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Solid-liquid phase equilibria on the $GdBa_2Cu_3O_{7-\delta}$ stability phase diagram in low oxygen pressures (1 - 100 mTorr)

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Abstract— **We report the solid-liquid phase equilibria on the $GdBa_2Cu_3O_{7-\delta}$ (GdBCO) stability phase diagram in low oxygen pressures (PO_2) ranging from 1 to 100 mTorr. On the basis of the GdBCO stability phase diagram experimentally determined in low oxygen pressures, the isothermal sections of three different phase fields on log PO_2 vs. $1/T$ diagram were schematically constructed within the Gd_2O_3-Ba_2CuO_y-Cu_2O ternary system, and the solid-liquid phase equilibria in each phase field were described. The invariant points on the phase boundaries include the following three reactions; a pseudobinary peritectic reaction of GdBCO ↔ Gd_2O_3 + liquid (L_1), a ternary peritectic reaction of GdBCO ↔ Gd_2O_3 + $GdBa_6Cu_3O_y$ + liquid (L_2), and a monotectic reaction of L_1 ↔ $GdBa_6Cu_3O_y$ +L_2. A conspicuous feature of the solid-liquid phase equilibria in low PO_2 regime (1 - 100 mTorr) is that the GdBCO phase is decomposed into Gd_2O_3 + L_1 or Gd_2O_3 + $GdBa_6Cu_3O_y$ + L_2 rather than Gd_2BaCuO_5 + L well-known in high PO_2 like air.**

***Keywords*: GdBCO, solid-liquid phase equilibria, peritectic reaction, monotectic reaction, low oxygen pressure.**

1. INTRODUCTION

GdBCO has been known to exhibit higher J_c in magnetic fields in comparison with YBCO [1], and thus regarded as a strong alternative to YBCO for coated conductors (CCs). In such a reason, high-performance GdBCO CCs have been fabricated by PLD (pulsed laser deposition) [2,3] and RCE-DR (reactive co-evaporation by deposition and reaction) [4,5] processes. Especially, a newly developed RCE-DR process for high-performance GdBCO CCs is surely promising technology for the commercialization of CCs because it is a cost-effective high-throughput process.

Since a liquid phase is involved in the RCE-DR process during the growth of GdBCO films [5], it is very important to understand the solid-liquid phase equilibria around the GdBCO phase in low PO_2 regime not only for a fundamental understanding of the conversion mechanism from amorphous precursor films to GdBCO films but also for further optimization of the RCE-DR process. Although several papers on the equilibrium solid-liquid phase relations for the RE-Ba-Cu-O systems (RE = Y and rare earth elements) [6-9] have been reported, the solid-liquid phase equilibria around the GdBCO phase has never been reported in low PO_2 regime yet, which is the motivation of this study. In this report, on the basis of the GdBCO stability phase diagram experimentally determined in low oxygen pressures [10], we schematically constructed the isothermal sections of three different phase fields on log PO_2 vs. $1/T$ diagram in the Gd_2O_3-Ba_2CuO_y-Cu_2O ternary system, and discussed the solid-liquid phase equilibria around the GdBCO phase.

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2. THE PHASE BOUNDARIES CONSIDERED ON THE LOG PO_2 VERSUS $1/T(K^{-1})$ DIAGRAM

Fig. 1 shows the stability phase diagram of GdBCO in low PO_2 region ranging from 1 to 100 mTorr [10], including the stability lines of GdBCO and the phase boundary line between two different phase fields above the GdBCO stability line. The stability lines for the reduction of CuO ↔ Cu_2O and the reaction of Gd_2CuO_4 ↔ Gd_2O_3 + Cu_2O, reported by W. Zhang and K. Osamura [11], are drawn in Fig. 1. The stability line for the reaction of $BaCuO_2$ ↔ Ba_2CuO_y + $BaCu_2O_2$, reported by T. B. Lindemer and E. D. Specht [12], is also drawn in this figure.

On the log PO_2 vs. $1/T$ diagram in Fig. 1, we selected eight points from "*a*" to "*h*" for the schematic construction of the isothermal sections representing the solid-liquid phase relations. One can see that the Cu_2O, Ba_2CuO_y and $BaCu_2O_2$ phases are stable around eight points while the stability line of Gd_2CuO_4 lies across the stability line of GdBCO. Therefore, the stability of Gd_2CuO_4 should be taken into account when we construct the isothermal sections.

It is known that a ternary eutectic point in the Y_2O_3-BaO-CuO system is very close to the $BaCu_2O_2$ composition [6,8]. Similarly, if we assume that the ternary eutectic point in the Gd_2O_3-BaO-CuO system is also located at the point close to the $BaCu_2O_2$ composition, a ternary liquid phase should form near the ternary eutectic point on the phase diagram. In this case, the solid phases compatible with the ternary liquid phase are Gd_2O_3,

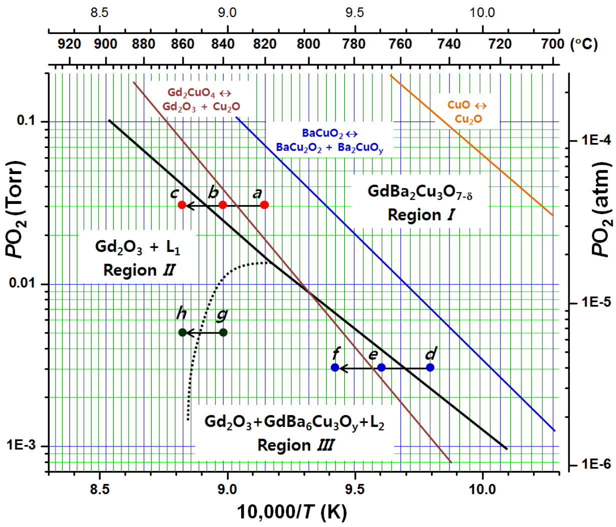

Fig. 1. The stability phase diagram of GdBCO in low PO_2 ranging from 1 to 100 mTorr [10]. The stability lines of $CuO \leftrightarrow Cu_2O$ [11], $BaCuO_2 \leftrightarrow BaCu_2O_2 + Ba_2CuO_y$ [12], and $Gd_2CuO_4 \leftrightarrow Gd_2O_3 + Cu_2O$ [11] are also represented.

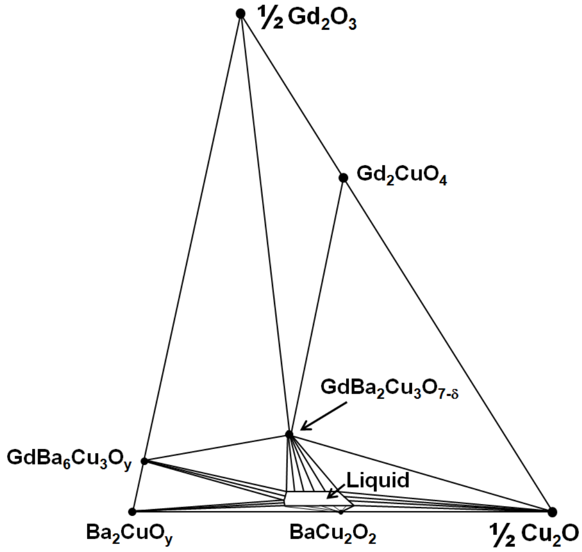

Fig. 2. Isothermal section of the Gd_2O_3-Ba_2CuO_y-Cu_2O system. The T - PO_2 condition is given at the point "*a*" and "*d*" in Fig. 1.

$GdBa_6Cu_3O_y$, Gd_2CuO_4, Ba_2CuO_y, $BaCu_2O_2$, Cu_2O, and GdBCO. Since the ternary liquid phase is incompatible with the compounds having the compositions of $Ba/Cu > 2$, it is sufficient to consider the isothermal sections within the Gd_2O_3-Ba_2CuO_y-Cu_2O ternary system for understanding the solid-liquid phase relations around the GdBCO phase.

3. ISOTHERMAL SECTION IN Gd_2O_3-Ba_2CuO_y-Cu_2O SYSTEM

Based on the stability phase diagram of GdBCO in low oxygen pressures in Fig. 1, we schematically construct the isothermal sections at the specific T - PO_2 conditions (i.e., "*a*" to "*h*" points) in order to clearly represent the solid-liquid phase equilibria around the GdBCO phase. As previously mentioned, the stability of Gd_2CuO_4 is also considered at each phase field for the construction of the isothermal sections. The isothermal sections at eight points in the Gd_2O_3-Ba_2CuO_y-Cu_2O system are illustrated in this section. We mainly focus on the variation in the isothermal sections across the invariant points including the pseudobinary peritectic reaction of $GdBCO \leftrightarrow Gd_2O_3 + L_1$, the ternary peritectic reaction of $GdBCO \leftrightarrow Gd_2O_3 + GdBa_6Cu_3O_y + L_2$, and the monotectic reaction of $L_1 \leftrightarrow GdBa_6Cu_3O_y + L_2$.

3.1. Pseudobinary peritectic reaction: $GdBCO \leftrightarrow Gd_2O_3 + L_1$

In the PO_2 region ranging from ~10 to 100 mTorr, GdBCO is decomposed into $Gd_2O_3 + L_1$ by the pseudobinary peritectic reaction. At the condition of the point "*a*" in Fig. 1, both GdBCO and Gd_2CuO_4 are stable, and the ternary liquid phase is compatible with GdBCO, $GdBa_6Cu_3O_y$, Ba_2CuO_y, $BaCu_2O_2$, and Cu_2O as shown in Fig. 2. It is noteworthy that since a binary liquid of BaO-CuO cannot exist in this condition and $BaCuO_2$ is unstable, $BaCu_2O_2$ near the ternary liquid phase should exist as a stable solid phase.

At the condition represented by the point "*b*" in Fig. 1, Gd_2CuO_4 is no more stable, and thus it is represented by a hollow circle as shown in Fig. 3. In comparison with Fig. 2, the ternary liquid region becomes wider because temperature is higher at the same PO_2.

At the point "*c*" above the GdBCO stability line in Fig. 1, GdBCO becomes unstable as represented by the hollow circle. Instead, Gd_2O_3 and the ternary liquid phase are stable as shown in Fig. 4. The area of the liquid region becomes much wider compared with that in Fig. 3. The $BaCu_2O_2$ phase also exists as the stable solid phase compatible with the ternary liquid phase.

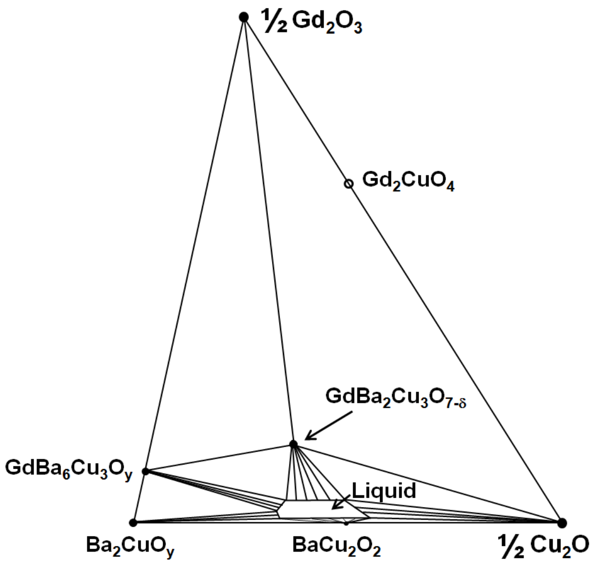

Fig. 3. Isothermal section of the Gd_2O_3-Ba_2CuO_y-Cu_2O system. The T - PO_2 condition is given at the point "*b*" in Fig. 1.

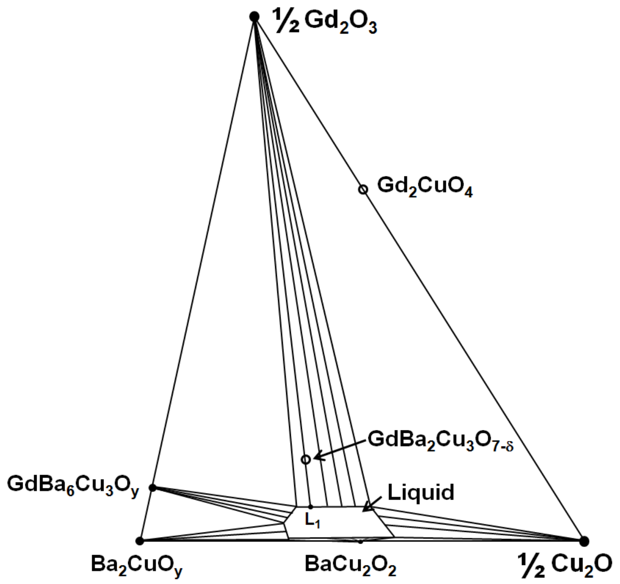

Fig. 4. Isothermal section of the Gd_2O_3-Ba_2CuO_y-Cu_2O system. The *T* - PO_2 conditions are given at the points "*c*" and "*h*" in Fig. 1.

3.2. Ternary peritectic reaction: GdBCO ↔ Gd_2O_3 + $GdBa_6Cu_3O_y$ + L_2

In the PO_2 region of ranging from 1 to ~10 mTorr, GdBCO is decomposed into Gd_2O_3 + $GdBa_6Cu_3O_y$ + L_2 by the ternary peritectic reaction. The isothermal section of the point "*d*" in Fig. 1 is similar to that of point "*a*", in which both GdBCO and Gd_2CuO_4 are stable. However, it is uncertain how the area of liquid region at the point "*d"* will be changed in comparison with that at the point "*a*" since the effects of lowering temperature and lowering oxygen pressure on the stability of the liquid phase are considered to be opposite each other [13]. At higher temperature (the point "*e*" in Fig. 1), GdBCO is unstable while Gd_2CuO_4 is still stable. At this condition, Gd_2CuO_4 becomes compatible with the liquid phase as shown in Fig. 5. The GdBCO composition locates within the composition triangle composed of Gd_2O_3, $GdBa_6Cu_3O_y$, and L_2, which indicates the ternary peritectic reaction of GdBCO ↔ Gd_2O_3 + $GdBa_6Cu_3O_y$ + L_2. At much higher temperature (the point "*f*" in Fig. 1), Gd_2CuO_4 becomes unstable, and the liquid region should be enlarged as shown in Fig. 6.

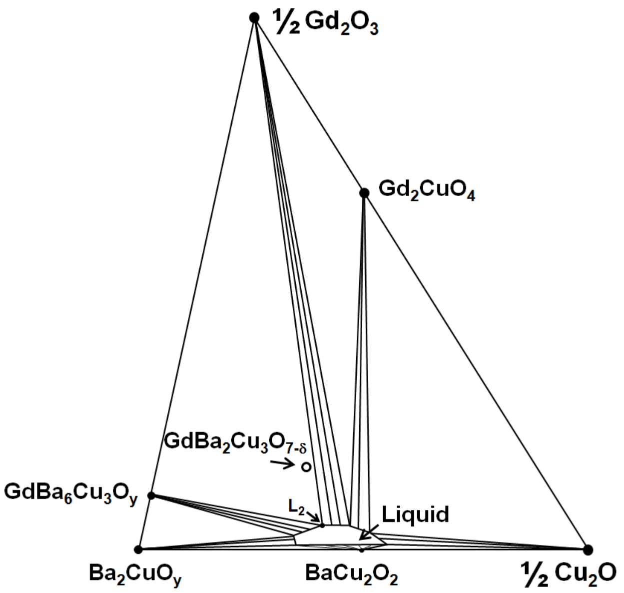

Fig. 5. Isothermal section of the Gd_2O_3-Ba_2CuO_y-Cu_2O system. The *T* - PO_2 condition is given at the point "*e*" in Fig. 1.

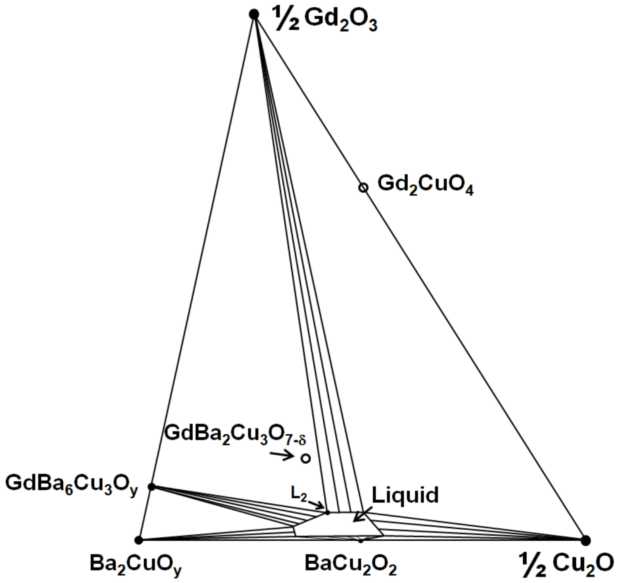

Fig. 6. Isothermal section of the Gd_2O_3-Ba_2CuO_y-Cu_2O system. The *T* - PO_2 conditions are given at the points "*f*" and "*g*" in Fig. 1.

3.3. Monotectic reaction: L_1 ↔ $GdBa_6Cu_3O_y$ + L_2

In the PO_2 region of ranging from 1 to ~10 mTorr, the monotectic reaction of L_1 ↔ $GdBa_6Cu_3O_y$ +L_2 occurs. Although the area of the ternary liquid phase is not identical, the isothermal section of the point "*g*" is considered to be similar to that of the point "*f*" as shown in Fig. 6. At much high temperature, the liquid phase region is enlarged so that the composition point of GdBCO lies on the tie-line between Gd_2O_3 and liquid phase (Fig. 4), indicating the monotectic reaction of L_1 ↔ $GdBa_6Cu_3O_y$ +L_2.

4. SUMMARY

We report the solid-liquid phase equilibria on the GdBCO stability phase diagram in low PO_2 regime ranging from 1 to 100 mTorr. Three invariant reactions, including a pseudobinary peritectic reaction of GdBCO ↔ Gd_2O_3 + liquid (L_1), a ternary peritectic reaction of GdBCO ↔ Gd_2O_3 + $GdBa_6Cu_3O_y$ + liquid (L_2), and a monotectic reaction of L_1 ↔ $GdBa_6Cu_3O_y$ +L_2, could be demonstrated by schematically constructing the isothermal sections at various *T*-PO_2 conditions. The solid-liquid phase equilibria around the GdBCO phase could be understood on the Gd_2O_3-Ba_2CuO_y-Cu_2O system. Interestingly, above the decomposition point of GdBCO, Gd_2O_3 is compatible with the liquid phase or $GdBa_6Cu_3O_y$ + liquid phases in the PO_2 region of 1 - 100 mTorr while Gd_2BaCuO_5 is compatible with the liquid phase in high oxygen pressure like air.

REFERENCES

[1] M. Murakami, N. Sakai, T. Higuchi, and S. I. Yoo, "Melt-processed light rare earth element-Ba-Cu-O," *Superconductor Science & Technology,* vol. 9, pp. 1015-1032, Dec. 1996.

[2] H. Kutami, T. Hayashida, S. Hanyu, C. Tashita, M. Igarashi, H. Fuji, Y. Hanada, K. Kakimoto, Y. Iijima, and T. Saitoh, "Progress in research and development on long length coated conductors in Fujikura," *Physica C-Superconductivity and Its Applications,* vol. 469, pp. 1290-1293, Aug-Oct. 2009.

[3] K. P. Ko, R. K. Ko, S. Y. Lee, H. K. Kim, S. H. Moon, S. S. Oh, and S. I. Yoo, "$GdBa_2Cu_3O_{7-\delta}$ Coated Conductor on $BaZrO_3$-Buffered IBAD-MgO Template," *IEEE Transactions on Applied Superconductivity,* vol. 19, pp. 3427-3430, Jun. 2009.

[4] S.H. Moon. "Advanced fast RCE process for REBCO coated conductor" Invited talk in 23rd International Symposium on Superconductivity, Nov. 1-3, 2010, Tsukuba, Japan.

[5] S.I. Yoo, "The high rate conversion mechanism of GdBCO coated conductors by a new high throughput process, RCE-DR," Invited talk in 2011 MRS spring meeting, Apr. 25-29, 2011, San Fransisco, USA.

[6] T. Aselage and K. Keefer, "Liquidus relations in Y-Ba-Cu oxides," *Journal of Materials Research,* vol. 3, pp. 1279-1291, Nov-Dec. 1988.

[7] J. L. MacManus-Driscoll, "Materials chemistry and thermodynamics of $REBa_2Cu_3O_{7-x}$," *Advanced Materials,* vol. 9, pp. 457-&, May 1997.

[8] W. Wong-Ng and L. P. Cook, "Liquidus diagram of the Ba-Y-Cu-O system in the vicinity of the $Ba_2YCu_3O_{6+x}$ phase field," *Journal of Research of the National Institute of Standards and Technology,* vol. 103, pp. 379-403, Jul-Aug. 1998.

[9] M. Kuznetsov, C. Krauns, Y. Nakamura, T. Izumi, and Y. Shiohara, "Ternary phase diagram of $SmO_{1.5}$-BaO-CuO_y system for melt processing," *Physica C,* vol. 357, pp. 1068-1072, Aug. 2001.

[10] J.W. Lee, S. M. Choi, J. H. Lee, S. H. Moon, and S. I. Yoo, to be submitted.

[11] W. Zhang and K. Osamura, "Oxygen-pressure dependence of Cu_2O-CuO-Gd_2O_3 phase-diagram," *Metallurgical Transactions B-Process Metallurgy,* vol. 22, pp. 705-710, Oct. 1991.

[12] T. B. Lindemer and E. D. Specht, "The BaO-Cu-CuO system - solid-liquid equilibria and thermodynamics of $BaCuO_2$ and $BaCu_2O_2$," *Physica C,* vol. 255, pp. 81-94, Dec. 1995.

[13] J. K. R. Weber, P. C. Nordine, K. C. Goretta, and R. B. Poeppel, "Effects of oxygen-pressure on the structure of Y-Ba-Cu-O materials formed by containerless melting and solidification," *Journal of Materials Research,* vol. 9, pp. 1657-1660, Jul. 1994.