liquid occur, which are then reflected in the structure of the crystallized solid. Similar structural changes have been found to occur in Al_2O_3 (*14*).

Acknowledgments

We thank Drs. G. G. Libowitz and E. Turi for their many helpful discussions. Also, we thank Drs. R. Morris and M. Kokta for relevant comments as well as T. Goble, Y. P. Khanna and W. M. Wenner for their assistance.

References

1. C. D. BRANDLE AND A. J. VALENTINO, *J. Cryst. Growth* **12**, 3 (1972).
2. B. COCKAYNE AND J. M. ROSLINGTON, *J. Mater. Sci.* **8**, 601 (1973).
3. C. D. BRANDLE, D. C. MILLER, AND J. W. NIELSEN, *J. Cryst. Growth* **12**, 195 (1972).
4. R. GILISSEN, A. J. FLIPOT, AND R. LECOCQ, *J. Amer. Ceram. Soc.* **57**, 6, 274 (1974).
5. M. MAREZIO, J. P. REMEIKA, AND P. D. DERNIER, *Mater. Res. Bull.* **1**, 247 (1966).
6. M. MAREZIO, J. P. REMEIKA, AND P. D. DERNIER, *Inorg. Chem.* **7**, 1337 (1968).
7. M. ALLIBERT, C. CHATILLON, J. MARESCHAL, AND F. LESSALDE, *J. Cryst. Growth* **23**, 289 (1974).
8. H. MAKINO, S. NAKAMURA, AND K. MATSUMI, *Japan. J. Appl. Phys.* **15**, 3, 415 (1976).
9. J. CZOCHRALSKI, *Z. Phys. Chem.* **92**, 219 (1918).
10. S. GELLER, P. J. CURLANDER, AND G. F. RUSE, *Mater. Res. Bull.* **9**, 637 (1974).
11. S. A. SCHUKAREV, G. A. SEMENOV, AND I. A. RAT'KOVSKII, *Russ. J. Inorg. Chem.* **14**, 1 (1969).
12. J. R. CARRUTHERS, M. KOKTA, R. L. BARNS, AND M. GRASSO, *J. Cryst. Growth* **19**, 204 (1973).
13. M. D. BARÓ, N. CLAVAGUERA, S. BORDAS, M. T. CLAVAGUERA-MORA, AND J. CASAS-VÁZQUEZ, *J. Therm. Anal.* **11**, 271 (1977).
14. A. NUKUI, H. TAGAI, H. MORIKAWA, AND S.-I. IWAI, *J. Amer. Ceram. Soc.* **59**, 11–12, 534 (1976).