

## A New Series of Layered Pure Perovskites $(ACuO_{2.5})_2(ATiO_3)_m$ <sup>†</sup>

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A new homologous series of layered "pure" perovskites  $(ACuO_{2.5})_2(ATiO_3)_m$  ( $m = 2 \sim 4$ ) was found. The distance between  $CuO_2$  planes can be changed by simply changing the number of  $TiO_6$  blocking layers. Among them,  $LaYCaBa_2Cu_2Ti_3O_{14}$  is a potential new superconductor.

### 1. INTRODUCTION

Copper-oxygen ( $CuO_2$ ) sheets, adequate hole/electron-doping levels and appropriate Cu-O distances have proven to be necessary conditions for high- $T_c$  superconductivity. Over the last several years, our interests have been in the structural/electrical properties of the quadruple perovskites  $Ln_2Ba_2Cu_2M_2O_{11}$  ( $M = Sn, Ti, Ln_2 = La_2 - Tb_2, LaY, NdDy$ ), which have  $CuO_2$  sheets separated by double  $MO_6$  octahedra and can be carrier-doped by substitutions for the cations in the blocking layer [1]. Although the band structure and several features of the internal chemistry, including the amount of holes, are similar to known superconductors, the long in-plane Cu-O distances ( $>1.94\text{\AA}$ ) appear to inhibit superconductivity. Recently, we have discovered the  $m = 3$  and 4 members of the layered "pure" perovskites,  $(ACuO_{2.5})_2(ATiO_3)_m$  [2, 3, 4]. Among them,  $LaYCaBa_2Cu_2Ti_3O_{14}$  has every property in order to show superconductivity.

### 2. EXPERIMENTAL SECTION

All samples were synthesized by usual solid

state reactions [4]. Powder XRD, TGA, magnetic susceptibility, HR-TEM and in-situ electrical conductivity/thermopower measurements were carried out as described before [1].

### 3. RESULTS AND DISCUSSION

The newly found perovskites,  $Ln_2CaBa_2Cu_2Ti_3O_{14}$  and  $Ln_2Ca_2Ba_2Cu_2Ti_4O_{17}$  form with a range of lanthanide ions,  $Ln_2 = La_2 - Dy_2, LaY - DyY$  and  $Ln_2 = Pr_2 - Dy_2$ , respectively. Along with the quadruple perovskites,  $Ln_2Ba_2Cu_2Ti_2O_{11}$  ( $Ln_2 = La_2 - Tb_2, LaY, NdDy$ ), they make a new family which has the generalized formula  $(ACuO_{2.5})_2(ATiO_3)_m$ , where  $m = 2 - 4$ .

In contrast to the many homologous series which have been reported for the intergrowth perovskites, this is the first example of a layered-cuprate "pure"-perovskite family. Whereas  $Ln_2Ba_2Cu_2Ti_2O_{11}$  ( $m = 2$ ) adopts a quadruple perovskite structure,  $Ln_2CaBa_2Cu_2Ti_3O_{14}$  ( $m = 3$ ) and  $Ln_2Ca_2Ba_2Cu_2Ti_4O_{17}$  ( $m = 4$ ) adopt a pentuple and sextuple  $c$ -axis-aligned perovskite structure, respectively [4]. In these structures, two, three or four sheets of  $TiO_6$  octahedra comprise the blocking

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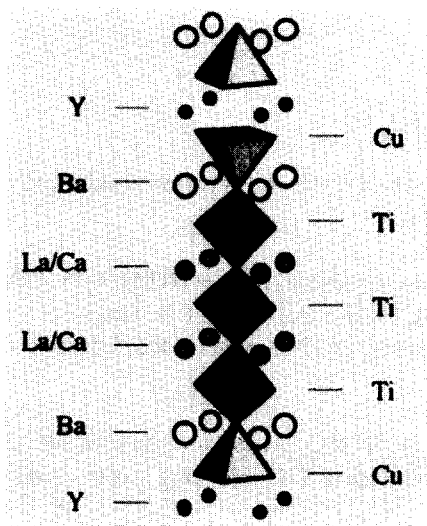


Figure 1. Suggested structure of  $\text{LaYCaBa}_2\text{Cu}_2\text{Ti}_3\text{O}_{14}$ .

layer and separate double planes of  $\text{CuO}_2$  pyramids. Thus the inter- $\text{CuO}_2$  plane distance can be varied by the number ( $m = 2 \sim 4$ ) of  $\text{TiO}_6$  sheets in the blocking layer.

The general formula can also be written as  $\text{Ln}_2\text{Ba}_2\text{Cu}_2\text{Ti}_2\text{O}_{11}(\text{CaTiO}_3)_n$  where  $n = 0 - 2$ , showing that the pentuple and sextuple perovskites are related by the addition of one or two  $\text{CaTiO}_3$  units, respectively, to the quadruple perovskite. The addition of the smaller  $\text{CaTiO}_3$  unit leads to Cu-O distances in the  $m = 3$  and 4 phases which are substantially shorter than that in the quadruple perovskite ( $1.925\text{\AA}$  in  $\text{Tb}_2\text{Ca}_2\text{Ba}_2\text{Cu}_2\text{Ti}_4\text{O}_{17}$ ).

Substituting Y for Ln is also an effective way to shorten the in-plane Cu-O bond length. It also helps ordering so that  $\text{LaYCaBa}_2\text{Cu}_2\text{Ti}_3\text{O}_{14}$  forms a tetragonal quintuple perovskite with the lattice parameters,  $a = 3.8675\text{\AA}$  and  $c = 19.337\text{\AA}$  (Figure 1, 2(a)), although its mother compound  $\text{La}_2\text{CaBa}_2\text{Cu}_2\text{Ti}_3\text{O}_{14}$  has a cubic structure with  $a = 3.9267\text{\AA}$ .

Figure 2(b) shows a TEM image of the oxygen high-pressure treated (HIP treated)  $\text{Eu}_2\text{CaBa}_2\text{Cu}_2\text{Ti}_3\text{O}_{14}$ , which has a quintuple structure under ambient conditions [3]. Obviously, the layered structure is destroyed after treatment. Oxygen insertion between the  $\text{CuO}_2$  planes is considered to be responsible. In  $\text{LaYCaBa}_2\text{Cu}_2\text{Ti}_3\text{O}_{14}$ , however, the small Y ions



Figure 2. TEM images of (a)  $\text{LaYCaBa}_2\text{Cu}_2\text{Ti}_3\text{O}_{14}$  and (b)  $\text{Eu}_2\text{CaBa}_2\text{Cu}_2\text{Ti}_3\text{O}_{14}$  (oxygen high-pressure treated (HIP)).

narrow the spacing between the  $\text{CuO}_2$  planes which can prevent oxygen diffusion.

These results and observations make  $\text{LaYCaBa}_2\text{Cu}_2\text{Ti}_3\text{O}_{14}$  an attractive candidate for a new superconductor.

#### 4. REFERENCES

1. P. A. Salvador et al, to be published in J. Am. Chem. Soc. and references therein.
2. W. J. Zhu et al., Mat. Res. Bull, **30** (1995) 243 - 246.
3. P. A. Salvador et al., to be published in proceedings of the 1996 Materials Research Society Fall Meeting in Boston, Solid-State Chemistry of Inorganic Materials.
4. Kenji D. Otzchi et al., J. Am. Chem. Soc., **118** (1996) 8951 - 8952.