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(3) Title: Synthesis and characterization of (Pb,Cu)Sr_2(*RE*,Ca)Cu_2O_z ($z≈7$; *RE*: Sm, Eu or Gd)

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(6) Abstract

By replacing Y with several kinds of rare-earth elements (*RE*'s), new members of high-temperature superconductor related cuprates, (Pb,Cu)Sr_2(*RE*,Ca)Cu_2O_z ($z≈7$, *RE*: Sm, Eu and Gd), are successfully prepared in a single-phase form. Chemical formula of these compounds proves to be $(Pb_{(1+x)/2}Cu_{(1-x)/2})Sr_2(RE_{1-x}Ca_x)Cu_2O_z$, which is completely same as that of (Pb,Cu)Sr_2(Y,Ca)Cu_2O_z. Single phase samples are obtained for x=0~0.5 in the cases of *RE*=Sm and Eu while in the case of *RE*=Gd, those are obtained for x values up to ~0.4. Solubility of Ca in the *RE* site varies in accordance with *RE* species and seems to strongly depend on its ionic radius, *i.e.*, large RE^{3+} results in large solubility. In addition, formation process of the present compounds is discussed based on the results of X-ray diffractometry, differential thermal analysis and scanning electron microscopy.

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1. Introduction

$(Pb,Cu)Sr_2(Y,Ca)Cu_2O_z$ ($z \approx 7$) ((Pb,Cu)-"1-2-1-2") [1-4] is known as one of high temperature superconducting cuprates (HTSC's) and to be isomorphous to $TlSr_2CaCu_2O_z$ ($z \approx 7$) having a so-called "1-2-1-2" type tetragonal crystallographic structure with a space group of P4/mmm. It characteristically contains (Pb,Cu)O monolayer in the structure. Some features of this compound have been reported by one of the present authors (TM) and his colleagues [4,5], that is, it forms in an oxidizing atmosphere and then the valence state of Pb is thought to be +4 being different from the case of $Pb_2Sr_2(Y,Ca)Cu_3O_8$ [6] in which the valence state of Pb is +2. Moreover, it exhibits large oxygen nonstoichiometry, *i.e.*, it tends to contain excess oxygen in the (Pb,Cu)O monolayer ($z=7+\delta$; $\delta=0\sim0.1$). The chemical composition of the (Pb,Cu)-"1-2-1-2" is described as a formula, $(Pb_{(1+x)/2}Cu_{(1-x)/2})Sr_2(Y_{1-x}Ca_x)Cu_2O_z$ ($x=0\sim0.4$) and an end member ($x=0.5$) was $(Pb_{0.5}Cu_{0.5})Sr_2YCu_2O_z$. Superconductivity appeared at $x>\sim0.25$ only when the excess oxygen is removed ($\delta \approx 0$). Critical temperature (T_c) raises with increasing x up to 52 K for $x=0.4$, and higher T_c of 72 K is obtained by partial substitution of Sr by Ca [7]. This seems to show that solubility of Ca in Y site plays an important role for determining T_c in the (Pb,Cu)-"1-2-1-2". In this study, other types of (Pb,Cu)-"1-2-1-2" were synthesized by replacing Y with other rare-earth elements (*RE*'s) such as Sm, Eu and Gd in order to increase solubility of Ca in the *RE* site. The results are discussed mainly based on the ionic radius of the rare-earth elements.

Additionally, $(Pb,Cu)Sr_2(Y,Ca)Cu_2O_z$ is featured by its remarkably rapid phase-formation. It has been reported that only 1 h firing at temperatures around 1000˚C results in highly crystallized samples [4, 8]. On this view point, phase evolution of the present $(Pb,Cu)Sr_2(RE,Ca)Cu_2O_z$ is also discussed.

2. Experimental

Samples of $(Pb,Cu)Sr_2(RE,Ca)Cu_2O_z$ (*RE*: Sm, Eu or Gd) were prepared by a solid-state reaction of commercial reagents of PbO, $SrCO_3$, RE_2O_3 (Sm_2O_3, Eu_2O_3 or Gd_2O_3), $CaCO_3$ and CuO with 3N-up purity. These powders were mixed according to nominal metallic compositions of $(Pb_{(1+x)/2}Cu_{(1-x)/2})Sr_2(RE_{1-x}Ca_x)Cu_2O_z$ (x=0~0.5) using an agate mortar. The obtained powder mixtures were calcined at 850˚C for 10 h in a flowing 21 vol.% O_2/N_2 gas mixture. The calcined powders were again pulverized and well mixed, and then pressed into disk-shaped pellets of 5 mm in diameter and 2 mm in thickness. Finally, these pellets were sintered at 950~970˚C for 1 h in a flowing 21 vol.% O_2/N_2 gas mixture. The both heating and cooling rates were set at 300˚C/h.

X-ray diffractometry (XRD) using CuKα radiation was carried out for the calcined powders and finally obtained black-colored ceramics samples for the purpose of phase identification and structural analysis. For the case of *RE*=Eu, differential thermal analysis (DTA) was carried out in a flowing air for the calcined powders of x=0 and 0.1 at elevated temperatures up to 950˚C (heating rate: 300˚C/h). Fractured-surface morphology of sintered samples with *RE*=Sm and *RE*=Gd was observed by using a scanning electron microscope (SEM).

3. Results and discussion

3-1. Synthesis of single-phase $(Pb,Cu)Sr_2(RE,Ca)Cu_2O_z$

Figure 1(a), (b) and (c) respectively show XRD profiles for samples with *RE* species of Sm, Eu or Gd finally sintered at temperatures around 960˚C. Almost all of the diffraction lines for each profile could be indexed according to the previously reported

“1-2-1-2” structure [2]. Formation of (nearly) single-phase sample was confirmed at x=0~0.5 for *RE*=Sm and *RE*=Eu, and at x=0~0.3 for *RE*=Gd. For the profiles for samples with *RE*=Gd, additional diffraction lines derived from Ca_2PbO_4 clearly appeared for x=0.4 or 0.5. Lattice constants, a and c, roughly estimated using 2θ values of (200) and (006) diffraction lines for present samples with *RE*=Sm, *RE*=Eu and *RE*=Gd are shown in Fig. 2. For all types of (Pb,Cu)-“1-2-1-2”, values of c systematically increase with increasing x. On the other hand, values of a keep constant and do not vary with x. This behaviour is quite similar to that reported for $(Pb,Cu)Sr_2(Y,Ca)Cu_2O_z$ [4]. These results show that chemical composition of the present (Pb,Cu)-“1-2-1-2” with *RE*=Sm, Eu or Gd is described as $(Pb_{(1+x)/2}Cu_{(1-x)/2})Sr_2(RE_{1-x}Ca_x)Cu_2O_z$ within the limitation of Ca solubility in the same way as $(Pb,Cu)Sr_2(Y,Ca)Cu_2O_z$.

A coordination number (*CN*) of the *RE* site of the (Pb,Cu)-"1-2-1-2" is 8 and the valence state of the *RE* ion is 3+. Solubility of Ca^{2+} in the *RE* site is expected to be strongly affected by ionic size of RE^{3+}. Ionic radius of Ca^{2+} is 0.112 nm for *CN*=8 [9] and that for the present RE^{3+}’s of Sm, Eu and Gd is 0.1079, 0.1066 and 0.1053 nm, respectively [9] . Ca^{2+} is larger than most of RE^{3+}, and difference in size between Ca^{2+} and present RE^{3+}’s is the smallest for Sm^{3+} and the largest for Gd^{3+}. The origin of the fact that the solubility of Ca for $(Pb,Cu)Sr_2(Sm,Ca)Cu_2O_z$ and $(Pb,Cu)Sr_2(Eu,Ca)Cu_2O_z$ is larger than that for $(Pb,Cu)Sr_2(Gd,Ca)Cu_2O_z$ (and $(Pb,Cu)Sr_2(Y,Ca)Cu_2O_z$; ionic radius of Y^{3+} is 0.1019 nm for *CN*=8) can be attributed to this.

T_c of $(Pb,Cu)Sr_2(Y,Ca)Cu_2O_z$ was reported to be strongly dependent on Ca content in the Y site, and that in $(Pb,Cu)Sr_2(Y,Ca)Cu_2O_z$ was reported to be ~0.3 [4]. Since present results showed that it can be increased by using larger RE^{3+}, such as Nd^{3+} instead of Y^{3+}, it is hopeful that T_c of the (Pb,Cu)-"1-2-1-2" can be raised to a higher temperature than 52 K which is the highest T_c reported so far for (Pb,Cu)Sr_2(Y,Ca)Cu_2O_z [4]. Evaluation of superconductivity of the present samples are now in progress and will be published elsewhere.

3-2. Phase evolution of (Pb,Cu)Sr_2(*RE*,Ca)Cu_2O_z

As mentioned before, remarkably rapid phase-formation is one of the most characteristic feature of the (Pb,Cu)-"1-2-1-2". Therefore, DTA for calcined powders of *RE*=Eu with x=0 and 0.1 was carried out up to 950˚C in order to investigate the formation process, and the results are given in Fig. 3. In both curves, clear endothermic peak was observed at ~925˚C for x=0 and at ~900˚C for x=0.1 which may be attributed to an existence of partially-melted state at somewhat lower temperatures than the final sintering temperature of ~950˚C at which (Pb,Cu)Sr_2(Eu,Ca)Cu_2O_z formed. Possible component of the liquid was supposed to be, for example, Sr(Ca)-Pb-O and/or Cu-Pb-O because it must contain Pb which formed low-melting-point phase(s). Appearance of similar endothermic peaks has been reported for the formation process of (Pb,Cu)Sr_2(Y,Ca)Cu_2O_z [8].

XRD measurements gave a result that, for the calcined powder, the formation-reaction of (Pb,Cu)Sr_2(Eu,Ca)Cu_2O_z had not been fully completed. Therefore, sintering process used in the present experiments was a reactive sintering. Since phase evolution in the reactive sintering process was quite enhanced when a liquid phase coexisted, this remarkably rapid formation of (Pb/Cu)-"1-2-1-2" might be a conclusion of the existence of partially melted state, *i.e.*, similarly as the case of the formation process of some Bi-containing HTSC's [10-12], partially melted state may play a crucial role for phase formation of the (Pb/Cu)-"1-2-1-2". As shown in Fig. 4 ((a) *RE*=Sm and x=0, (b)

RE=Gd and x=0), this was also suggested by the results of SEM observation for the fractured surface. Surface morphology shown in these photographs seemed to suggest that some kind of liquid phase participated in the formation reaction of the (Pb/Cu)-"1-2-1-2".

4. Conclusion

Chemical composition of $(Pb,Cu)Sr_2(RE,Ca)Cu_2O_z$ (RE: Sm, Eu or Gd) proved to be described as $(Pb_{(1+x)/2}Cu_{(1-x)/2})Sr_2(RE_{1-x}Ca_x)Cu_2O_z$. Single-phase samples were successfully prepared by a solid-state reaction method for x=0~0.5 for both *RE*=Sm and *RE*=Eu and for x=0~0.3 for *RE*=Gd. It was suggested that solubility of Ca in the *RE* site was strongly affected by ionic radius of RE^{3+}.

The results of DTA and SEM observation seemed to show that there appeared a partially melted state at temperatures somewhat lower than the formation temperatures around 960˚C of the (Pb,Cu)-"1-2-1-2", which seemed to play an important role for its phase evolution.

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Figure captions

Fig. 1. XRD profiles for samples with nominal compositions of $(Pb_{(1+x)/2}Cu_{(1-x)/2})Sr_2(RE_{1-x}Ca_x)Cu_2O_z$; (a) *RE*=Sm, (b) *RE*=Eu and (c) *RE*=Gd.

Fig. 2. Lattice constants, *a* and *c*, for samples of $(Pb,Cu)Sr_2(RE,Ca)Cu_2O_z$ (*RE*=Sm, Eu and Gd).

Fig. 3. DTA curves for samples of *RE*=Eu with x=0 and 0.1. Arrows indicate endothermic peaks near at 925˚C and 900˚C respectively for x=0 and for x=0.1. Detail in the vicinity of the endothermic peaks is shown in the inset.

Fig. 4. SEM photographs of fractured surface of sintered samples of $(Pb,Cu)Sr_2RECu_2O_z$ (x=0); (a) *RE*=Sm and (b) *RE*=Gd.

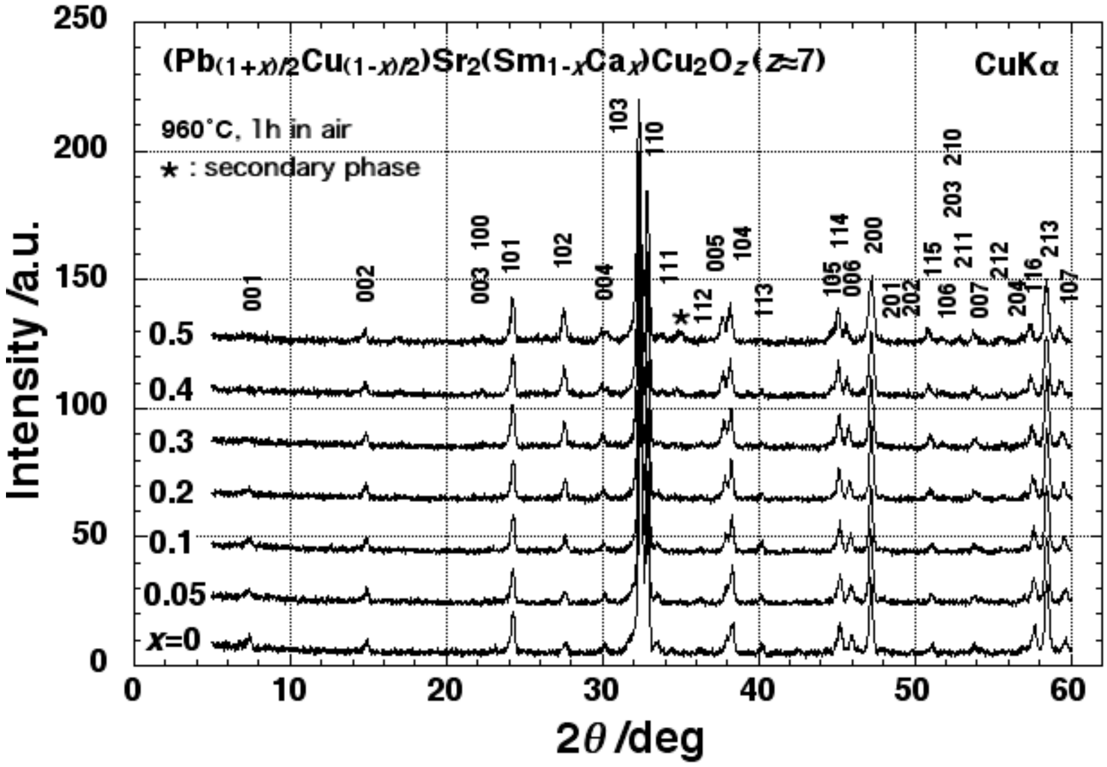

Fig. 1(a) T. Maeda *et al*.

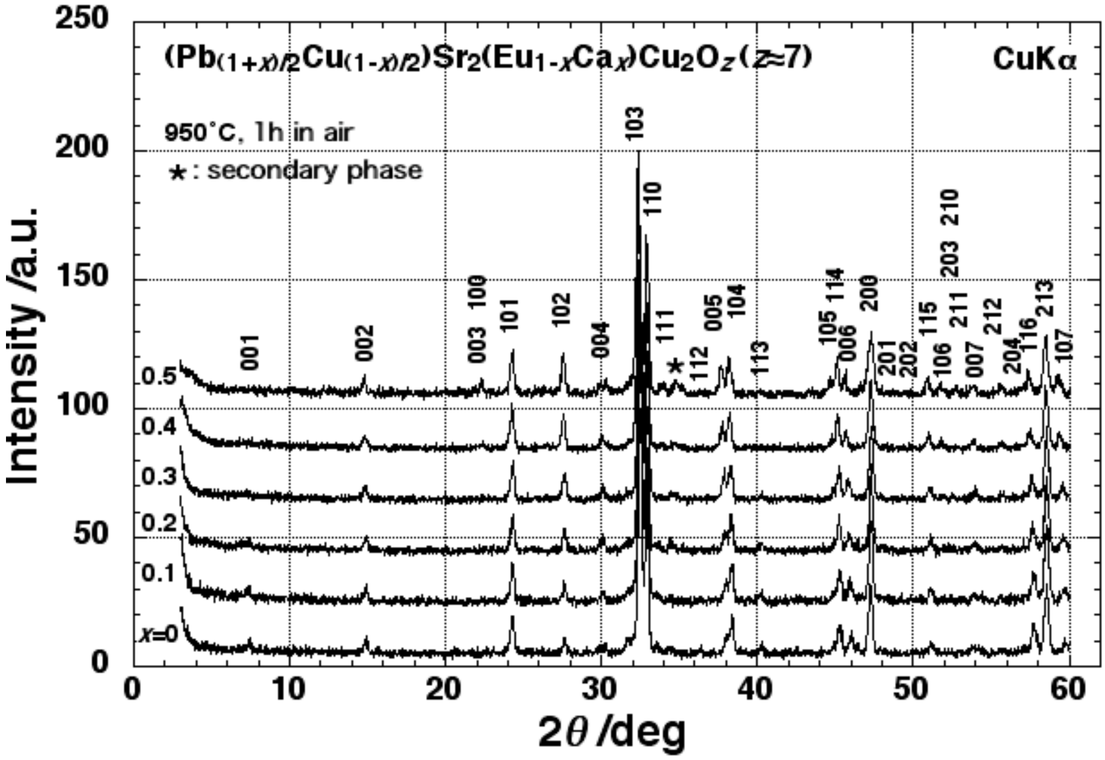

Fig. 1(b)   T. Maeda *et al*.

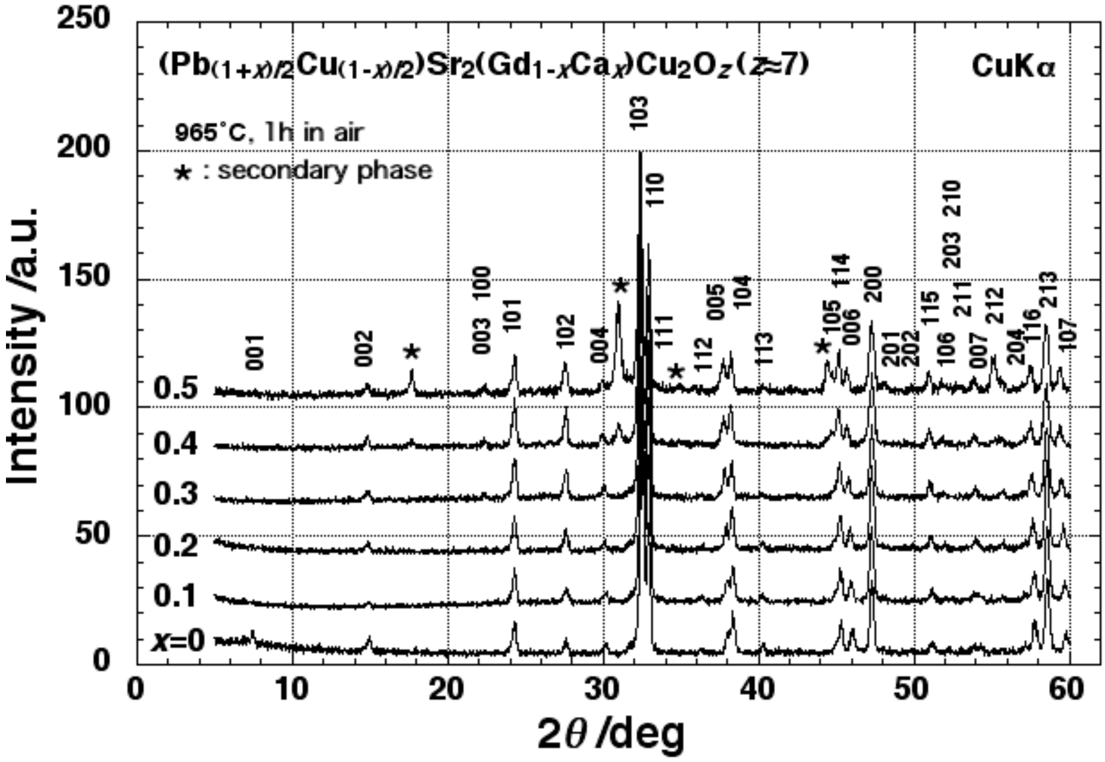

Fig. 1(c)   T. Maeda *et al*.

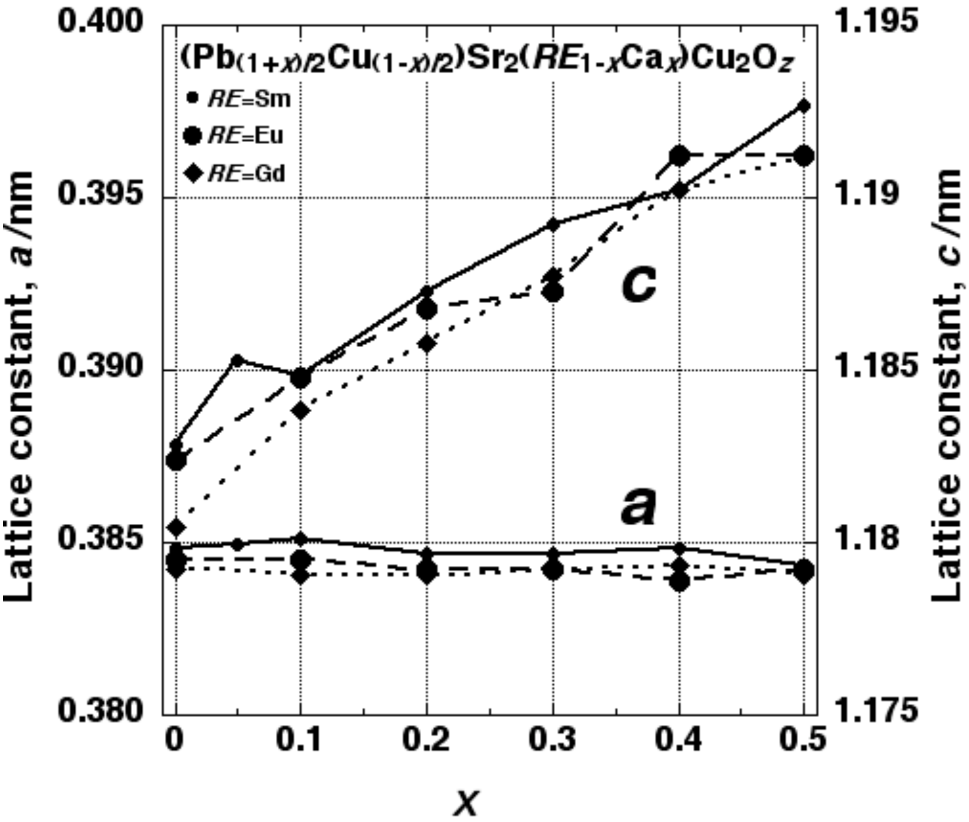

Fig. 2 T. Maeda *et al*.

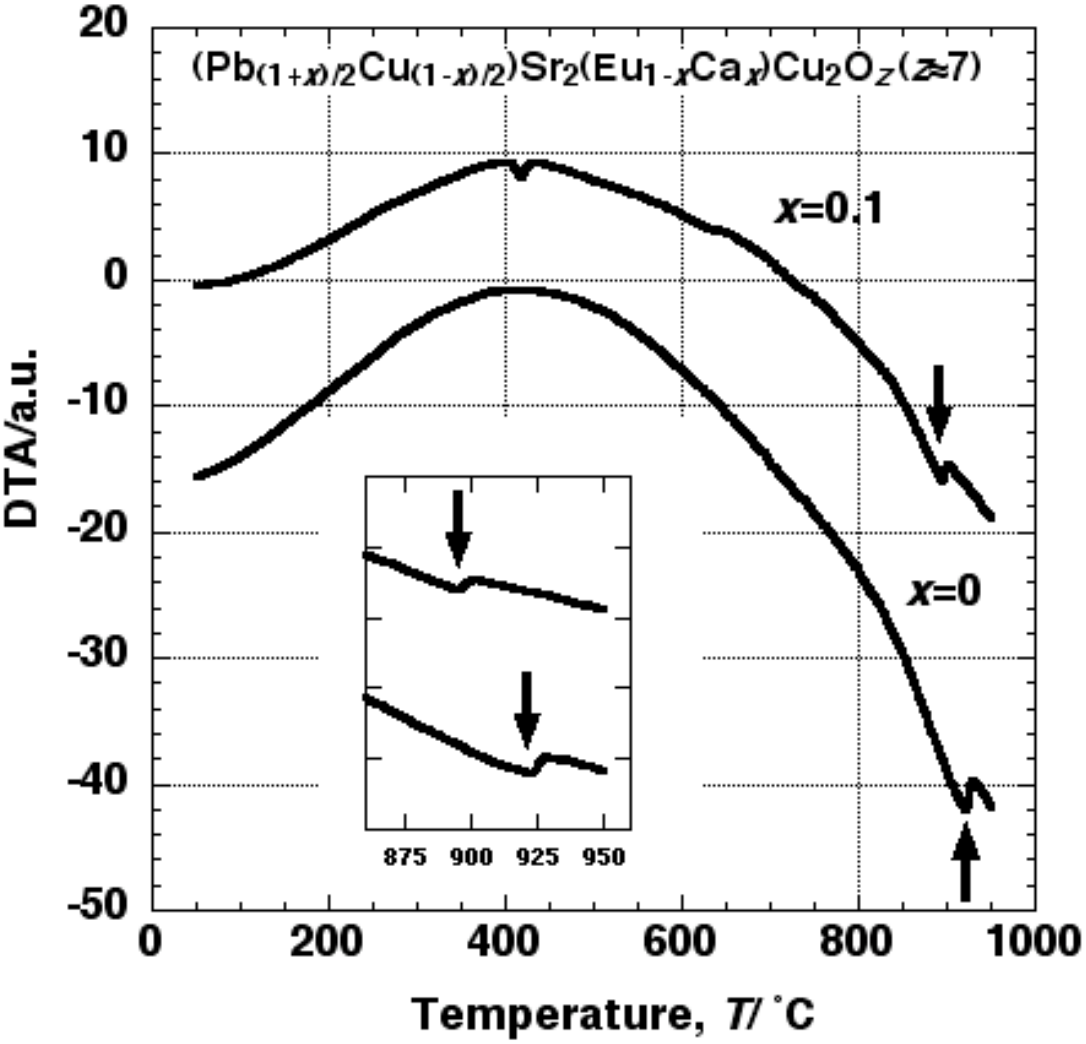

Fig. 3. T. Maeda *et al*.

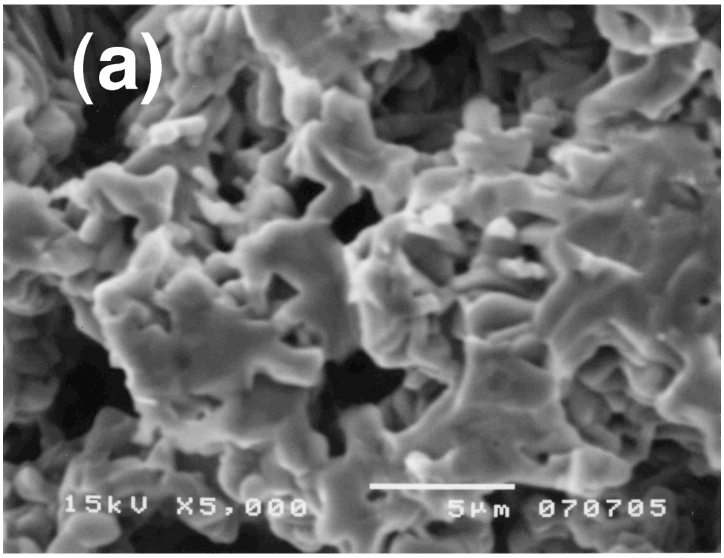

Fig. 4(a). T. Maeda *et al.*

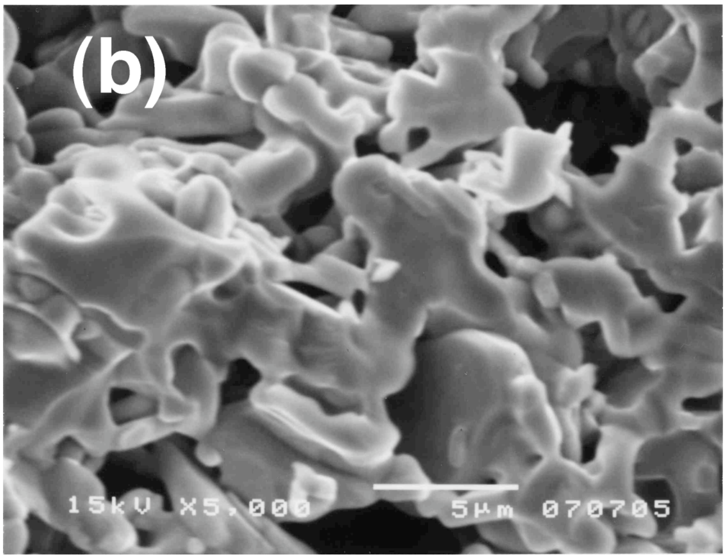

Fig. 4(b). T. Maeda *et al*.