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Use of DSC for study of the complex setting reaction and microstructural stability of a gallium-based dental alloy

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Abstract

Gallium-based alloys have been introduced as mercury-free restorative dental materials. However, these alloys undergo a complex setting reaction, and problems of clinical corrosion and fractures of restored teeth have been reported. The purpose of this study was to investigate the use of DSC for study of the setting reaction and microstructural stability of a commercial product (Galloy, Southern Dental Industries, Australia). Specimens (~20 mg) were prepared with variations in mixing times, condensation techniques, surface conditions and storage times. The DSC analyses were performed from room temperature to 225°C, using a heating rate of 10°C/min. Interpretation of the thermograms was aided by comparison to complementary X-ray diffraction (XRD) patterns of specimens subjected to the same experimental conditions. An exothermic peak was associated with absorption of liquid gallium by the starting Ag–Sn–Cu particles, and four endothermic peaks were associated with the formation of metallurgical phases during setting. The results show the great utility of DSC for study of the present gallium-based alloys and the development of improved alloy compositions. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Differential scanning calorimetry; Gallium-based alloys; Dental amalgam; Trituration; Condensation; Setting reaction

1. Introduction

Puttkammer [1] first suggested the replacement of mercury by gallium to formulate a mercury-free dental amalgam, since liquid gallium has the ability to wet the surfaces of many solids, including human teeth. Smith and Caul [2] subsequently reported the compositions of powdered alloys that could be mixed with gallium to serve as a possible replacement for dental amalgam. For many years thereafter little attention was paid to development of gallium-based dental restorative alloys. Within recent years, in response to continuing concerns about the biocompatibility of dental amalgam, three commercial gallium-based restorative alloys have been marketed: Gallium Alloy GF and Gallium Alloy GF II, Tokuriki Honten, Tokyo, Japan; Galloy, Southern Dental Industries, Bayswater, Vic., Australia. These products are described as alternatives to dental amalgam having similar manipulative procedures, suitable physical and mechanical properties, and superior biocompatibility. The setting dimensional changes and mechanical properties [3–5], handling characteristics [6,7], in vitro and in vivo

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corrosion characteristics [3,8–10], and biocompatibility [11–14] of these alloys have been reported.

Clinical preparation of these restorative materials involves mixing (termed *trituration*) a metallic powder and a gallium-based liquid. The overall setting reaction has two components and may be written as follows [3]:

$$Ag_4Sn + Ga \rightarrow Ga_{28}Ag_{72} + Sn$$

$$Cu_3Sn + Ga \rightarrow CuGa_2 + Sn$$

The two reactions arise because the starting Ag–Sn–Cu metallic powder (termed the *pre-alloy particles*) contains two phases: Ag_4Sn and Cu_3Sn [3]. In addition to formation of the $CuGa_2$ and $Ga_{28}Ag_{72}$ phases, both setting reactions result in the formation of a third β-Sn phase. Reaction between Ag in the pre-alloy particles and In present in the Ga-based liquid yields a fourth phase (In_4Ag_9). Thus, the microstructure of the gallium-based restorative alloys is highly complex, containing the two starting Ag_4Sn and Cu_3Sn phases (since the powder particles are incompletely consumed during setting) and four reaction phases ($CuGa_2$, $Ga_{28}Ag_{72}$, β-Sn and In_4Ag_9). Formation of these reaction phases (collectively termed the *matrix*) is intimately related to the clinically relevant dimensional changes that occur during setting, as well as to the mechanical properties, corrosion resistance and biocompatibility of these materials [3].

The objective of this study was to use differential scanning calorimetry (DSC) to obtain insight into the setting reaction kinetics and microstructural stability of a commercial gallium alloy prepared under different experimental conditions. Such thermal analyses, which have previously been reported for dental amalgams [15], can provide the basis for greater understanding of the gallium-based alloys and yield insight for the scientific development of improved materials [16]. The present thermal analyses complement a recently reported X-ray diffraction (XRD) and scanning electron microscopic study [17] of gallium alloy specimens prepared under nominally identical conditions.

2. Experimental

The gallium-based alloy (Galloy) and an appropriate trituration apparatus were contributed by the manufacturer (Southern Dental Industries). The Galloy product was in the form of preproportioned capsules with the powder (60% Ag, 28% Sn and 12% Cu) in one compartment and the liquid (62% Ga, 25% In and 13% Sn) in the other compartment (elemental compositions in weight percent).

Seven groups of specimens were prepared for DSC analyses, as summarized in Table 1. Specimens were triturated for either the manufacturer's recommended time of 8 s or a longer time of 10 s. The mixed specimens were either dispensed onto a clean, white paper sheet or into a 5 mm diameter × 5 mm height mold fabricated from poly(methyl) methacrylate (PMMA). The specimens in groups 1 and 4 were not condensed (i.e., no packing of the material to minimize voids), whereas specimens in groups 2, 5 and 7 were hand-condensed (the normal clinical procedure), using a smooth, round-ended amalgam condenser (2 mm diameter). The specimens in groups 3 and 6 were machine-condensed, using a slow-speed dental handpiece with the same smooth, round-ended condenser. For the specimens in group 7, an approximately 1 mm thick surface layer of material was

Table 1
Summary of specimen groups for DSC experiments ($n = 3$)

Experimental group	Trituration time (s)	Location of dispensed specimen	Condensation procedure
1	8	Paper sheet	No condensation, surface layer not removed
2	8	PMMA mold	Hand condensation, surface layer not removed
3	8	PMMA mold	Machine condensation, surface layer not removed
4	10	Paper sheet	No condensation, surface layer not removed
5	10	PMMA mold	Hand condensation, surface layer not removed
6	10	PMMA mold	Machine condensation, surface layer not removed
7	8	PMMA mold	Hand condensation, 1 mm surface layer removed

removed following hand condensation, which would be the normal clinical procedure for placement of a Galloy dental restoration. No surface layer of material was removed for any of the other six specimen groups.

Three specimens for DSC analysis were prepared for each of the seven groups ($n = 3$), using a fresh mix of Galloy for each specimen. The prepared mass of material was cut with a razor blade, yielding small irregularly shaped test specimens (typically about 10 mg weight) that were randomly selected for the analyses. Each specimen was analyzed in the freshly mixed condition, and after storage times of 1 h, 1 day, 1 week and 1 month at room temperature, except for specimens in the seventh group where analyses were not performed after 1 month.

The DSC analyses were performed with a TA 910 apparatus (TA Instruments, Wilmington, DE), using a heating rate of 10°C/min over the temperature range from 25 to 225°C. Each specimen was placed in a small, open aluminum pan, and a second empty aluminum pan served as the reference material. The computer software associated with the DSC apparatus was used to construct tangent lines to the sides of each peak and to calculate the change in enthalpy (ΔH) associated with the given transformation. The starting and ending temperatures for each transformation were determined from the intersections of the baseline and the two tangent lines. As described in Section 3, an incompletely resolved, double endothermic peak was observed for some Galloy specimens, and the area of this double peak was computed as a single peak.

Three-way analysis of variance (ANOVA) was used to compare the temperature and enthalpy change (ΔH) for each of the peaks on the DSC plots, where the three factors were trituration time, condensation method and storage time. The specimens where an approximately 1 mm thick surface layer was removed were excluded from the statistical analysis due to their different conditions compared to the other groups, and the specimens analyzed after 1 month of storage were excluded due to the presence of only one sample for each group.

3. Results

Figs. 1–4 present DSC plots for four representative Galloy specimens and illustrate the types of peaks that were observed. Table 2 summarizes the peak positions and enthalpy changes for these four specimens, and provides information about the peaks observed for

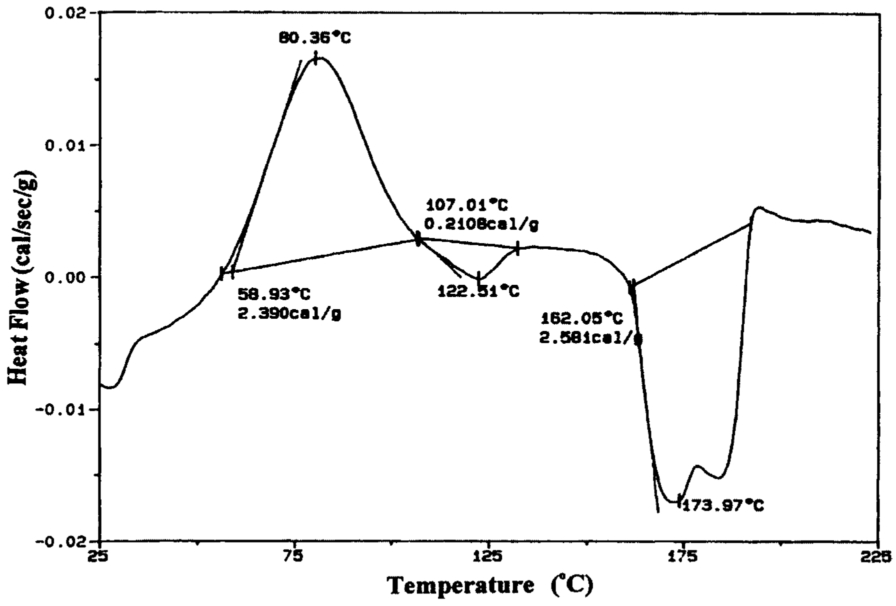

Fig. 1. DSC thermogram for a freshly prepared Galloy specimen that was triturated for 8 s and hand-condensed.

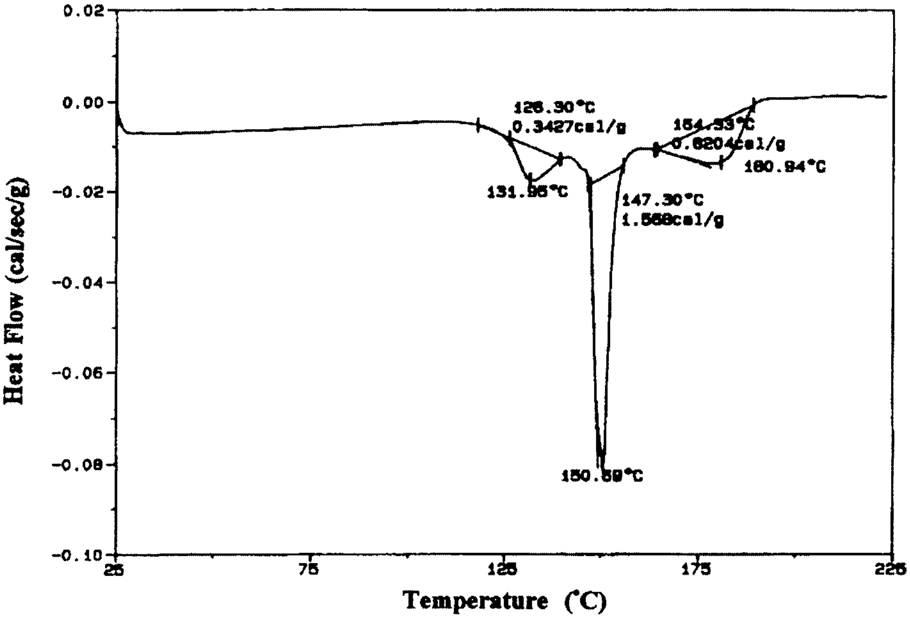

Fig. 2. DSC thermogram after 1 day for a Galloy specimen that was triturated for 8 s and hand-condensed.

four additional representative specimens. The DSC plots for these latter specimens are available elsewhere [18]. There was little effect of trituration time (8 or 10 s) on the DSC plots for specimens where the rest of the preparation conditions were the same, although other factors (condensation procedure, surface condition and storage time before analysis) could have substantial effects.

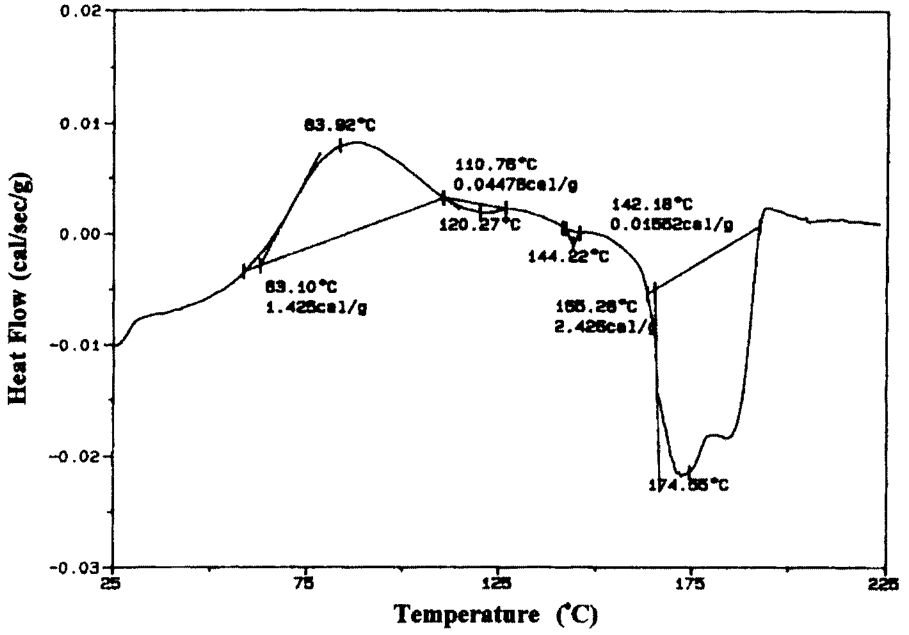

Fig. 3. DSC thermogram for a freshly prepared Galloy specimen that was triturated for 8 s and machine-condensed.

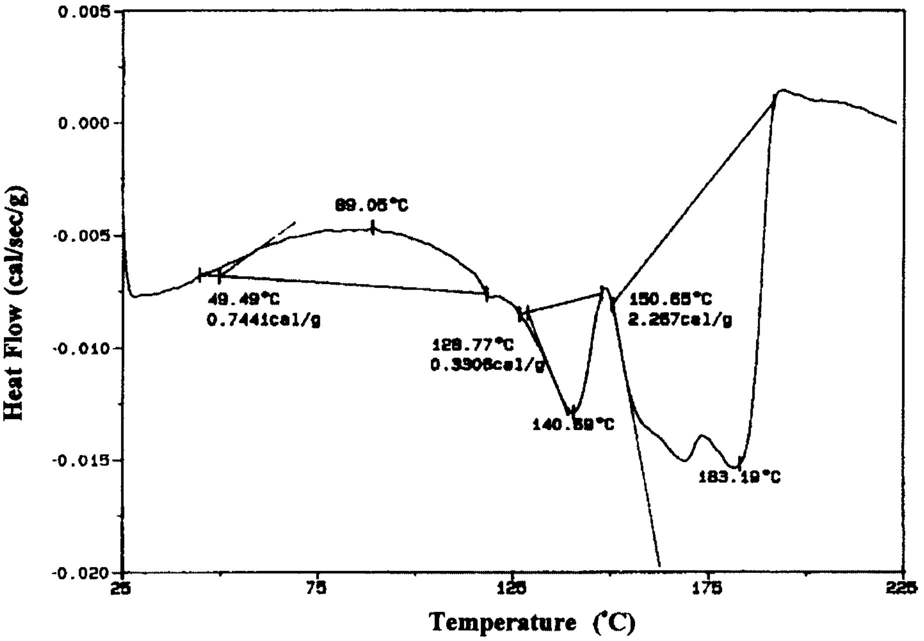

Fig. 4. DSC thermogram after 1 h for a Galloy specimen that was triturated for 8 s and hand-condensed, with a 1 mm surface layer removed.

Table 2 shows that there were generally five DSC peaks for the Galloy specimens, an exothermic peak and four endothermic peaks. The two endothermic peaks occurring at the highest temperatures for some specimens were not separately resolved, and the enthalpy changes listed in Table 2 for those cases correspond to the total area for both peaks. Interpretation of the DSC peaks was possible from the results of a complementary XRD study [17] that used nominally identical specimens, where the XRD patterns were obtained at different time periods after trituration. Identification of the phases in the XRD patterns [17] was based upon previously published results by Herø and Okabe [3] and upon peak positions in the appropriate ICDD polycrystalline powder standards (International Center for Diffraction Data, Swarthmore, PA) for the six microstructural phases.

The exothermic first peak, occurring at temperatures between approximately 80 and 100°C, is attributed to absorption of the gallium-rich liquid by the pre-alloy particles, which should occur spontaneously after the powder and liquid are mixed. As would be expected, this peak becomes smaller with increasing time after preparation of the hand-condensed specimens, since the gallium-rich liquid is consumed during the setting reaction. Table 2 shows that this peak was absent for the hand-condensed specimens at times of 1 day and longer. This peak also becomes smaller for the machine-condensed specimens and for the hand-condensed specimens after removal of the approximately 1 mm thick surface layer.

The endothermic second peak, occurring at temperatures between approximately 120 and 140°C, is attributed to the formation of the $CuGa_2$ phase. The relatively small size of this peak is consistent with the relatively small size of the XRD peaks for the $CuGa_2$ phase [17]. Herø and Okabe [3] suggest that $CuGa_2$ is the first setting reaction phase to form. Table 2 shows that this peak is relatively stable with time up to 1 week for the hand-condensed specimens. However, this peak becomes much smaller when the hand-condensed specimens are analyzed 1 month after preparation, or when machine-condensed specimens or specimens where the approximately 1 mm thick surface layer has been removed are analyzed.

The endothermic third peak, occurring at temperatures between approximately 140 and 150°C, is interpreted as arising from the formation of the β-Sn phase, based upon the changes in XRD intensity with time for the β-Sn peaks [17]. Table 2 shows that for both the

Table 2
Summary of the DSC peak positions and enthalpy changes for representative Galloy specimens (the specimen groups are provided in Table 1, and the figures showing the corresponding DSC plots for four of these specimens are indicated in brackets)

Condition/time for analysis	Peak 1 (exothermic)	Peak 2 (endothermic)	Peak 3 (endothermic)	Peaks 4 and 5 (endothermic)
Triturated 8 s, hand-condensed; fresh (group 2) (Fig. 1)	80°C, 2.4 cal/g	123°C, 0.2 cal/g	Absent	173 and 184°C, 2.6 cal/g
Triturated 8 s, hand-condensed; 1 h (group 2)	82°C, 0.8 cal/g	123°C, 0.1 cal/g	Absent	172 and 184°C, 2.8 cal/g
Triturated 8 s, hand-condensed; 1 day (group 2) (Fig. 2)	Absent	132°C, 0.3 cal/g	151°C, 1.6 cal/g	181°C (one peak), 0.8 cal/g
Triturated 8 s, hand-condensed; 1 week (group 2)	Absent	136°C, 0.2 cal/g	151°C, 1.7 cal/g	184°C (one peak), 0.8 cal/g
Triturated 8 s, hand-condensed; 1 month (group 2) (Fig. 3)	Absent	138°C, 0.01 cal/g	152°C, 0.2 cal/g	184°C (one peak), 0.05 cal/g
Triturated 8 s, machine-condensed; fresh (group 3)	84°C, 1.4 cal/g	120°C, 0.04 cal/g	144°C, 0.02 cal/g	172 and 184°C, 2.4 cal/g
Triturated 8 s, hand-condensed; 1 h, 1 mm removed (group 7)	104°C, 1.0 cal/g	133°C, 0.03 cal/g	147°C, 0.1 cal/g	166 and 181°C, 1.6 cal/g
Triturated 8 s, hand-condensed; 1 h, 1 mm removed (second specimen from group 7) (Fig. 4)	89°C, 0.7 cal/g	Absent	141°C, 0.3 cal/g	166 and 181°C, 2.3 cal/g
Interpretation	Absorption of Ga	$CuGa_2$	β-Sn	$Ga_{28}Ag_{72}$ and In_4Ag_9

hand-condensed and machine-condensed specimens, this peak is absent or weak for freshly prepared specimens or specimens analyzed 1 h after preparation, and then becomes strong after 1 day and 1 week, followed by a substantial decrease in intensity after 1 month.

The fourth and fifth peaks are adjacent endothermic peaks occurring at temperatures ranging from approximately 170 to 185°C. For simplicity, this unresolved double peak was considered as a single peak for enthalpy calculation. Table 2 shows that an apparent single peak was observed for hand-condensed specimens analyzed 1 day, 1 week and 1 month after preparation. These two peaks are hypothesized to be due to the formation of the $Ga_{28}Ag_{72}$ and In_4Ag_9 phases, which have strong XRD peaks [17]. The intensities of these peaks decrease substantially after 1 day to 1 month, as the setting reaction becomes completed, and are moderately decreased with removal of the gallium-rich surface layer.

4. Discussion

The results from the DSC analyses that are summarized in Table 2 are consistent with the general nature of the setting reaction and the procedures used to prepare the Galloy specimens. For exothermic peak 1, attributed to the incorporation of the gallium-rich liquid into the pre-alloy particles, there was no significant difference in the peak temperature for the hand-condensed specimens in the freshly prepared condition and after 1 h storage ($P > 0.05$), although values of ΔH were significantly different ($P < 0.05$). Differences in peak positions and values of ΔH for the machine-condensed specimens, compared to the hand-condensed specimens, are attributed to the differences in the amount of gallium available to be absorbed by the pre-alloy particles.

For endothermic peak 2, attributed to the formation of the $CuGa_2$ phase, statistically significant increases in ΔH and peak temperature ($P < 0.05$ in both cases) were found when comparing the freshly prepared specimens with specimens stored 1 h, 1 day and 1 week before DSC analysis. However, the values of ΔH for the hand-condensed specimens and storage times up to 1 week remain small. The decrease in peak intensity for the machine-condensed specimens and for the hand-condensed specimens after 1 month storage, where no surface layer was removed, and for the hand-condensed specimens where the surface layer was removed, is considered due to the lack of availability of free gallium to form the $CuGa_2$ phase.

The endothermic peak 3, attributed to the formation of β-Sn, was observed in specimens after 1 day, 1 week and 1 month storage times before DSC analysis, but this peak was absent or weak for freshly prepared specimens or after 1 h storage time (Table 2). Statistical analysis of peaks for specimens stored for periods of 1 day and longer revealed significant differences in values of both temperature and ΔH ($P < 0.05$) [18]. The present DSC analyses and the results from complementary XRD analyses [17] show that this phase forms relatively slowly during the setting reaction, requiring periods longer than 1 h to become prominent (Table 2). However, this peak is diminished greatly when specimens stored for 1 month are analyzed, indicating that formation of the β-Sn phase has been nearly completed.

The fourth and fifth peaks (both endothermic), attributed to the formation of the $Ga_{28}Ag_{72}$ and In_4Ag_9 phases, were considered to be a single peak for simplicity in the statistical analysis, where the mean temperature of the two peaks was used when both were evident (Table 2). Statistical analysis indicated that interaction occurred between the effects of the different independent variables (trituration time, condensation method and storage time) on the peak temperature. Subsequent two-way ANOVA for all of the DSC specimens showed that there were significant differences ($P < 0.05$) in the mean peak temperature and ΔH, depending upon specimen storage time, trituration time and condensation method. However, these results should be viewed with some caution, because of the necessity of considering only a single peak instead of separate peaks for the two reaction phases. Nonetheless, it is evident from Table 2 that the values of ΔH for these peaks decreased greatly as the setting reaction was completed.

Recently, the Galloy product was withdrawn from the United States market because of reports of problematic in vivo corrosion behavior and fractured teeth due to excessive expansion of restorations [17]. Future metallurgical development may focus on elimination of the $CuGa_2$ phase [10], which has been implicated for the in vivo corrosion of gallium-based alloys, and to develop new alloy compositions that do not undergo excessive expansion in vivo. The present research suggests that DSC will be a highly convenient technique to study the setting reaction and microstructural development for future gallium-based alloys, but complementary XRD analyses will be required.

5. Conclusions

1. Formation of peaks on the DSC plots indicated that phase transformation began in Galloy within a few minutes after trituration.
2. XRD provided information about the sequence of matrix phase formation in setting Galloy that was essential for interpretation of the DSC results. An exothermic peak was associated with absorption of liquid gallium by the starting Ag–Sn–Cu particles, and four endothermic peaks were associated with formation of new metallurgical phases ($CuGa_2$, $Ga_{28}Ag_{72}$, β-Sn and In_4Ag_9) during setting.
3. Varying the condensation method and removing an approximately 1 mm thick surface layer from the condensed Galloy can have a substantial effect on the setting reaction, whereas there is little effect from a small increase in the recommended trituration time.
4. DSC is expected to be a powerful, highly convenient technique to study the microstructural development and stability of future gallium-based restorative materials, although complementary XRD analyses are required.

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