



## The high-pressure synthesis and characterization of some praseodymium-substituted rare-earth based $R_2Ba_4Cu_7O_{14+\delta}$ ( $R = Nd, Sm, Eu, Gd, Ho, Tm$ )\*

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Samples of the  $(R_{1-x}Pr_x)_2Ba_4Cu_7O_{14+\delta}$  ( $R = Nd, Sm, Eu, Gd, Ho, Tm$ ; Pr-doped R247) systems with  $x = 0$  to 1.0 and with an increment of 0.1 in  $x$  was investigated. Single-phased samples were obtained with substitution limit equal to 0.4, 0.6, 0.5, 0.6, 0.8 and 0.5 for phases with  $R = Nd, Sm, Eu, Gd, Ho$  and  $Tm$ , respectively, as indicated by x-ray diffraction (XRD) data.  $T_c$ 's of the Pr-doped R247 phases were found to be suppressed from 66, 69, 75, 70, 92 and 88K down to 41K ( $x=0.3$ ), 20 K ( $x= 0.4$ ), 52K( $x=0.4$ ), 18K ( $x= 0.5$ ), 8K ( $x= 0.7$ ) and 50K ( $x = 0.4$ ) and the corresponding composition coefficients of  $T_c$ ,  $dT_c/dx$ , were found to be -41.3, -50.4, -28.0, -47.7, -53.0 and -46.0 K/Pr-atom per formula unit for Pr-doped R247 phases with  $R = Nd, Sm, Eu, Gd, Ho$  and  $Tm$ , respectively. The variation of  $T_c$  and  $|dT_c/dx|$  coefficients of the Pr-doped R247 phases upon Pr doping are described and their implications are discussed.

### 1. INTRODUCTION

The effect of Pr substitution for Y on the superconducting properties of the  $Y_2Ba_4Cu_{6+n}O_{14+n-\delta}$  ( $n = 1, 2, 3$ ) homologous series has been extensively investigated and the superconductivity in these cuprates were found dramatically suppressed, which reveals a contrast to the similar substitution by other rare-earths. However, to our knowledge there have been limited number of investigations reported in the literature regarding the Pr substitution in the  $R_2Ba_4Cu_7O_{14+\delta}$  ( $R =$  rare earths other than Y) phases, with the exceptions of those (*i.e.*, Pr-substituted R247,  $R = Y, Er, Dy$ ) studied by Tarntair et al. [1] We have extended our efforts to further investigate the crystal chemistry and the possible size effect of  $R^{3+}$  on the superconductivity of Pr-doped R247 phases.

In this paper we summarize the results of our study on the crystal structural and physical properties of six series of Pr-doped R247 phases and the size effect of  $R^{3+}$  on the suppression of  $T_c$  of title phases is also discussed.

### 2. EXPERIMENTAL

The method of sample preparation of the three Pr-doped R247 series was previously reported.[2] The oxygen content of samples was determined by a modified iodometric titration method.[3] The lattice

parameters were estimated from XRD data obtained from an automatic powder diffractometer. The field-cooled dc magnetic susceptibility (Meissner effect) was measured with a dc SQUID magnetometer over the temperature range of 100-5 K under a field of 1.5 mT.

### 3. RESULTS AND DISCUSSIONS

Samples of the Pr-doped  $(R_{1-x}Pr_x)_2Ba_4Cu_7O_{14+\delta}$  phases with  $x$  smaller than 0.4, 0.6, 0.5, 0.6, 0.8 and 0.5, respectively, were found to be single-phased and the substitution limit of Pr for R atoms was also determined to be 0.3-0.4, 0.5-0.6, 0.4-0.5, 0.5-0.6, 0.7-0.8 and 0.4-0.5 for  $R = Nd, Sm, Eu, Gd, Ho$  and  $Tm$ , respectively, as indicated by x-ray diffraction data. With increasing Pr content the crystallographic orthorhombicity (*i.e.*,  $2(b-a)/(b+a)$ ) of unit cell was found to reduce significantly and the structural anisotropy of the title R247 lattice was found to decrease for all six series of R247 phases investigated.

The  $T_c$ 's, as determined from field-cooled magnetization measurements (Meissner effect) on samples of Pr-doped R247 ( $R = Nd, Sm, Eu, Gd, Ho, Tm$ ), are plotted as a function of Pr content ( $x$ ) and summarized in Fig.1. In general,  $T_c$  was found to decrease with increasing Pr content for all R247.

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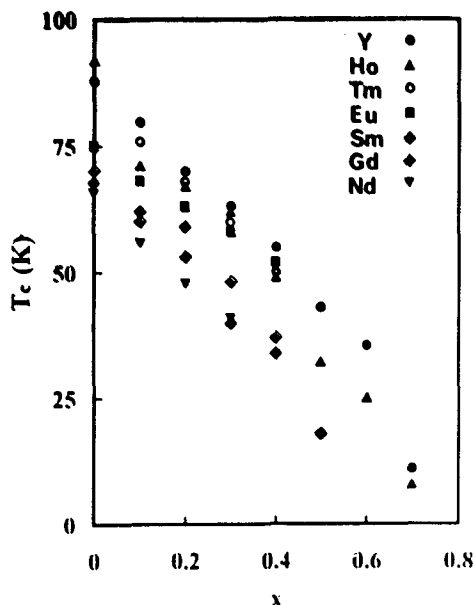


Fig. 1.  $T_c$  as a function of Pr content ( $x$ ) for Pr-doped R247 phases with  $R = Y, Nd, Sm, Eu, Gd, Ho,$  and  $Tm$ .

However, the oxygen stoichiometry of Pr-doped R247 with different R's tends to vary slightly or decreases with increasing  $x$ , as indicated by iodometric titration data.

In an attempt to investigate the effect of Pr doping on the superconductivity of R247 phases, the composition coefficient of  $T_c$ ,  $|dT_c/dx|$  for all Pr-doped R247 was then calculated from Fig. 1. The  $|dT_c/dx|$  coefficient was estimated to be 41.7, 50.4, 28.0, 47.7, 53.0 and 46.0 K/Pr atom per formula unit (f.u.) for Pr-doped 247 phases with  $R = Nd, Sm, Eu, Gd, Ho$  and  $Tm$ , respectively. Four of these values appear to be much greater as compared to that of Pr-doped Y247 phases (*i.e.*, 43.9 K/Pr atom per f.u.) reported earlier.[1] To further study the size effect of  $R^{3+}$  on and the trend of the variation of  $T_c$ , the coefficient of  $|dT_c/dx|$  was plotted as a function of ionic radii of  $R^{3+}$  for Pr-doped R247 phases and represented in Fig. 2. However, we did not observe any systematic correlation between  $R^{3+}$ -size and the  $|dT_c/dx|$  coefficients. Our observations may suggest that the difference of oxygen compositions and inhomogeneous distribution of oxygen are likely to exist in most of Pr-doped R247 samples investigated in this work.

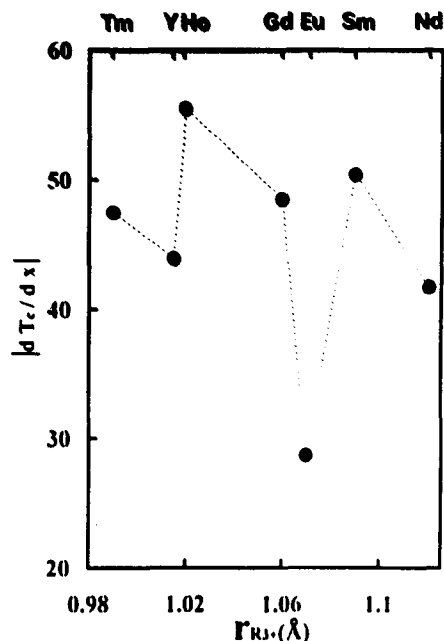


Fig. 2. The  $|dT_c/dx|$  coefficient for Pr-doped R247 phases with  $R = Y, Nd, Sm, Eu, Gd, Ho$  and  $Tm$ .

#### 4. CONCLUSIONS

The substitution limits of Pr for R of Pr-doped R247 cuprates were determined to be less than 0.4, 0.6, 0.5, 0.6, 0.8 and 0.5 for  $R = Nd, Sm, Eu, Gd, Ho$  and  $Tm$ , respectively. With increasing Pr dopant content both  $T_c$  and the crystallographic orthorhombicity of the Pr-doped R247 phases were found to decrease monotonically. The variation of  $T_c$  was found to be strongly correlated to both dopant and oxygen contents for all of the Pr-doped R247 series. No systematic correlation between  $R^{3+}$ -size and  $|dT_c/dx|$  was observed in the six Pr-doped R247 series.

#### REFERENCES

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