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LETTER TO THE EDITOR

Characterization of a new Pb-based 1222 cuprate $\text{Pb}(\text{Sr}_{1.2}\text{La}_{0.8})\text{Gd}_2\text{Cu}_2\text{O}_{9.06}$

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Abstract. A new compound $\text{Pb}(\text{Sr}_{1.2}\text{La}_{0.8})\text{Gd}_2\text{Cu}_2\text{O}_{9.06}$ has been synthesized and characterized in this letter. The Pb ions in the rock-salt-type monolayer of this compound occur in the form of mixed valence states, i.e., Pb^{4+} and Pb^{2+} , and the average cationic valence is 3.14, close to that in $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_7$. It seems to us that the single-Pb-layer Pb-based layered compounds are stable only when the average cationic valence in this layer is close to three. The crystal structure refinement results indicate that the PbO layer is highly distorted, and no Cu ions enter this monolayer. The high distortion of the PbO layer makes the Pb-1222 phase preferentially orientate more readily. This compound does not superconduct. The nonsuperconductivity is not caused by low charge carrier concentration. It may be caused by the Gd_2O_2 layers, which affect not only the buckling degree of conducting CuO_2 planes but the coupling effect between adjacent CuO_2 planes as well.

According to Shaked *et al* [1], all the layered cuprates can be named by four numbers, representing the number of insulating layers, spacing layers, separating layers and conducting layers, respectively. Based on the naming scheme, all the Pb-based layered compounds can be classified into three categories according to the number of insulating layers, i.e.

(i) $(\text{Pb}_2\text{Cu})(\text{Sr}, \text{La})_2\text{A}_{n-1}\text{Cu}_n\text{O}_z$ ($n = 1, 2$) [2, 3] and $(\text{Pb}_2\text{Cu})\text{Sr}_2(\text{Ln}, \text{Ce})_n\text{Cu}_2\text{O}_z$ ($n = 2, 3, 4, \dots$) [4, 5] with PbO–Cu–PbO insulating layers,

(ii) $(\text{PbCu})(\text{Ba}, \text{Sr})_2(\text{Y}, \text{Ca})\text{Cu}_2\text{O}_7$ [6] and $(\text{PbCu})(\text{Ba}, \text{Sr})_2(\text{Ln}, \text{Ce})_n\text{Cu}_2\text{O}_z$ ($n = 2, 3, 4, \dots$) [5, 7] with a PbO– CuO_x insulating bilayer and

(iii) $(\text{Pb}, \text{M})(\text{Sr}, \text{La})_2(\text{Y}, \text{Ca})_{n-1}\text{Cu}_n\text{O}_z$ ($n = 1, 2$) [8–11] and $(\text{Pb}, \text{Cu})(\text{Sr}, \text{Pr})_2\text{Pr}_2\text{Cu}_2\text{O}_9$ [12] with a (Pb, M)O insulating monolayer (M = divalent metal element, such as Cu, Cd).

It is noted that all the insulating layers in the Pb-based cuprates consist of mixed cations of different valences. Thus, it is very intriguing to synthesize a compound with its cations in the insulating layer consisting of pure Pb. In this work, we have successfully synthesized such a new compound $\text{Pb}(\text{Sr}_{1.2}\text{La}_{0.8})\text{Gd}_2\text{Cu}_2\text{O}_{9.06}$, whose cations in the insulating layer consist of pure Pb.

Samples were prepared by the solid state reaction method using PbO, SrCO_3 , La_2O_3 , Gd_2O_3 , CuO as starting materials. Stoichiometric amounts of starting materials were

appropriately weighed, and ground together in an agate mortar. The well mixed powders were calcined at 850 °C in air overnight and then furnace cooled to room temperature. The prereacted material was reground and pressed into pellets. The pellets were sintered at 920 °C in air for 20 hours with intermediate grinding. X-ray diffraction (XRD) analyses were performed on a M18AHF x-ray diffractometer with Cu K α radiation (50 kV \times 200 mA). The structure refinement data were collected on the same diffractometer at ambient temperature. The scattering slit is 0.50°, the divergence slit 0.50° and the receiving slit 0.15 mm. The scanning step width is 0.02° in 2θ and the sampling time is 2 s per step. The 2θ range was from 10 to 110°. A standard four-probe method was used for electrical resistivity measurements. The valences of Pb and Cu as well as the oxygen content of the samples were determined by iodometric titrations.

The phase identification results reveal that pure Pb-1222 phase can be obtained only at 920 °C in air in the composition of $\text{Pb}(\text{Sr}_{1.2}\text{La}_{0.8})\text{Gd}_2\text{Cu}_2\text{O}_z$. The Pb-1222 phase is very sensitive to sintering temperature and atmosphere. We have tried different sintering temperatures (900 °C, 920 °C, 940 °C and 960 °C) on $\text{Pb}(\text{Sr}_{1.2}\text{La}_{0.8})\text{Gd}_2\text{Cu}_2\text{O}_z$ in air, but found that pure Pb-1222 phase can only be obtained at 920 °C. Because the components of our Pb-1222 phases are very complex and some of them can form Pb-1212 phase and 214 phase, inappropriate sintering temperature will lead to the formation of impurity phases. Besides, we have tried to anneal these samples in O₂ or N₂, and found that the Pb-1222 phase is unstable in these atmospheres. This can be understood from the iodometric titration results of $\text{Pb}(\text{Sr}_{1.2}\text{La}_{0.8})\text{Gd}_2\text{Cu}_2\text{O}_{9.06}$ synthesized in air, which indicate that the formal valence state of Pb ions is +3.14. This result suggests that the Pb ions in the insulating layer actually exist in the form of mixed valence states, i.e., Pb⁴⁺ and Pb²⁺, and the proportion of Pb⁴⁺ and Pb²⁺ is 0.57:0.43. In our previous work, we have found that pure $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_7$ can be easily synthesized when the ratio of Pb⁴⁺ and Cd²⁺ in the insulating monolayer is close to 1:1 [9]. Thus, it is not difficult to understand that annealing the sample in O₂ or N₂ will result in the appearance of impurity phases, taking into account the fact that a reasonable proportion of Pb⁴⁺ and Pb²⁺ (about 1:1) will be destroyed in these atmospheres. Therefore, it seems to us that the single-Pb-layer layered compounds are stable only when its average cationic valence in this Pb layer is close to three. In order to meet this condition, some fraction of the Pb ions in the rock-salt-type Pb layer in this kind of compound must be replaced by low-valence cations as in $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_7$, or Pb ions must exist in the form of mixed valences as in the present compound.

The crystal structure of $(\text{Pb}, \text{Cu})(\text{Sr}, \text{Nd})_2(\text{Ho}, \text{Ce})_2\text{Cu}_2\text{O}_{9.06}$ has been reported by Maeda *et al* [13]. Based on the structure model described in [13], we have refined the structure parameters of $\text{Pb}(\text{Sr}_{1.2}\text{La}_{0.8})\text{Gd}_2\text{Cu}_2\text{O}_{9.06}$ by the Rietveld method [14] using x-ray powder diffraction data. Figure 1 shows the schematic representation of the crystal structure of $\text{Pb}(\text{Sr}_{1.2}\text{La}_{0.8})\text{Gd}_2\text{Cu}_2\text{O}_9$. In the refinement, the thermal parameters (B) were assumed to be isotropic, and the thermal parameters of all oxygen atoms were arbitrarily fixed at 1 Å². Furthermore, we assumed that the relatively large Sr and La ions reside in the ninefold 4e site, and the relatively small Gd ions reside in the eightfold 4e site (see figure 1). Table 1 lists the final R factors, the refined lattice constants, structure parameters and their estimated standard deviations in parentheses for $\text{Pb}(\text{Sr}_{1.2}\text{La}_{0.8})\text{Gd}_2\text{Cu}_2\text{O}_{9.06}$. Table 2 lists the selected metal–oxygen interatomic distances of this compound. Figure 2 shows the Rietveld refinement patterns for $\text{Pb}(\text{Sr}_{1.2}\text{La}_{0.8})\text{Gd}_2\text{Cu}_2\text{O}_9$. The dotted line represents the observed diffraction patterns, the solid line represents the calculated patterns and the curve at the bottom of the figure represents the difference between the observed and calculated patterns. The short vertical lines mark the positions of possible Bragg reflections for the (Pb, Cd)-1222 phase. In the refinement, we found that the sample had obvious preferred

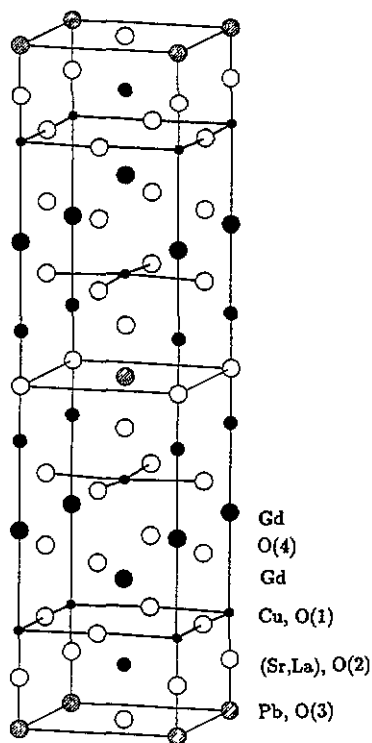


Figure 1. The schematic representation of the crystal structure of $\text{Pb}(\text{Sr}_{1.2}\text{La}_{0.8})\text{Gd}_2\text{Cu}_2\text{O}_9$.

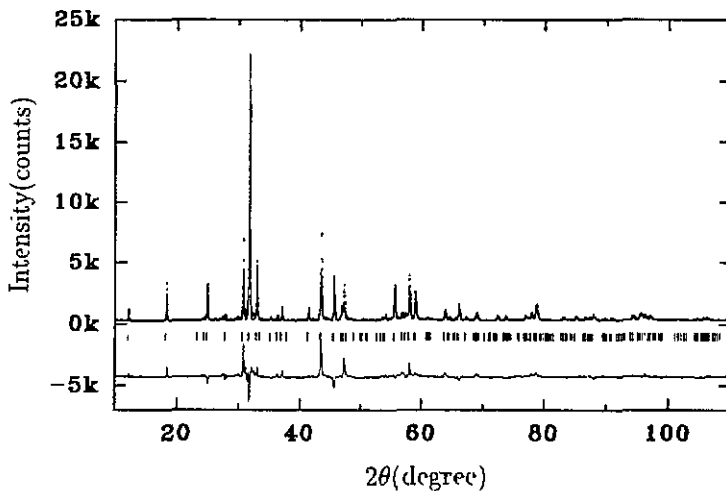


Figure 2. The Rietveld refinement patterns for $\text{Pb}(\text{Sr}_{1.2}\text{La}_{0.8})\text{Gd}_2\text{Cu}_2\text{O}_9$. The dotted line represents the observed diffraction patterns, the solid line represents the calculated patterns and the curve at the bottom of the figure represents the difference between the observed and calculated patterns. The short vertical lines mark the positions of possible Bragg reflections for the Pb-1222 phase.

orientation (00 l). The preferred orientation was refined with the March–Dollas function. But the final result is not very good. The orientation in the Pb-1222 phase may be due to the high distortion of the PbO layer (see below) and/or the existence of Pb^{2+} with lone

electron pairs which make the PbO layer cleave more easily.

Table 1. Refined structure parameters for $\text{PbSr}_{1.2}\text{La}_{0.8}\text{Gd}_2\text{Cu}_2\text{O}_{9.06}$ from powder x-ray Rietveld analysis. Space group $14/mmm$. The numbers in parentheses are estimated standard deviations in the last significant digit, and those without deviations were fixed. g denotes the site occupancy. $R_p = 12.26\%$, $R_{wp} = 17.14\%$, $a = 3.8599(1)$ Å, $c = 29.2361(5)$ Å.

| Atom | Site | x | y | z | g | B (Å ²) |
|---|------|------------|-----|-----------|----------------------------|-----------------------|
| (Pb ⁴⁺ /Pb ²⁺ /Cu ²⁺) | 8i | 0.1181(26) | 0 | 0 | 0.139(1)/0.105(1)/0.006(1) | 0.57(9) |
| (Sr, La) | 4e | 0.5 | 0.5 | 0.0832(1) | 0.6/0.4 | 0.66(4) |
| Gd | 4e | 0.5 | 0.5 | 0.2043(1) | 1 | 0.33(4) |
| Cu | 4e | 0 | 0 | 0.1464(2) | 1 | 0.53(6) |
| O(1) | 8g | 0 | 0.5 | 0.1456(5) | 1 | 1 |
| O(2) | 4e | 0 | 0 | 0.0750(7) | 1 | 1 |
| O(3) | 8j | 0.4356(6) | 0.5 | 0 | 0.25 | 1 |
| O(4) | 4d | 0 | 0.5 | 0.25 | 1 | 1 |
| O(5) | 4c | 0 | 0.5 | 0 | 0.03 | 1 |

Table 2. Selected metal–oxygen interatomic distances and bond valence sum of Pb ions in the Pb layer for $\text{Pb}(\text{Sr}_{1.2}\text{La}_{0.8})\text{Gd}_2\text{Cu}_2\text{O}_{9.06}$. For convenience, the displaced atoms were placed at their ideal positions while calculating the interatomic distances. N is the number of equivalent bonds.

| Bonds | Distance (Å) | N |
|------------------|--------------|-----|
| Pb–O(2) | 2.193 | 2 |
| Pb–O(3) | 2.729 | 4 |
| (Sr, La)–O(1) | 2.656 | 4 |
| (Sr, La)–O(2) | 2.740 | 4 |
| (Sr, La)–O(3) | 2.432 | 1 |
| Gd–O(1) | 2.583 | 4 |
| Gd–O(4) | 2.347 | 4 |
| Cu–O(1) | 1.930 | 4 |
| Cu–O(2) | 2.087 | 1 |
| Bond valence sum | | |
| Pb | 2.16 | |

During the refinement of the thermal parameter of the Pb atom in the rock-salt-type PbO monolayer in the present Pb-1222 compound assuming the ideal 2a site, an extraordinarily large thermal parameter is obtained for this atom, which implies a displacement of the Pb atom from the ideal 2a site (0,0,0) to the 8i site ($x,0,0$). Moreover, the O(3) atom in the PbO layer is also displaced from the ideal 2b site ($\frac{1}{2}, \frac{1}{2}, 0$) to the 8j site ($x, \frac{1}{2}, 0$). Besides, the oxygen content result determined by iodometric titrations indicates that a very small amount of excess oxygen exists in the 1222 compound. We assume that the small amount of excess oxygen resides in the interstitial O(5) site ($0, \frac{1}{2}, 0$) [13], and the occupancy is fixed at 0.03 from the oxygen content. Therefore, the PbO layer is highly distorted. We suggest that the distortion may be related to a structural incompatibility between the PbO layer and the CuO plane. Generally, the lattice parameter a of high- T_c layered cuprates is primarily determined by the Cu–O bond, which is strong and almost invariant through all the cuprates (about 1.9 Å for the Cu–O bond length). As a result, the Pb–O(3) distances within the PbO layer will be constrained by the Cu–O bond lengths (about 2.7 Å for the

Pb–O(3) distance within the PbO layer), while, on the other hand, the ideal interatomic distance can be approximately defined as the sum of the ionic radii. For example, the ideal $\text{Pb}^{4+}\text{--O}^{2+}$ distance is 2.175 Å from ionic radius considerations. Thus, the Pb–O(3) distance expected from ionic radius considerations is not compatible with the constrained Pb–O(3) distance imposed by the crystal structure, and the bonds are strained. This can be seen from the bond valence sum of Pb ions (table 2), calculated from the bond valence theory advanced by Brown *et al* [15]. The result indicates that the calculated bond valence sums of Pb (+2.16) from the strained bonds do not coincide properly with the true oxidation states measured from the iodometric titrations (+3.14). We suggest that the difference between the interatomic distances imposed by the crystal structure and that expected from ionic radius considerations is a potential origin of the atomic distortion. Besides, the Pb^{2+} with the $4f^{14}5d^{10}6s^2$ electron configuration shows the ‘inert pair effect’, which manifests itself structurally by a distortion of the cation coordination environment [16]. Finally, the coexistence of Pb^{4+} and Pb^{2+} in the PbO layer, which have different valences and different ionic radii (0.775 Å and 1.19 Å for Pb^{4+} and Pb^{2+} respectively, CN = 6), is also a potential origin of the atomic distortion.

In order to verify that no Cu ions enter the rock-salt-type PbO monolayer in the present Pb-1222 phase, we have refined the site occupancy of the cations in the PbO layer. The result reveals that this site is nearly completely occupied by Pb ions (see table 1). In the refinement, the ratio of Pb^{4+} and Pb^{2+} is fixed at 0.57:0.43.

Table 3. Bond angles of Cu–O(1)–Cu for some 1212 and 1222 phases.

| Phase | Composition | Cu–O(1)–Cu (°) | T_c (K) | Reference |
|---------|---|----------------|-----------|-----------|
| Pb-1212 | $(\text{Pb}_{0.5}\text{Cd}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_7$ | 166.93 | 76 | [9] |
| Pb-1222 | $\text{Pb}(\text{Sr}_{1.2}\text{La}_{0.8})\text{Gd}_2\text{Cu}_2\text{O}_{9.06}$ | 178.61 | < 5 | this work |
| Y-123 | $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ | 164.63 | 92 | [17] |
| Cu-1222 | $(\text{Eu}, \text{Ce})_2(\text{Ba}, \text{Eu})_2\text{Cu}_3\text{O}_{10-\delta}$ | 173.74 | 25 | [18] |
| Bi-2212 | $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_z$ | 171.63 | 80 | [19] |
| Bi-2222 | $\text{Bi}_2\text{Sr}_2(\text{Gd}, \text{Ce})_2\text{Cu}_2\text{O}_{10}$ | 180 | 34 | [20] |
| Tl-1212 | $\text{TlBa}_2\text{CaCu}_2\text{O}_{7-\delta}$ | 176.59 | 103 | [21] |
| Tl-1222 | $\text{TlBa}_2(\text{Eu}, \text{Ce})_2\text{Cu}_2\text{O}_{7-\delta}$ | 173.89 | 40 | [22] |

The electrical resistivity measurements indicate that the $\text{Pb}(\text{Sr}_{1.2}\text{La}_{0.8})\text{Gd}_2\text{Cu}_2\text{O}_{9.06}$ sample does not superconduct and exhibits a semiconductor-like behaviour. The iodometric titration results indicate that the valence state of Cu in $\text{Pb}(\text{Sr}_{1.2}\text{La}_{0.8})\text{Gd}_2\text{Cu}_2\text{O}_{9.06}$ is +2.09. Because this sample could not be doped by annealing in O_2 to increase its carrier concentration, we synthesized another compound $(\text{Pb}_{0.5}\text{Cd}_{0.5})(\text{Sr}_{1.2}\text{La}_{0.8})\text{Gd}_2\text{Cu}_2\text{O}_z$. This sample is stable when it is annealed in both O_2 and air. But, it does not superconduct, either, whether it is annealed in air or O_2 . The valence states of Cu for $(\text{Pb}_{0.5}\text{Cd}_{0.5})(\text{Sr}_{1.2}\text{La}_{0.8})\text{Gd}_2\text{Cu}_2\text{O}_z$ annealed in air and O_2 are 2.12 and 2.16, respectively, from the iodometric titration measurement. It is suggested that the fact that the Pb-1222 samples do not superconduct is not caused by low charge carrier concentration. In our previous work, we have demonstrated that (Pb,Cd)-1212 can superconduct in appropriate synthesis conditions. Therefore, we think that the fact that the Pb-1222 phase is not superconducting may be caused by the Gd_2O_2 layers. To our knowledge, the superconductivity of all high- T_c oxide superconductors deteriorates when their oxygen-deficient (Y,Ca) layer is replaced by Ln_2O_2 layers. First, the coupling effect between adjacent CuO_2 planes weakens when the (Y,Ca) layer is replaced by the thick Ln_2O_2

layers sandwiched between two adjacent CuO_2 planes. The superconductivity of high- T_c oxides strongly depends on the spacing distance between adjacent CuO_2 planes. Second, the substitution of the oxygen-deficient (Y, Ca) layer by Ln_2O_2 layers flattens the conducting CuO_2 planes for these layered cuprates containing two CuO_2 planes. This can be seen from the bond angles of Cu-O(1)-Cu within the conducting CuO_2 planes. The bond angles of Cu-O(1)-Cu for Pb-1222 and (Pb, Cd)-1212 have been calculated from the refined structure parameters, and are listed in table 3. For comparison, the bond angles of Cu-O(1)-Cu for other 1212 and 1222 phases have been calculated, too. From the bond angles of Cu-O(1)-Cu for these 1212 and 1222 phases, we found that the introduction of Ln_2O_2 layers, indeed, flattens the buckled CuO_2 planes for most cases, which may lead to the deterioration of the superconductivity of these 1212 phases, although the buckling degree of conducting CuO_2 planes is not monotonically correlated with the superconducting transition temperatures of those layered copper oxides. Third, the Ln_2O_2 layers may provide electron-type carriers as in $(\text{Nd, Ce})_2\text{CuO}_4$. From the above, we can conclude that the layer sandwiched between adjacent CuO_2 planes is a critical factor in controlling the superconductivity of copper oxides.

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