Synthesis and Properties of $TiSr_2(RE_{1-x}Ce_x)_2Cu_2O_z$ (RE = Sm, Eu, Gd)

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Abstract

The result of the synthesis for $TiSr_2(RE_{1-x}Ce_x)_2Cu_2O_z$ (Ti-1222) (RE = Sm, Eu, Gd) are reported. The single phase of Ti-1222 were not synthesized under ambient pressure, but three phased samples with Ti-1222 and $SrTiO_3$, CeO_2 were obtained. The crystal structures for Ti-1222 phases were analyzed using X-ray diffraction data. Resistivity measurements for the all samples showed insulating behaviors.

Key words: Ti-1222;Titanium-Cuprate;Superconducting related materials;Structure Refinement

Since the discovery of Superconductivity in $(Ln,Ce)_2(Ba,Ln)_2Cu_3O_{10}$[1], several types of 1222-type copper oxide series has been synthesized, such as $MSr_2(Ln,Ce)_2Cu_2O_z$ (M = Bi[4], Pb[3], Tl[2], Fe[5], Ru[6], In[7]). These homologous series consisted with the fluorite block, $[(Ln,Ce)_2O_2]$ and charge reservoir, MO-layer. Rukang *et.al.* [8] reported that the Ti based 1222 series of $TiSr_2(Ln,Ce)_2Cu_2O_y$ (Ln = Pr, Nd). These Ti-1222 compounds were semiconductor behavior. In this experiments, we have synthesized rare earth substituted Ti-1222 phase, $TiSr_2(RE_{1-x}Ce_x)_2Cu_2O_y$ (RE = Sm, Eu, Gd; x = 0.3) and reported crystal structure and resistivity measurements.

The samples were prepared by solid state reaction from CuO_2, $SrCO_3$, TiO_2, CeO_2, Sm_2O_3, Eu_2O_3 and Gd_2O_3. The mixed powder are calcined at 960 $\sim$ 1000°C in air or Ar gas. They were reground, pelletized and fired at 1050°C in O_2 gas flow. We also make high pressure firing under 3.5GPa at 1050°C, but Ti-1222 was not synthesized in this condition. The obtained samples were characterized by powder X-ray diffraction with Cu Kα radiation (RINT system, Rigaku). The range of the XRD was from 20° to 100° in 2θ and step width was 0.04°. The resistivities were measured using a standard four-probe DC method above 20K.

The X-ray diffraction pattern of all samples showed the Ti-1222 phase as well as two impurities. These impurity phases were identified as $SrTiO_3$ and CeO_2.

The multi-phase Rietveld analysis was using RIETAN-2000 program.[9] The structure models of Ti-1222 are based on tetragonal M-1222 structure with the space group I4/mmm (No.139). The atomic coordinate are Ti in 2a (0, 0, 0) Cu(2), Sr, M', O(2) in 4e (0, 0, z) O(1) in 4c (0, $\frac{1}{2}$, 0) O(3) in 8g (0, $\frac{1}{2}$, z) O(4) in 4d (0, $\frac{1}{2}$, $\frac{1}{4}$). The occupation factors, g, of RE and Ce for the M' site were fixed at 0.7 and 0.3, respectively.

In course of refinement, the result suggested that the Ti site was partially substituted by Cu atom. It is in good agreement with the existence of the $SrTiO_3$ in diffraction pattern. Therefore, we assigned Ti and Cu(1) atom at same site and linear constraint was imposed on the occupation factor, g: $g_{Cu(1)}$ = 1 - g_{Ti}. According to the large thermal parameter, O(1) atom on z = 0 plane was shifted from 4c site to split site 8j site (x, $\frac{1}{2}$, 0) and refined the occupation factor. It is difficult to refine simultaneously the occupation factor and the atomic coordinate in oxygen atom, we fixed the occupation factor of O(1) site. Finally, the thermal parameter, B, of all oxygen sites were fixed 1.0.

Table 1 list the final lattice constants and structure parameters of the $(Ti,Cu)Sr_2(RE_{0.7}Ce_{0.3})_2Cu_2O_y$.

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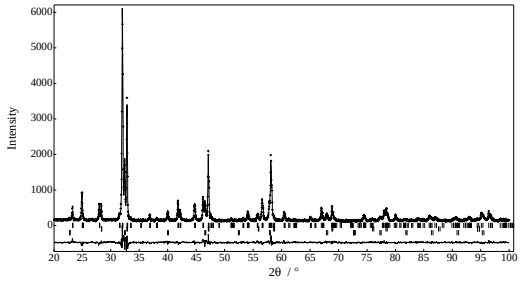

Fig. 1. The Rietveld patterns for (Ti,Cu)$Sr_2(Sm_{0.7}Ce_{0.3})_2Cu_2O_y$. The dots and the continuous lines shows the raw diffraction and calculated data, respectively. The difference between the observed and calculated intensities are displayed the bottom of therefore. The short vertical lines mark the position of the bragg peaks of Ti-1222 (upper), CeO_2 (middle) and $SrTiO_3$ (lower).

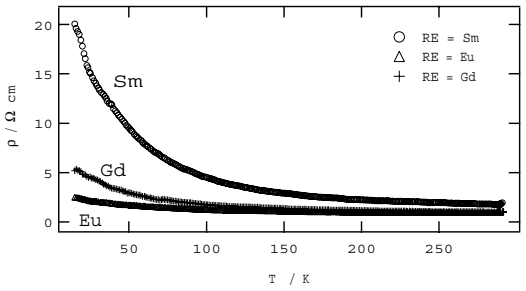

Fig. 2. The temperature dependence of the resistivity for (Ti,Cu)$Sr_2(RE_{0.7}Ce_{0.3})_2Cu_2O_y$ (RE = Sm, Eu, Gd).

The mass fractions of each phases evaluated from scale factors are also presented in Table 1.

Figure 2 shows the temperature dependence of resistivity of (Ti,Cu)$Sr_2(RE_{0.7}Ce_{0.3})_2Cu_2O_z$. All samples showed the insulating behavior in all temperature range and did not showed superconducting above 20K.

The valence of Cu(2) site calculated using the bond valence sum[10] calculation from structural parameters is 2.24 in Sm sample. This is not so high in cuprate superconductors, however the sample showed the insulating behavior. It is difficult to discuss the relation between structure and properties for multi-phased sample. We are now making to synthesize with a modified synthesis condition to obtain a single phase sample.

We have synthesized (Ti,Cu)$Sr_2(RE_{0.7}Ce_{0.3})_2Cu_2O_y$ (RE = Sm, Eu, Gd) and refined the crystal structure parameters. Single phase of Ti-1222 were not synthesized, but three phased samples were obtained in our synthesis conditions.

Table 1
Structural Parameters of (Ti,Cu)$Sr_2(RE_{0.7}Ce_{0.3})_2Cu_2O_y$ (RE = Sm, Eu, Gd). Refined mass fractions of Ti-1222, $SrTiO_3$ and CeO_2 is also listed below.

RE	Sm	Eu	Gd
a/nm	0.385486(14)	0.385098(17)	0.384487(11)
c/nm	2.83511(13)	2.83521(14)	2.83006(11)
g_{Ti}	0.74(10)	0.79(10)	0.60(12)
B_{Ti}/nm^2	0.006(5)	0.017(5)	0.017(5)
$z_{\mathrm{Cu(2)}}$	0.1418(3)	0.1422(3)	0.1426(3)
$B_{\mathrm{Cu(2)}}$/nm^2	0.0136(16)	0.0144(14)	0.0096(15)
z_{Sr}	0.42079(14)	0.42016(12)	0.42005(14)
B_{Sr}/nm^2	0.0031(14)	0.0078(13)	0.0046(14)
$z_{M'}$	0.29444(11)	0.29410(10)	0.29425(11)
$B_{M'}$/nm^2	0.0110(11)	0.0074(9)	0.0086(11)
$g_{\mathrm{O(1)}}$	0.24	0.18	0.20
$x_{\mathrm{O(1)}}$	0.193(16)	0.232(18)	0.265(18)
$z_{\mathrm{O(2)}}$	0.0624(11)	0.0614(9)	0.0615(10)
$z_{\mathrm{O(3)}}$	0.1458(10)	0.1463(8)	0.1466(9)
R_{wp}	8.56%	7.18%	7.84%
R_{p}	6.86%	5.60%	6.10%
R_I(Ti1222)	3.27%	2.57%	2.74%
R_F(Ti1222)	2.59%	2.00%	2.06%
R_{e}	6.60%	5.42%	6.59%
S	1.386	1.326	1.190
Ti-1222	0.807	0.787	0.780
$SrTiO_3$	0.170	0.190	0.190
CeO_2	0.023	0.023	0.031

$M' = RE_{0.7}Ce_{0.3}$ (RE = Sm, Eu, Gd)
$g_{\mathrm{Cu(1)}}$ = 1 - g_{Ti}, $B_{\mathrm{Cu(1)}} = B_{\mathrm{Ti}}$

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