The high-pressure synthesis and characterization of some praseodymium-substituted rare-earth based $R_2\text{Ba}_4\text{Cu}_7\text{O}_{14+\delta}$ ($R = \text{Nd, Sm, Eu, Gd, Ho, Tm}$)*

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Samples of the $(R_{1-x}\text{Pr}_x)\text{Ba}_4\text{Cu}_7\text{O}_{14+\delta}$ ($R = \text{Nd, Sm, Eu, Gd, Ho, Tm}$; Pr-doped $R_247$) 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, 0.6, 0.8 and 0.5 for phases with $R = \text{Nd, Sm, Eu, Gd, Ho and Tm}$, respectively, as indicated by x-ray diffraction (XRD) data. $T_c$'s of the Pr-doped $R_247$ 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 $R_247$ phases with $R = \text{Nd, Sm, Eu, Gd, Ho and Tm}$, respectively. The variation of $T_c$ and $dT_c/dx$ coefficients of the Pr-doped $R_247$ 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 $Y_2\text{Ba}_4\text{Cu}_6\text{O}_{14+\delta}$ ($n = 1, 2, 3$) 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 $R_2\text{Ba}_4\text{Cu}_7\text{O}_{14+\delta}$ ($R = \text{rare earths other than Y}$) phases, with the exceptions of those (i.e., Pr-substituted $R_247$, $R = \text{Y, Er, Dy}$) studied by Tamtaat 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 $R_247$ phases.

In this paper we summarize the results of our study on the crystal structural and physical properties of six series of Pr-doped $R_247$ 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 $R_247$ 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 magnetization 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 $(R_{1-x}\text{Pr}_x)\text{Ba}_4\text{Cu}_7\text{O}_{14+\delta}$ phases with $x$ smaller than 0.4, 0.6, 0.5, 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 $R = \text{Nd, Sm, Eu, Gd, Ho and Tm}$, 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 $R_247$ lattice was found to decrease for all six series of $R_247$ phases investigated.

The $T_c$'s, as determined from field-cooled magnetization measurements (Meissner effect) on samples of Pr-doped $R_247$ ($R = \text{Nd, Sm, Eu, Gd, Ho, Tm}$), 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 $R_247$. 

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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 $|dT_c/dx|$ 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.

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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