

Superconductivity of (Pb_{0.75}W_{0.25})Sr₂(RE_{0.5}Ca_{0.5})Cu₂₀z (RE = Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, and Y) by Annealing in N₂ Gas

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雑誌名	Journal of Superconductivity and Novel Magnetism
巻	33
号	12
ページ	3667-3672
発行年	2020-12
権利	This is a post-peer-review, pre-copyedit version of an article published in Journal of Superconductivity and Novel Magnetism. The final authenticated version is available online at: https://doi.org/10.1007/s10948-020-05628-6 .
URL	http://hdl.handle.net/10466/00017196

doi: <https://doi.org/10.1007/s10948-020-05628-6>

RUNNING TITLE: Superconductivity of $(\text{Pb}, \text{W})\text{Sr}_2(\text{RE}, \text{Ca})\text{Cu}_2\text{O}_z$ by N_2
annealing

Superconductivity of $(\text{Pb}_{0.75}\text{W}_{0.25})\text{Sr}_2(\text{RE}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_z$ Cu_2O_z (RE=Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Y) by annealing in N_2 gas

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(Received _____)

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Abstract

We have synthesized the Pb-1212 compounds in the $(\text{Pb}_{0.75}\text{W}_{0.25})\text{Sr}_2(\text{RE}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_z$ (RE=Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Y) system. Every sample shows an onset of resistivity-drop phenomenon near 80K and zero-resistivity. Moreover, the samples with RE = Y and Yb show diamagnetic signals starting from about 78 K and 76 K with lowering temperature, respectively. From these experimental results, we can see that these phenomena originate from superconductivity of the Pb-1212 phase in the present system. The T_c value of about 80 K for the sample with RE = Y in the present system is higher than the already reported values for the superconductors annealed under N_2 gas. The important thing is that annealing under N_2 atmosphere is essential for making the Pb-1212 samples exhibit superconductivity in the present system.

Keywords: Superconductivity · Pb-1212 compound · $(\text{Pb}_{0.75}\text{W}_{0.25})\text{Sr}_2(\text{RE}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_z$ · RE= Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Y · Annealing under N_2 gas

1. Introduction

The Pb-1212 compound showing superconductivity was first discovered by Rouillon *et al.* [1]. The nominal composition was $\text{Pb}_{0.5}\text{Sr}_{2.5}\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_z$. They reported that the compound had the potential to show superconductivity up to 100 K and this report was drawing the interests of researchers throughout the world. The Pb-1212 compound has (Pb,*M*)-O monolayers for the charge reservoir block in the crystal structure, the chemical formula can be expressed as (Pb,*M*) $\text{Sr}_2\text{ACu}_2\text{O}_z$. In the case of the Pb-1212 compound by Rouillon *et al.*, *M* corresponds to Sr, and *A* corresponds to a mixture of Y and Ca. After this discovery, the superconducting Pb-1212 compounds with *M* = Cu [2, 3], Ca [4], In [5], Cd [6, 7], Mg [8] have been synthesized. These compounds needed annealing in O₂ atmosphere for exhibiting the superconductivity. Then, the Pb-1212 samples with *M* = V [9], W [10] and Mo [11] have been discovered, their compositions are $(\text{Pb}_{0.7}\text{V}_{0.3})\text{Sr}_2(\text{Y}_{0.6}\text{Ca}_{0.4})\text{Cu}_2\text{O}_{7-\delta}$, $(\text{Pb}_{0.8}\text{W}_{0.2})\text{Sr}_2(\text{Nd}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_{7-\delta}$ and $(\text{Pb}_{0.75}\text{Mo}_{0.25})\text{Sr}_2(\text{Nd}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_{7-\delta}$ respectively. Moreover, in the second and the third of these three compounds, *A*-site was occupied by a mixture of Nd and Ca. Interestingly, these three samples needed annealing not under O₂ atmosphere but in argon or N₂ gas for showing superconductivity. Following, we also have synthesized new Pb-1212 compounds substituted *M*-site of (Pb,*M*)-O monolayer by other oxy-anions of BO₃³⁻ [12], PO₄³⁻ [13], SO₄²⁻ [14]. These Pb-1212 compounds needed partial substitution of Ba for Sr and/or annealing under 1 atm O₂ gas for showing superconductivity.

Thus, it is very interesting that the Pb-1212 compounds are very flexible to substitutable cations for *M*-site in the (Pb,*M*)-O monolayers and that the annealing condition for obtaining the superconductivity changes such as under O₂ gas or N₂ due to what the cations occupy the *M*-site of (Pb,*M*)-O monolayers.

Recently, we have successfully synthesized new Pb-1222 compounds in the $(\text{Pb}_{0.75}\text{W}_{0.25})\text{Sr}_2(\text{Eu}_{2.0-x}\text{Ce}_x)\text{Cu}_2\text{O}_z$ system [15]. Among them, we discovered that the sample

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with $x = 0.3$ showed superconductivity with an onset of about 15 K. These Pb-1222 samples have the same (Pb,W)-O monolayers as the Pb-1212 samples of $(\text{Pb}_{0.8}\text{W}_{0.2})\text{Sr}_2(\text{Nd}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_{7-\delta}$ have, however our Pb-1222 compound exhibited superconductivity only when the samples were annealed not in N_2 gas but under high-pressure O_2 gas. This experimental fact shows that the condition for obtaining the superconductivity depend on not only what the cations occupies the M -site of (Pb, M)-O monolayer but what the crystal structure the Pb-compounds have.

Now, there is a question whether other RE elements besides Nd can be used for synthesizing the Pb-1212 samples in the $(\text{Pb}_{0.75}\text{W}_{0.25})\text{Sr}_2(\text{RE}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_z$ system or not? If this is possible, what is the RE element of the Pb-1212 sample showing the highest T_c in the system. Moreover, what is the most suitable annealing condition for the samples to exhibit the superconductivity; under N_2 atmosphere or in O_2 gas? The results are reported in detail.

2. Experimental

A conventional solid-state reaction method was employed for sample preparation. For starting materials, high-purity powders of PbO (Kojundo Chemical Laboratory Co.; 99.99 %), WO_3 (Kojundo Chemical Laboratory Co.; 99.99 %), SrCO_3 (Wako Pure Chemical Co.; 99.99 %), RE_2O_3 (RE=Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm and Yb; Kojundo Chemical Laboratory Co.; 99.9 %), Y_2O_3 (Kojundo Chemical Laboratory Co.; 99.99 %), CaCO_3 (Kojundo Chemical Laboratory Co.; 99.99 %), CuO (Kojundo Chemical Laboratory Co.; 99.99 %) were used. Appropriate amounts of the powders were weighed for the samples in two groups with $x = 0.2$ and 0.25 in a nominal composition of $(\text{Pb}_{1-x}\text{W}_x)\text{Sr}_2(\text{RE}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_z$. The mixed powders were thoroughly ground and cold-pressed into disk-shaped pellets. The pellets were

1 preheated at 850°C for about 20 h in air and cooled down to room temperature. Then, the
2 pellets were pulverized, pelletized again and they were sintered at 950°C for about 20 h in air
3 and cooled down to room temperature. Next, the resulting pellets were annealed under 1
4 atm N₂ gas at 950°C for 20 h and cooled down to 800°C at a rate of 10°C/min, kept at this
5 temperature for 2 h, then quenched to room temperature (hereafter, N₂ annealing). Moreover,
6 we tried to anneal the resulting pellets in 1 atm O₂ gas at 400°C for about 4 h, after the
7 annealing they were cooled down to room temperature at a rate of 2.5°C/min (hereafter, O₂
8 annealing). The resulting samples were checked for the homogeneity and the phase purity
9 by X-ray powder diffraction measurements using CuK α radiation. The diffraction intensities
10 were collected by step scanning at 0.02° intervals for 2 seconds in the range from 5° to 50° in 2θ . The
11 temperature dependence of the electrical resistivity (hereafter, ρ - T dependence) was measured from 4.2 K to 273 K
12 by a standard four-probe method. Moreover, the temperature dependence of the DC magnetic susceptibility
13 (hereafter, χ - T dependence) was measured for the powdered samples using a SQUID magnetometer. The data
14 were obtained for two processes of ZFC and FC. ZFC process means that the measurement was performed from
15 2.0 K to 300 K on heating under a magnet field of 10 Oe after cooling from room temperature to 2.0 K under
16 zero-magnet field, while FC process means that the measurement was performed from 2.0 K to 300 K on heating
17 under a magnet field of 10 Oe after cooling from room temperature to 2.0 K under a magnet field of 10 Oe.
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49 3. Results and Discussion

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54 X-ray diffraction analysis was carried out to investigate for the samples in two systems with $x = 0.2$ and
55 0.25 in a composition of (Pb_{1-x}W_x)Sr₂(RE_{0.5}Ca_{0.5})Cu₂O_z (RE=Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb
56 and Y). As a result, we found that almost the samples in these two systems were mainly
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1 composed of the 1212 phase for the above-specified rare-earth elements, but the samples
2 belonging to the system with $x=0.2$ contained more impurity phases than those with $x = 0.25$.
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4 Then, we have investigated on physical properties of the samples with a nominal composition of
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7 $(\text{Pb}_{0.75}\text{W}_{0.25})\text{Sr}_2(\text{RE}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_z$ (RE=Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Y), namely, the
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9 samples with $x = 0.25$.
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11 Figure 1 shows X-ray diffraction patterns for the powdered samples with various RE elements in the
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13 $(\text{Pb}_{0.75}\text{W}_{0.25})\text{Sr}_2(\text{RE}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_z$ system. Here, we pay attention to the diffraction pattern of the sample
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15 with RE= Y (hereafter, Y-sample) at the top of the patterns. The diffraction peaks are mainly originated from
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17 the Pb-1212 phase and they are indexed on the basis of a tetragonal unit cell with the lattice parameters of $a = 0.3820$
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19 nm and $c = 1.184$ nm. Then, diffraction peaks originating from impurities marked by closed circles are also seen in
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21 the figure. They are Pb-Sr(Ca)-Cu-O solid solution with a typical composition of $\text{Pb}_{2.05}(\text{Sr}, \text{Ca})_3\text{Cu}_{0.73}\text{O}_{7.70}$ [16] and
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23 unknown phases. As seen from the figure, the samples with RE except Yb are also mainly consisted of the Pb-1212
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25 phase, judging from the fact that each diffraction pattern resembles that of the Y-sample each other. While, the sample
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27 with RE=Yb (hereafter, Yb-sample) shows peaks from the Pb-1212 phase and also shows higher peaks from the
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29 impurities. From this result, Yb may be on the edge of RE elements required for composing the
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31 Pb-1212 structure because the ion radius of Yb^{3+} is too small in comparison with that of Ca^{2+}
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41 Figure 2 shows the lattice parameters a and c as a function of r in the present
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43 $(\text{Pb}_{0.75}\text{W}_{0.25})\text{Sr}_2(\text{RE}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_z$ (RE=Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Y) system,
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45 where r means the radius of RE^{3+} in eight-coordination by Shannon [17]. The values of a and c are
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47 shown by *open* and *closed circles*, respectively. Each straight line is a guide for the eye. Here, we can see that the
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49 lattice parameters a and c are both linearly increasing with the increase of the ion radius of RE^{3+} . These results can be
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51 considered to indicate that each RE^{3+} preferentially occupies A site of $(\text{Pb}, M)\text{Sr}_2\text{ACu}_2\text{O}_z$ expressed in chemical
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53 formula for the Pb-1212 compounds.
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58 Figure 3 shows ρ - T dependence for the samples in the present $(\text{Pb}_{0.75}\text{W}_{0.25})\text{Sr}_2(\text{RE}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_z$
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(RE=Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Y) system. These samples were treated by N₂ annealing. From the figure, we can see such a tendency as that with the decrease of the ion radius of RE³⁺, the slope of the resistivity versus temperature above 80 K becomes more gradual and the value of resistivity at 273 K is gradually decreasing. Moreover, we can see that each sample shows a two step-like resistivity-dropping phenomenon. The origin of the two-step-like phenomenon is not clear at present, we expected that the phenomenon was caused by weak link connection *unknown superconducting phase* with homogeneous cations and oxygen and the *main superconducting phase*. Hereafter, the lower and the higher onset temperatures of the resistivity-dropping phenomena are defined as T_{on}^l and T_{on}^h , respectively. Then, we can see that with the decrease of the ionic radius of RE³⁺, the value of T_{on}^l is rising. This result is suggestive of homogeneous cations and oxygen in the *unknown superconducting phase* related to T_{on}^l . While the value of T_{on}^h is almost constant of about 80 K, this value is originate from superconducting transition of the *main superconducting phase*. This *main superconducting phase* is obviously the Pb-1212 phase from the facts that the value of T_{on}^h is about 80 K and the samples are mainly consisted of the Pb-1212 phase as seen in Fig.1. Here, we emphasize that only the samples treated by N₂ annealing showed this resistivity-dropping phenomenon. While after O₂ annealing, each of the samples showed a semiconducting ρ - T dependence without the resistivity-dropping phenomenon. The *inset* shows an enlargement of the temperature range of the resistivity-dropping phenomenon for the samples with RE = Dy, Ho, Er, Ho, Yb and Y. The left and right *down arrows* specifically indicate the points of T_{on}^l and T_{on}^h for the Y-sample respectively. Then, the left and right *up arrows* specifically indicate the points of T_{on}^l and T_{on}^h for the Yb-sample, respectively. The values of T_{on}^l and T_{on}^h for the Y-sample are 65K and 80 K, respectively. Then, the values of T_{on}^l and T_{on}^h for the Yb-sample are 72 K and 79 K, respectively. Looking closely, we can see that the Y-sample have the highest T_{on}^h of 80 K in the present (Pb_{0.75}W_{0.25})Sr₂(RE_{0.5}Ca_{0.5})Cu₂O_z system.

Figure 4 shows χ - T dependence in a powder form of the Yb-sample and the Y-sample. In the figure, *black closed circles* and *black open ones* are values of magnetic susceptibility for the Y-sample obtained on ZFC and FC processes, respectively. Then, *light-blue closed circles* and *light-blue open ones* are the values of magnetic susceptibility for the Yb-sample obtained on ZFC and FC processes, respectively. As seen from the figure, the

1 Y-sample shows only a diamagnetic response with decreasing temperature, but the Yb-sample shows
 2 Curie-Weiss-like behavior originating from the magnetism of Yb^{3+} in addition to the diamagnetic response. The
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 4 important thing is that the two step-like change is not seen in the χ - T dependence unlike the ρ - T dependence.
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 6 This result can be considered to indicate that the *unknown superconducting phase* exist in the grain
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 8 boundary and weak link connection this *unknown superconducting phase* and the *main superconducting phase*
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 10 was cut off by the powdering of the sample, and then only the diamagnetic response for the *main*
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 12 *superconducting phase* appeared in the χ - T dependence. Moreover, considering the results of X-ray diffraction
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 14 patterns and χ - T dependences, we can see that the impurities found in Fig. 1 are non- magnetic substances and
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 16 that they does not contribute to the χ - T dependence. The *inset* shows an enlargement of the temperature range
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 18 near the diamagnetic response. *Down arrow* shows a starting temperature of the response T_c^m for Yb-sample and *up*
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 20 *arrow* shows T_c^m for the Y-sample. The values of T_c^m are seen to be about 76 K and 78 K for Yb-sample and
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 22 Y-sample, respectively. These values are consistent with those of T_{on}^h estimated from the ρ - T dependences for
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 24 Yb-sample and Y-sample. Then, the superconducting volume fraction for the Y-sample is calculated to be about
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 26 4.0 % in the FC process, assuming the density to be about 6.5 g/cm^3 . Besides, the superconducting volume fraction
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 28 for the Yb-sample is calculated to be about 5.0 % in the FC process, assuming the density to be about 7.0 g/cm^3 .
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 30 Considering the experimental facts from the resistivity and the magnetic measurements, we can see that the
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 32 resistivity-dropping phenomenon of the *main superconducting phase* is originate from
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 34 superconductivity and the superconductivity phase is rightly the Pb-1212 one in the present
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 36 system, although the superconducting volume fractions somewhat small.
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their crystal structure, why the annealing conditions for each of them are so different. In the (Pb,W)-O monolayers of these compounds, Pb is estimated to be present partly as Pb^{2+} and partly in Pb^{4+} , and almost all W estimated to be present as W^{6+} . When the Pb-1212 structure was formed in the samples of $(Pb_{0.75}W_{0.25})Sr_2(RE_{0.5}Ca_{0.5})Cu_2O_z$ (RE=Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Y), Pb in the (Pb,W)-O monolayers may be present as a mixture of Pb^{2+} and Pb^{4+} . Probably, the sum of valence number of Pb and W being 3 is considered to be necessary for the Pb-1212 compounds to exhibit superconductivity. Therefore, almost all Pb^{4+} in the (Pb,W)-O monolayers changes into Pb^{2+} after annealing under N_2 atmosphere, so the sum of valence number of Pb^{2+} and W^{6+} come to be 3 ($= 2 \times 0.75 + 6 \times 0.25$) as the portion of Pb^{2+} and W^{6+} is 75 % and 25 % in the $(Pb_{0.75}W_{0.25})$ -O monolayers of the present Pb-1212 system, respectively. On the other hand, when the Pb-1222 structure was formed in the samples of $(Pb_{0.75}W_{0.25})Sr_2(Eu_{2.0-x}Ce_x)Cu_2O_z$, almost all Pb in the (Pb,W)-O monolayers is probably present as Pb^{2+} because of lacking of the oxygen atoms in the fluorite $(Eu_{2.0-x}Ce_x)O_2$ layers, then the sum of valence number of Pb and W is 3. However, the Pb-1222 compounds do not show superconductivity as the number of the carriers is not adequate to that claimed necessary for appearance of superconductivity because of lacking of the oxygen atoms in the fluorite layers.

Summarizing the above, we speculate that annealing in N_2 or He gas is needed for the Pb-1212 compounds with (Pb,M)-O monolayers to show superconductivity when the sum of the valence number of Pb and M exceeds 3, while annealing in O_2 is needed for the Pb-1212 compounds to show superconductivity when the sum is less than 3. This speculation can give an explanation about differences in the annealing conditions for appearance of superconductivity for the Pb-1212 compounds with $M = Cu$ [2, 3], Ca [4], In [5], Cd [6, 7], Mg [8], V [9], W [10] and Mo [11].

4. Conclusions

We have synthesized the Pb-1212 compounds with RE= Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Y in the $(\text{Pb}_{0.75}\text{W}_{0.25})\text{Sr}_2(\text{RE}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_z$ system. Each sample showed the resistivity-dropping phenomenon starting from about 80 K and zero-resistivity. Moreover, the Yb-sample and the Y-sample, for examples, showed diamagnetic responses starting from about 76 K and 78 K, respectively. Although the superconducting volume fractions were somewhat small, we could see that the resistivity-dropping phenomenon was resulted from superconductivity and the superconductivity was originated rightly from the Pb-1212 phase. The important thing is that annealing under N_2 atmosphere is absolutely essential for the samples to become superconductors in the $(\text{Pb}_{0.75}\text{W}_{0.25})\text{Sr}_2(\text{RE}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_z$ system. Moreover, the Y-sample in the present $(\text{Pb}_{0.75}\text{W}_{0.25})\text{Sr}_2(\text{RE}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_z$ system showed superconductivity at 80 K. This superconducting transition temperature is higher than the already reported values for the superconductors annealed under N_2 gas.

References

1. Rouillon, T., Provost, J., Hervieu, M., Groult, D., Michel, C., Raveau, B.: *Physica C* **159**, 201 (1989)
2. Lee, J.Y., Swinnea, J. S., Steinfink, H.: *J. Mater. Res.* **4**, 763 (1989)
3. Ono, A., Uchida, Y.: *Jpn. J. Appl. Phys.* **29**, L586 (1990)
4. Rouillon, T., Maignan, A., Hervieu, M., Michel, C., Groult, D., Raveau, B.: *Physica C* **171**, 7 (1990)
5. Liu, R. S., Wu, P. T., Wu, S. F., Wang, W. N., Edwards, P. P.: *Physica C* **165**, 111 (1990)
6. Beales, T. P., Dineen, C., Freeman, W. G., Hall, S. R., Harrison, M. R., Jacobson, D. M., Zammattio, S. J.,

Supercond. Sci. Technol. **5**, 47 (1992)

7. Liu, R. S., Groult, D., Maignan, A., Hu, S. F., Jefferson, D. A., Raveau, B., Michel, C., Hervieu, M., Edwards, P. P.: Physica C **195**, 35 (1992)
8. Liu, H. B., Morris, D. E., Sinha, A. P. B.: Physica C **204**, 262 (1993)
9. Widder, W., Franz, M., Bauernfeind, L., Braun, H. F.: Physica C **217**, 121 (1993)
10. Zhao, Y. D., Qian, Y. T., Tang, K. B., Zhang, Y. H.: J. Supercond. **11**, 729 (1998)
11. Zhao, Y. D., Qian, Y. T., Tang, K. B., Liu, W., Chen, X. H., Zhang, Y. H.: Supercond. Sci. Technol. **11**, 898 (1998)
12. Sasakura, H., Akagi, Y., Tsukui, S., Adachi, M.: Physica C **468**, 925 (2008)
13. Sasakura, H., Akagi, Y., Tanaka, M., Tsukui, S., Adachi, M.: J. Supercond. Nov. Magn. **23**, 1529 (2010)
14. Tanaka, M., Sasakura, H., Akagi, Y., Tsukui, S., Adachi, M.: J. Supercond. Nov. Magn. **24**, 1673 (2011)
15. Sasakura, H., Akagi, Y., Tanaka, M., Tsukui, S., Adachi, M.: J. Supercond. Nov. Magn. **27**, 5 (2014)
16. Kitaguchi, H., Takada, J., Oda, K., Miura, Y.: J. Mater. Res. **5**, 1397 (1990)
17. Shannon, R. D.: Acta Crystallogr. A **32**, 751 (1976)

Figure captions

Fig. 1. X-ray diffraction patterns for the samples with various RE elements in the $(\text{Pb}_{0.75}\text{W}_{0.25})\text{Sr}_2(\text{RE}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_z$. (RE=Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Y) system. Each sample shows diffraction peaks originating from the Pb-1212 phase and impurities. The pattern of the sample with RE = Y is shown at the top, for comparison, the diffraction peaks originating from the Pb-1212 phase are indexed on the basis of a tetragonal unit cell with the lattice parameters of $a = 0.3820$ nm and $c = 1.184$ nm. Then, peaks marked by *closed circles* are coming from unknown impurity phases and Pb-Sr(Ca)-Cu-O

solid solution with a typical composition of $\text{Pb}_{2.03}(\text{Sr}, \text{Ca})_3\text{Cu}_{0.73}\text{O}_{7.70}$ [16].

Fig. 2. The lattice parameters a and c as a function of r in the present $(\text{Pb}_{0.75}\text{W}_{0.25})\text{Sr}_2(\text{RE}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_z$ ($\text{RE}=\text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$ and Y) system, where r means the radius of RE^{3+} in eight-coordination by Shannon [17]. *Open and closed circles* show the values of a and c , respectively. Each *straight line* is a guide for the eye.

Fig. 3. ρ - T dependences for the samples with $\text{RE}=\text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$ and Y in the present $(\text{Pb}_{0.75}\text{W}_{0.25})\text{Sr}_2(\text{RE}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_z$ system. Each sample shows a two step-like resistivity-dropping phenomenon. The *inset* shows an enlargement of the temperature range near the resistivity-dropping phenomenon for the samples with $\text{RE} = \text{Dy}, \text{Ho}, \text{Er}, \text{Ho}, \text{Yb}$ and Y . The left and right *down arrows* specifically indicate the points of T_{on}^{l} and T_{on}^{h} (see the text) for the Y -sample respectively. Then, the left and right *up arrows* specifically indicate the points of T_{on}^{l} and T_{on}^{h} for the Yb -sample, respectively. The values of T_{on}^{l} and T_{on}^{h} for the Y -sample are 65K and 80 K, respectively. Then, the values of T_{on}^{l} and T_{on}^{h} for the Yb - sample are 72 K and 79 K, respectively.

Fig. 4. χ - T dependences in a powder form of the Y -sample and the Yb -sample. *Black closed circles* and *black open ones* are the values of magnetic susceptibility for the Y -sample obtained on ZFC and FC processes (see the text), respectively. And, *light-blue closed circles* and *ligh-blue open ones* are the values of magnetic susceptibility for the Yb -sample obtained on ZFC and FC processes, respectively. Each sample shows a diamagnetic response. The *inset* shows an enlargement of the temperature range near the diamagnetic response. *Down arrow* shows a starting temperature of the response T_{c}^{m} for Yb -sample, and *up arrow* shows T_{c}^{m} for the Y -sample. The values of T_{c}^{m} are seen to be about 76 K and 78 K for Yb -sample and Y -sample, respectively.







