

Relation between size and phase structure of gallium: Differential scanning calorimeter experiments

Hao He, Guang Tao Fei,* Ping Cui, Kang Zheng, Li Min Liang, Yong Li, and Li De Zhang

Key Laboratory of Materials Physics, Institute of Solid State Physics, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230031, People's Republic of China

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The relation between sizes and phase structures of gallium has been studied. Gallium droplets with different sizes dispersed in poly(methyl methacrylate) and silicone oil were studied by differential scanning calorimeter and transmission electron microscopy. The results showed that particles with different sizes corresponded to stable or metastable phases of gallium. The stable phase α -gallium is dominantly formed when the average size of particles is no less than 0.8 micron, and the metastable phases β -, γ - and δ -gallium are mainly formed when the average particle size is 0.8–0.6 micron, 0.6–0.3 micron, and below 0.3 micron, respectively. The phase selection in the solidification process under undercooling is used to explain the results.

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It is well known that physical properties of materials vary with dimensions. Recent work shows that particle sizes can induce structural changes in nanocrystalline Se, Ag, and various oxides.^{1–3} In this communication, we reported the size-induced structural changes in submicron-sized gallium (Ga) particles.

Ga is a low freezing point (29.9 °C) metal and its phase structures have been widely studied.^{4–6} In general, four orthorhombic crystalline structural phases, α -, β -, δ -, and γ -phase with melting points of 29.9 °C, –16.2 °C, –19.4 °C, and –35.6 °C,⁶ respectively, have been investigated. In these phases, only α is the stable phase, and others are metastable ones. Some theoretical and experimental results on Ga have been reported.^{7–18} Di Cicco *et al.*^{11,16} have studied phase transitions and undercooling phenomenon of confined Ga. Konrad *et al.*¹² have studied the kinetics of Ga films confined at Al₂O₃ grain boundaries. Teske *et al.*¹³ have found a possible new phase θ -Ga and mentioned that it was necessary to combine Ga with other kinds of excessive small size particles in order to get more Ga particles with θ -phase. In addition, some researchers have studied Ga confined in porous glass.^{17,18} From all the reference works above, we can know that metastable and stable Ga phases are related to undercooling small Ga droplets and bulk Ga, respectively, which indicates that the phase structures seem to be dependent on size of Ga particles.

In this report, Ga particles with gradient size distribution were dispersed in poly(methyl methacrylate) (PMMA) matrix with a size of 75 × 45 × 2 mm³ by means of ultrasonic vibration and sedimentation method. These Ga/PMMA composites have been sliced at different distance from the bottom of the same sample and the distance from the bottom of sample was defined as D . The evaluation of the Ga particle size and its distribution was carried out with transmission electron microscopy (TEM), and the statistics was carried out with 345 particles for each sample. TEM observation showed that for the samples obtained at the position $D=0, 9, 10, 11, 39$ mm, the average size of the Ga particles was about 0.8–1, 0.8–0.6, 0.6–0.3, 0.2–0.1, and below 0.1 μm , respectively.

Differential scanning calorimeter (DSC) experiments were carried out with a Perkin-Elmer Pyris Diamond DSC equipment. The DSC and TEM measurements are carried out on the same samples with corresponding positions. The same measurement procedure for each sample was done as follows. The sample was first cooled down to –150 °C with a cooling rate of 80 °C/min and kept at –150 °C for 10 minutes to allow the solidification of all the Ga droplets, then measured the heat flow up to 60 °C with a scanning rate of 20 °C/min.

As a comparison, the DSC measurement of bulk Ga was also conducted and only one single endothermic peak with onset temperature of 30 °C was observed, which is in agreement with the melting point of α -Ga reported in the literature.⁶

Figure 1 shows the DSC heating trace of Ga dispersed in PMMA for the samples taken at the position $D=0, 9, 10, 11, 39$ mm. Four endothermic peaks can be observed at onset temperature of 30 °C, –16 °C, –19 °C, and –36 °C, but not all of these four peaks appear at each curve. These four peaks were attributed to the melting endotherm of α -, β -, δ -, and γ -phases of Ga, respectively.⁶ Compared with the result obtained in bulk Ga, it can be found that the metastable phases only appear in small Ga particles.

In order to reveal the relation between the increase and the decline of those four phases, Eq. (1) was used to evaluate the weight percentage of relative quantities of the various phases,

$$M_p \% = \frac{\frac{A_p}{\Delta H_p}}{\frac{A_\alpha}{\Delta H_\alpha} + \frac{A_\beta}{\Delta H_\beta} + \frac{A_\gamma}{\Delta H_\gamma} + \frac{A_\delta}{\Delta H_\delta}} \times 100 \% , \quad (1)$$

where p denotes α, β, γ , and δ , M_p is the weight of each phase, ΔH_p is the latent heat value obtainable from Ref. 6 and A_p is the areas under the peaks of the various phases. From Eq. (1) the relations between the relative weight percentage of various phases and D can be obtained (Fig. 2).

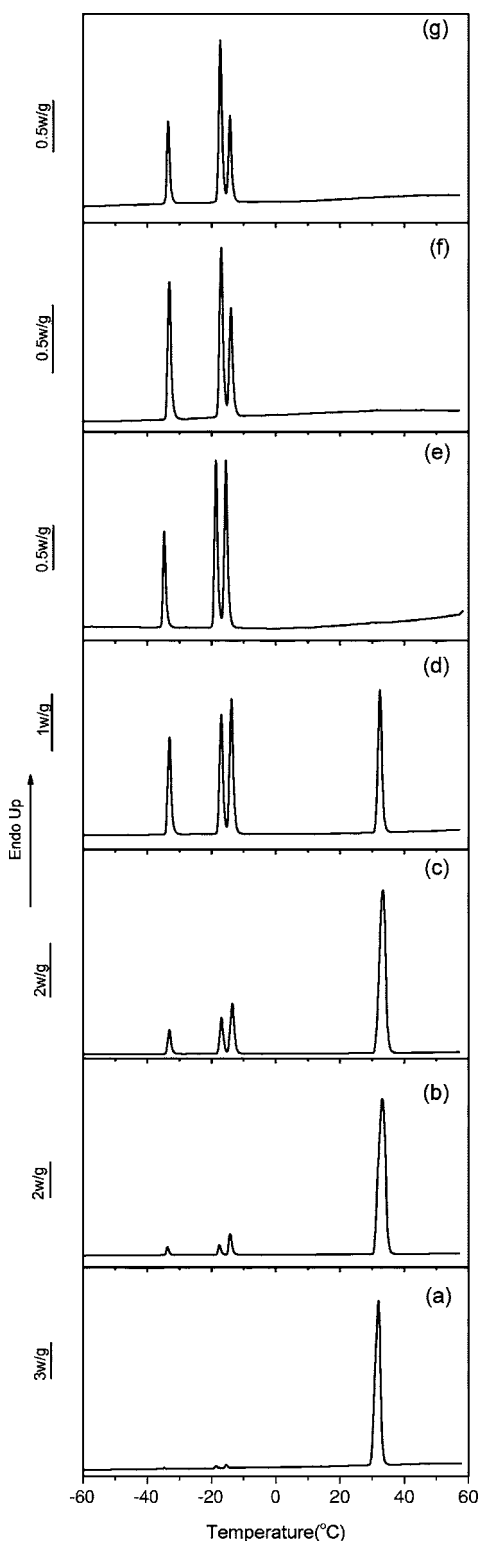


FIG. 1. DSC trace of heating measurement for Ga/PMMA samples with $D=0$ (a), 6 (b), 9 (c), 10 (d), 11 (e), 24 (f), and 39 mm (g), and the average diameters of particles are in the range of (a) $\geq 0.8 \mu\text{m}$, (c) $0.8\text{--}0.6 \mu\text{m}$, (d) $0.6\text{--}0.3 \mu\text{m}$, and (g) $\leq 0.3 \mu\text{m}$, respectively. The scanning rate is $20^\circ\text{C}/\text{min}$. D is defined as the distance to bottom of the sample and vertical axis is heat flow.

From Figs. 1 and 2 it can be found that the weight percentage of α -Ga decreased sharply with the increase in D ,

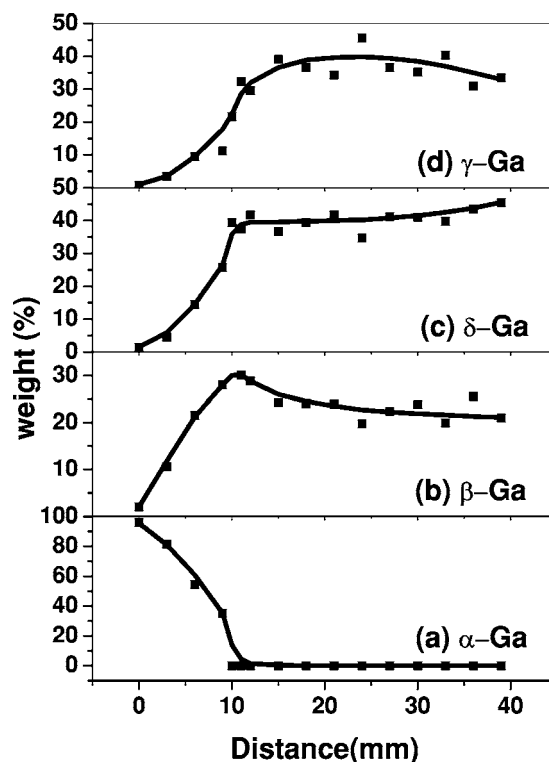


FIG. 2. The relative weight percentage of various phases of Ga dispersed in PMMA matrix with the different distance to bottom (D). The horizontal axes are the distance to bottom and the vertical axis is the relative weight percentage of various phases. (a), (b), (c), and (d) denote the α -Ga, β -Ga, δ -Ga, and γ -Ga, respectively.

which revealed that the stable phase structure α -Ga could easily form as the size of Ga particles is large or even bulk. For β - and γ -Ga, they have similar tendency, that is, the quantities of β - and γ -Ga increase rapidly to a maximum value and then decrease slowly, and the maximum percentage was found to locate at D of about 10 and 25 mm, respectively, which shows that the possibility of forming β -Ga and γ -Ga phases is higher when particle size is in the range of $0.8\text{--}0.6 \mu\text{m}$ and $0.6\text{--}0.3 \mu\text{m}$, respectively. For δ -Ga, there is a gradual increase in weight percentage from a negligible quantity at the bottom to $40\text{--}50 \text{ wt. } \%$ at the top, which indicates that the possibility of forming this phase structure is much higher in small particles with size below $0.3 \mu\text{m}$.

It has been reported that gallium can easily form two stable phases, Ga(II) with a tetragonally distorted fcc structure and Ga(III) with a tetragonally distorted bcc structure at a high pressure (about $11.4\text{--}26.9 \text{ Kba}$).^{6,8} As is well known, the volume of PMMA will shrink during the polymerization process, which will induce internal pressure on the Ga particles. Therefore, to solve the problem whether the relation between the particle size and phase structure is intrinsic or not, it is necessary to eliminate the effect of pressure. At the same time, the influence of boundary effect on the phase structure should be checked. Thus, Ga was also dispersed in the silicon-oil (freezing point about -60°C) by means of ultrasonic vibration method. In this case, the effect of pressure can be negligible owing to the liquid state of silicon oil in the Ga phase transition temperature region. Meanwhile,

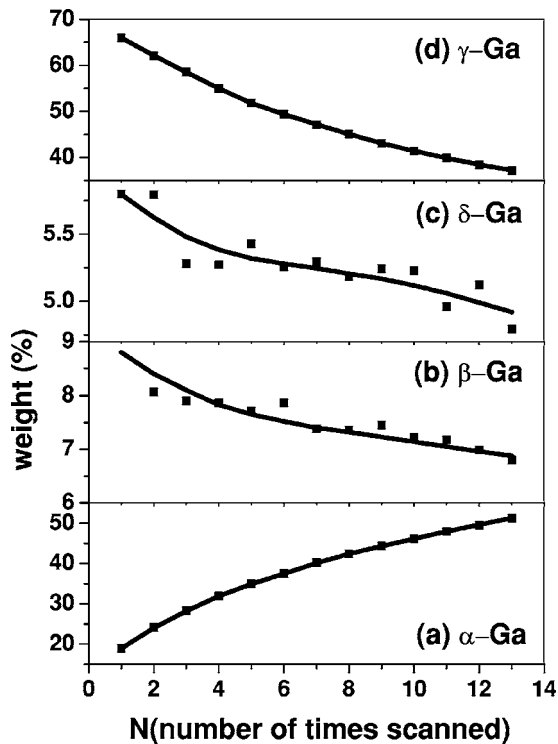


FIG. 3. The relations between the relative quantity of the various phases of Ga dispersed in silicon-oil matrix and the number of times scanned. (a) α -Ga, (b) β -Ga, (c) δ -Ga, and (d) γ -Ga. The horizontal axes are the number of times scanned and the vertical axes are the relevant percent of various phases.

the boundary between silicon oil and Ga should be different from that of between PMMA and Ga, so the boundary effect can be known. The DSC measurement for the Ga dispersed in silicon oil was conducted for many times with the same procedure and four melting peaks show the growth and the decline (or fluctuation) among them under the repeating measurements. Equation (1) was also used to evaluate the change of relative quantities of those four phases under the repeating measurement and the results are shown in Fig. 3. It can be seen that the relative weight of α -Ga (curve *a*) increases with the increase in the number of times scanned but that of other phases descends (curves *b*, *c*, and *d*). This fact means that with increasing the number of times scanned, the quantity of α -Ga increases and that of β -Ga, δ -Ga, and γ -Ga decreases.

The difference between the system of Ga/PMMA and that of Ga/silicone oil is as follows. Ga particles in PMMA are isolated and have no opportunity to collide, aggregate, and grow even as they melt; namely, the particle size keeps unchanged during the whole DSC measurement process because PMMA keeps in the solid state all the time. In Ga/silicone-oil sample, the Ga droplets may have a strong stochastic motion and collision possibility at the temperature above the melting points. The small droplets can coalesce to become bigger ones to reduce the surface energy.

The curves shown in Fig. 3 were measured with one sample, so it means that the phases may change from one to another. Increasing the resident time of above the melting point of Ga by increasing the number of times scanned may

increase the possibility of droplets aggregation; in other words, the number of small droplets decreases and the number of bigger droplets increases. From Fig. 3, we can see that the particle sizes have a relation to the Ga phases. The bigger particles tend to form α -phase and the smaller particles with different sizes tend to form β -, δ -, and γ -phases, respectively.

The boundary between PMMA and Ga is different from that between silicon oil and Ga because of the different chain structure of PMMA from that of silicon oil. In the Ga/silicone oil samples, the relation between particle sizes and phase structures is the same as that appears in the Ga/PMMA samples, which shows that the boundary does not have influence on the relationship between particle size and phases. All these results indicate that the relation between particle sizes and phases is an intrinsic phenomenon.

The phase selection principle, which generally categorizes as nucleation control and growth control, may account for the various phase formation in undercooled solidification of droplets with different sizes.^{19–21} Nucleation control plays a dominating role in the phase formation in an undercooled melt when competing stable and metastable phases share the same crystalline characters and have comparable interface kinetic coefficients. In terms of the four phases of Ga (α -, β -, γ -, and δ - phase) with the same orthorhombic crystalline and different cell parameters (*a*, *b*, and *c*), the nucleation control of the phase selection principle might be invoked to explain the relationship between droplet sizes and phases. The interfacial energies σ between crystal nuclei and liquid, and the supercooling ΔT are two very important parameters in the nucleation process. Based on the Turnbull-Fisher theory of homogeneous nucleation,²² the gram-atomic interfacial energies σ_g between liquid and nuclei and the gram-atomic heats of fusion ΔH_f have a relation: $\sigma_g/\Delta H_f \approx \text{constant}$. The σ_g of four phases of Ga can be calculated from the correlation $\sigma_g/\Delta H_f \approx 0.436$ (for Ga, the constant ≈ 0.436).^{6,22} $\sigma_\alpha = 8.35$ cal/g, $\sigma_\beta = 3.96$ cal/g, $\sigma_\gamma = 3.64$ cal/g, $\sigma_\delta = 2.71$ cal/g. The potential barrier of formation nuclei is sensitive to the change of interfacial energies σ , so the different σ_g of four phases would make great effect on the nuclei formation. On the other hand, as we know, the ratio of surface area to volume and surface energy are inversely proportional to the size of droplets, so the smaller droplets need more driving force that generates from undercooling than that of larger ones during the process of solidification, and different size gallium droplets show different undercooling characteristics. Undercooling is an important factor for many liquids in determining solidification microstructure development. Therefore the supercooling ΔT that is related with the different sizes of Ga droplets and the interfacial energies σ would deeply affect the structure and growth of the nuclei. This kind of nucleus in the gallium droplets with different sizes may dominate to grow up as the winning structure and solidify to different phases in the following growth process. This phenomenon that various metastable phases can be obtained at the different levels of undercooling has also been observed in the Pb-Sn alloy system.²³ Considering that the liquid and solid structures of Ga are more complicated than that of most metals, further investigations on the solidification process of Ga droplets are necessary to do in details.

In summary, we have found that the phase structures have a relation with volumes of gallium particles. From the DSC results, Ga particles with different sizes are corresponding to the different phases. There is a strong tendency to form the stable phase α -Ga, metastable phases β -Ga, γ -Ga, and δ -Ga, when the average diameters of particles are in the range of $\geq 0.8 \mu\text{m}$, $0.8\text{--}0.6 \mu\text{m}$, $0.6\text{--}0.3 \mu\text{m}$, and $\leq 0.3 \mu\text{m}$, respectively. The phase selection principle plays a very important

role in the solidification process of gallium droplets with different sizes.

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*Corresponding author. Electronic address: gtfci@issp.ac.cn

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