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

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Abstract

The stability of phases in the $(R_{1-x}Pr_x)_2Ba_4Cu_7O_{14+\delta}$ ($R = Sm, Gd, Ho$; Pr-doped R247) systems with $x = 0$ to 1.0 and with an increment of 0.1 in x was investigated. Samples of the title Pr-doped R247 phases were prepared at 980–990°C under 20–36 bar of oxygen atmosphere, followed by long-time annealing at 300–320°C under 110–115 bar of oxygen. Single-phased samples were obtained with substitution limit (x) equal to 0.5, 0.6 and 0.7 for phases of the title $(R_{1-x}Pr_x)_2Ba_4Cu_7O_{14+\delta}$ series with $R = Sm, Gd$ and Ho , respectively, as indicated by X-ray diffraction data. With increasing Pr content (x) both the lattice parameters and unit-cell volume were found to increase monotonically and, however, the corresponding crystallographic orthorhombicity, $2(b-a)/(b+a)$, was found to decrease with increasing x for all three Pr-doped series. The T_c of the Pr-doped R247 phases were found to be suppressed from 69, 70 and 92 K down to 20 K ($x = 0.4$), 18 K ($x = 0.5$) and 8 K ($x = 0.7$) for Pr-doped R247 phases with $R = Sm, Gd$ and Ho , respectively. The composition coefficients of T_c , dT_c/dx , were found to be -50.4 , -48.5 and -55.5 K/Pr-atom per formula unit for the title Pr-doped R247 series with $R = Sm, Gd$ and Ho , respectively. The crystal structure, temperature-dependent resistivity and magnetization data of the Pr-doped R247 phases synthesized in our study are described and their implications are discussed. © 1997 Elsevier Science B.V.

Keywords: Substitution effect; Meissner effect; High-pressure synthesis of $(R,Pr)_2Ba_4Cu_7O_{14+\delta}$

1. Introduction

The effect of Pr substitution for Y on the structural and superconducting properties of the $n = 0$ [1–3], $n = 1$ [4–6] and $n = 2$ [7–10] members of the $Y_2Ba_4Cu_{6+n}O_{14+n-\delta}$ homologous series have been

extensively investigated and the superconductivity in these cuprates were found to be dramatically suppressed, which reveals a contrast to the substitution by other rare earths. There have been different as well as controversial interpretations proposed to rationalize the dramatic effect of superconductivity suppression due to Pr doping. For instance, hole-filling and magnetic pairing-breaking models were suggested by Soderholm et al. [1] and Peng et al. [2], respectively, to explain their observations of super-

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conducting transition temperature (i.e. T_c) depression in the $(Y_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$ system. On the other hand, Fink et al. [11] proposed the carrier-localization model which was attempted to rationalize similar observations.

However, to our best knowledge there have been a limited number of, if not none, investigations reported in the literature regarding the Pr substitution in the $R_2Ba_4Cu_7O_{14+\delta}$ phases (R247, R = rare earths other than Y), which was found to crystallize in a structure consisting of intergrown $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$ subunits [12]. The only exceptions are those (i.e. Pr-substituted R247, R = Y, Er, Dy) studied by Tarntair et al. [13]. We have extended our efforts to investigate the preparation, structures and, in particular, the size effect of R^{3+} on superconductivity of Pr-doped rare-earth based R247 phases since the study of the $(Y_{1-x}Pr_x)_2Ba_4Cu_7O_{14+\delta}$ series was initiated in our group [13]. There has been a large number of studies reported regarding R247 phases with R partially or fully substituted by Pr. For instance, $Pr_2Ba_4Cu_7O_{14+x}$ was reported to be metallic but not superconducting down to 4.2 K by Yamada et al. [14]. Investigations of several series of $(R_{1-x}Pr_x)_2Ba_4Cu_7O_{14+\delta}$ phases with R = Y, Dy and Er [13,15], and Nd, Eu and Tm [16] have also been reported by our group. In general, when R in R247 phases was partially substituted by Pr, T_c of the parent phases were gradually suppressed with increasing Pr content.

The strength of the Pr doping effect on the superconductivity of various R247 phases is generally represented by a composition coefficient of T_c , i.e. $|dT_c/dx|$, with which the strength of the Pr doping effect on T_c of R247 can be compared among various R247 series with different R. On the other hand, in addition to Pr dopant content, oxygen stoichiometry is also one of the crucial factors in determining T_c of Pr-doped R247 phases. We have therefore investigated the possibility of a variation of the oxygen composition in R247 upon Pr doping. Iodometric titration data indicated that oxygen stoichiometry of Pr-doped samples varied with different extents for R247 phases. For example, the ranges of oxygen composition were determined to be 14.765–14.906, 14.525–14.603, 14.632–14.788 and 14.652–14.732 for the Pr-doped R247 phases with R = Y [15], and Nd, Eu and Tm [16], respectively. With a

better understanding of the materials parameters such as oxygen composition, dopant content and T_c , it will be easier for us to rationalize and understand the observations of T_c depression upon Pr doping in different series of R247 phases.

The synthesis of Pr-doped R247 phases has provided us with an opportunity to probe the origin of T_c depression and structure changes upon Pr doping. Furthermore, the possible correlations between magnetic properties of doped Pr ion and R^{3+} ions and high-temperature superconductivity of R247 phases can be understood. In this paper we describe the synthesis, oxygen compositions, structural and physical properties of three series of Pr-doped R247 phases with R = Sm, Gd, and Ho, respectively. The possible size effect of R^{3+} on the suppression of T_c of title phases is also discussed.

2. Experimental

Samples of the three title $(R_{1-x}Pr_x)_2Ba_4Cu_7O_{14+\delta}$ series were synthesized by reacting a stoichiometric amount of R_2O_3 (R = Gd, Sm, Ho), $Ba(NO_3)_2$, CuO and Pr_6O_{11} under high temperature and high pressure conditions. The optimal conditions to obtain X-ray pure single phases have been summarized in Table 1. The Pr-doped R247 phases appear to exist in a limited range of pressure, whereas their stabilities are less sensitive to temperature variation.

The oxygen contents of samples of the $(Ho_{1-x}Pr_x)_2Ba_4Cu_7O_{14+\delta}$ series with $0 \leq x \leq 0.7$ have been determined by a modified iodometric titra-

Table 1
Optimal conditions for the preparation of $(R_{1-x}Pr_x)_2Ba_4Cu_7O_{14+\delta}$ (R = Sm, Gd, Ho) phases using a high-pressure reactor

	R		
	Ho	Gd	Sm
Sintering temperature (°C)	980–986	980–990	980–985
Oxygen pressure (bar)	19–21	28.5–30.5	35.8–37.5
Duration (h)	20–24	20–24	20–24
Annealing temperature (°C)	300–320	300–320	300–320
Oxygen pressure (bar)	110–115	110–115	110–115
Duration (h)	36–48	36–48	36–48

tion method previously described by Appelman et al. [17]. The XRD patterns of samples were obtained from an automatic powder diffractometer (Mac Science MXP3, Japan) using a graphite-monochromatized Cu K α radiation and equipped with a Ni filter. The temperature-dependent electrical resistivity was measured on sintered bar-specimens by a DC (10 mA) four-probe method. The field-cooled DC magnetic susceptibility (Meissner effect) was measured with a DC SQUID magnetometer (MSMP system, Quantum Design, USA) over the temperature range of 100–5 K under a field of 1.5 mT. The SEM micrographs of $(R_{1-x}Pr_x)_2Ba_4Cu_7O_{14+\delta}$ (R = Ho, Gd) phases were taken on a Hitachi model S-400 field emission scanning electron microscope.

3. Results and discussion

Samples of the Pr-doped $(R_{1-x}Pr_x)_2Ba_4Cu_7O_{14+\delta}$ phases with $x \leq 0.5, 0.6$ and 0.7 were found to be single-phased and the substitution limit of Pr for R atoms was simultaneously determined to be $0.4\text{--}0.5, 0.6\text{--}0.7$ and $0.7\text{--}0.8$ for R = Gd, Sm, and Ho, respectively, as indicated by X-ray diffraction

data. The diffraction peak due to impurity appearing at $2\theta = 28.78^\circ$ was attributed to $BaPrO_3$ in addition to the Pr-doped R247 phases when the substitution limit was exceeded, as indicated by XRD data. Typically, a systematic shifting of major peaks in the XRD patterns of all the three Pr-doped R247 phases was observed in our investigations. For simplicity we have shown in Fig. 1 the XRD patterns of the $(Ho_{1-x}Pr_x)_2Ba_4Cu_7O_{14+\delta}$ ($x = 0\text{--}0.8$) series in which a systematic shifting of eight major peaks ($30^\circ \leq 2\theta \leq 40^\circ$) towards the lower 2θ side was observed. Unit cell expansion was clearly observed in Pr-doped Ho247 phases when the smaller Ho^{3+} ion was gradually substituted by a larger Pr ion, as revealed by XRD data. We have also found that both the pristine and Pr-doped R247 phases only exist in a relatively narrow range of pressure (i.e. 19–38 bar of oxygen), whereas their stability is less sensitive to temperature variation when pressure is controlled in the optimal range.

Summarized in Fig. 2 are the lattice parameters a, b, c , and the unit cell volume of the three Pr-doped R247 phases determined from the XRD data by using a least-square refinement method. The dimensions of a, b, c , and volume of all three Pr-doped

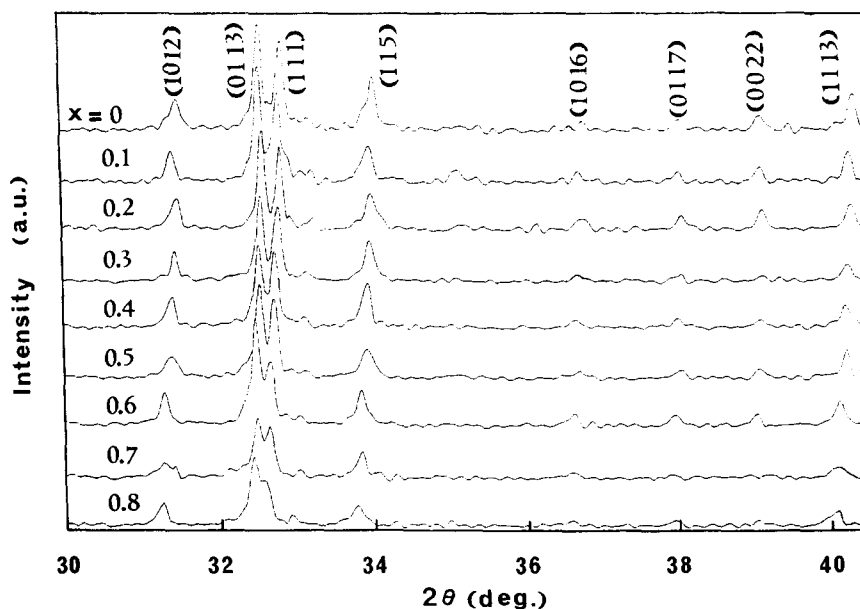


Fig. 1. The systematic shifting of major peaks located at $2\theta = 30\text{--}42^\circ$ in XRD patterns of $(Ho_{1-x}Pr_x)_2Ba_4Cu_7O_{14+\delta}$ phases with $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7$ and 0.8 , respectively.

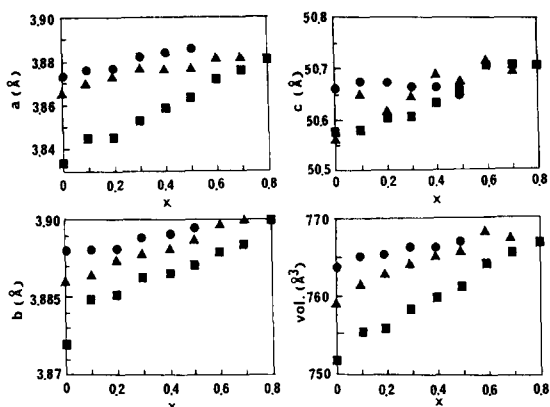


Fig. 2. The lattice parameters a , b , c and cell volume of Pr-doped R247 phases as a function of Pr content (x) for $R = \text{Gd}$ (\blacktriangle), Sm (\bullet) and Ho (\blacksquare), respectively.

R247 phases were found to expand monotonically with increasing Pr contents, with the c -parameter varying slightly irregularly. This observation may suggest that the Pr ion is to be present in a valence state of $3+$, because the ionic radius of eight-coordinated Pr^{3+} (Pr^{4+}) is relatively larger (smaller) than that of any of the following R^{3+} ions with the same coordination number, i.e. Pr^{4+} (0.96 \AA) $<$ Y^{3+} (1.015 \AA) \approx Ho^{3+} (1.02 \AA) $<$ Gd^{3+} (1.06 \AA) $<$ Sm^{3+} (1.09 \AA) $<$ Pr^{3+} (1.14 \AA) [18]. An opposite trend of cell dimension variation would have been observed if the Pr ions were to be present in a valence state of $4+$ since they are significantly smaller than any of the Sm^{3+} , Gd^{3+} and Ho^{3+} ions. For the same reason the possibility that Pr substituted for Ba and entered the Ba-sites has been ruled out.

Represented in Fig. 3 is the variation of structural anisotropy (i.e. orthorhombicity) of the Pr-doped R247 phases as a function of Pr content. We have noticed that the crystallographic orthorhombicity (i.e. $2(b-a)/(b+a)$) of the unit cell was found to reduce significantly with increasing Pr content for R247 phases with $R = \text{Sm}$ and Ho , whereas phases with $R = \text{Gd}$ showed a scattered distribution as Pr content increases. Our observations indicated that the structural anisotropy of the title R247 phases decreases upon Pr substitution, the same trend has also been reported in other Pr-doped R247 series with $R = \text{Y}$, Dy and Er [13] and Nd , Eu , and Tm [16], respectively.

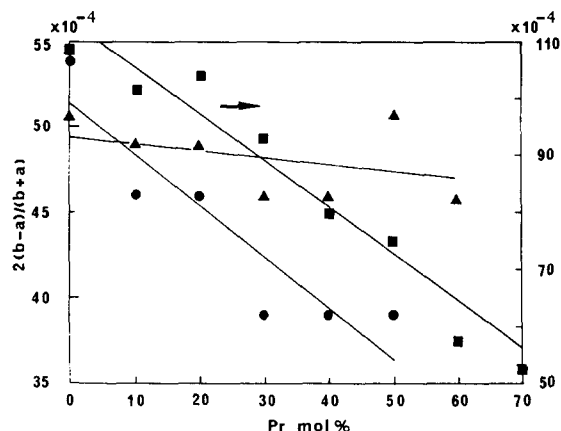


Fig. 3. The variation of orthorhombicity as a function of Pr content (x) for Pr-doped R247 phases with Gd (\blacktriangle) Sm (\bullet) and Ho (\blacksquare), respectively.

Shown in Fig. 4 are the temperature-dependent resistivity data for the title Pr-doped R247 phases. Normal-state resistivity ($\rho_{298 \text{ K}}$) was found to in-

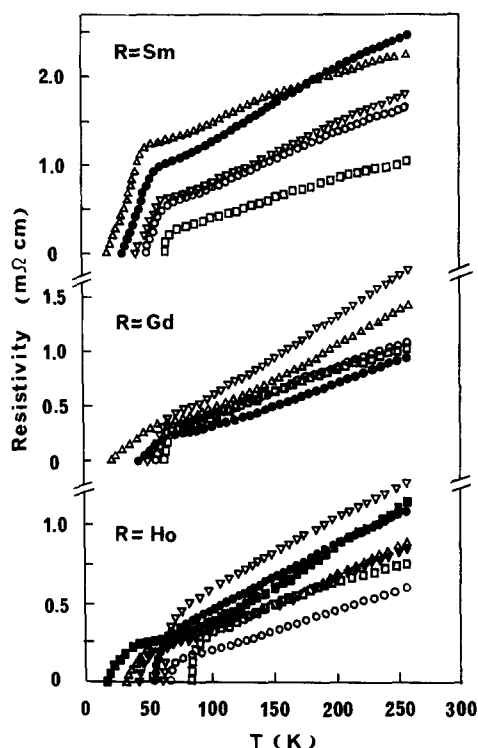


Fig. 4. The electrical resistivity as a function of temperature for samples of the $(\text{R}_{1-x}\text{Pr}_x)_2\text{Ba}_4\text{Cu}_7\text{O}_{14+\delta}$ ($R = \text{Gd}, \text{Sm}, \text{Ho}$) series with $x = 0$ (\square), 0.1 (\circ), 0.2 (∇), 0.3 (\bullet), 0.4 (\triangle), 0.5 (∇) and 0.6 (\blacksquare), respectively.

Table 2

Comparison of T_c and ΔT_c as a function of x for samples of the $(R_{1-x}Pr_x)_2Ba_4Cu_7O_{14+\delta}$ ($R = Sm, Gd, Ho$) phases

	x							
	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7
R = Sm								
T_c	69	62	58	40	36	20	–	–
ΔT_c	4	12	18	24	25	–	–	–
R = Gd								
T_c	70	60	53	48	37	18	–	–
ΔT_c	4	8	15	22	25	–	–	–
R = Ho								
T_c	92	71	67	62	49	32	25	–
ΔT_c	8	12	13	15	16	18	20	–

crease systematically with increasing Pr content only in the series of Pr-doped Sm247 phases, whereas no such trend was observed in the corresponding Pr-doped Gd247 or Ho247 series. Summarized in Table 2 is the comparison of T_c and ΔT_c (i.e. $T_{c,onset} - T_{c,zero}$) as a function of x for samples of $(R_{1-x}Pr_x)_2Ba_4Cu_7O_{14+\delta}$ ($R = Sm, Gd, Ho$) phases. Within each series T_c of the Pr-doped R247 phases was found to decrease monotonically with increasing Pr content for all samples with $R = Sm, Gd$ and Ho , respectively. At constant x , T_c of the Pr-doped R247 phases decreases linearly with increasing radius of the R ion. The width of superconducting transition (i.e. ΔT_c) for the Pr-doped R247 phases was found to broaden as the content of Pr dopant increases, as indicated by the temperature-dependent resistivity data. In addition, the correlation between T_c and empirical oxygen content, which can be translated into hole concentrations, for the Pr-doped Ho247 series is summarized in Table 3. The depression of T_c can not be attributed to simple reasons since the empirical oxygen contents ($14 + \delta$) were found to decrease from 14.891 to 14.482 as nominal Pr content (i.e. x) increases from 0 to 0.60. Both oxygen and Pr compositions in samples of the $(Ho_{1-x}Pr_x)_2Ba_4Cu_7O_{14+\delta}$ series are very likely to be dependent of each other.

The results of field-cooled temperature-dependent magnetization measurements on the samples of Pr-doped R247 phases are shown and summarized in Fig. 5. The transition temperatures (T_c) determined from the Meissner effect are in good agreement with

Table 3

The correlation between T_c and oxygen content ($14 + \delta$) for samples with nominal composition of $(Ho_{1-x}Pr_x)_2Ba_4Cu_7O_{14+\delta}$

x (%)	δ^a	T_c (K)
0	0.8906	92
10	0.8279	71
20	0.8762	67
30	0.8113	62
40	0.6645	49
50	0.5148	32
60	0.4819	25

^a Relative standard deviation in δ is < 5% except that of the specimen with $x = 0.5$ whose standard deviation in δ is 12%.

those obtained from temperature-dependent resistivity data represented in Fig. 4. The volume fraction of superconducting Pr-doped R247 phases was found to decrease systematically with increasing Pr content for samples with all R.

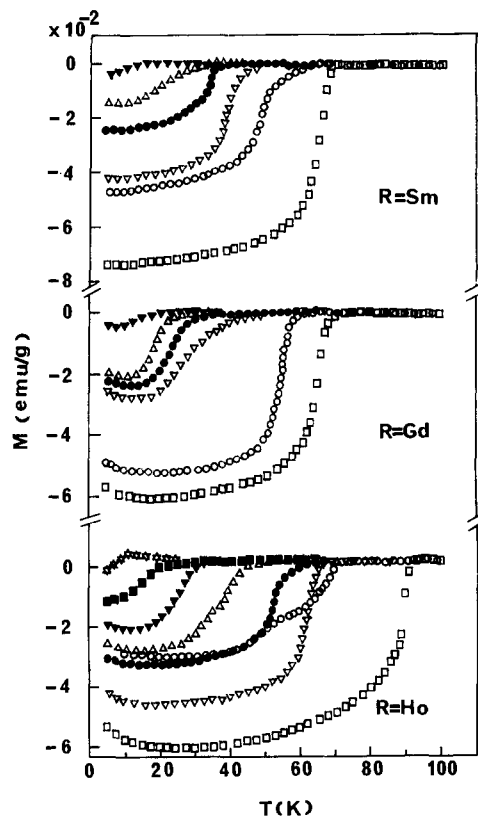


Fig. 5. The field-cooled temperature-dependent magnetic susceptibility M for samples of $(R_{1-x}Pr_x)_2Ba_4Cu_7O_{14+\delta}$ ($R = Gd, Sm, Ho$) with $x = 0$ (\square), 0.1 (\circ), 0.2 (∇), 0.3 (\bullet), 0.4 (\triangle), 0.5 (\blacktriangledown), 0.6 (\blacksquare) and 0.7 (\star), respectively.

The composition coefficients of T_c , $|dT_c/dx|$, determined to be 50.4, 48.5 and 55.5 K/Pr atom per formula unit (f.u.) for R-doped 247 phases with R = Sm, Gd and Ho, respectively, appear to be much greater compared to that of Pr-doped Y247 phases (i.e. 43.9 K/Pr atom per f.u.) reported earlier [13]. The Pr content dependence of T_c for Pr-doped R247 phases (R = Y, Sm, Gd, Ho) are summarized and compared in Fig. 6. However, we did not observe any R^{3+} -size dependence of the $|dT_c/dx|$ values in our investigation, as might have been expected for a series of Pr-doped R247 phases with different sizes of R. Our observations may presumably be attributed to the variation of oxygen compositions and inhomogeneous distribution of oxygen in different series of Pr-doped R247 samples.

In order to investigate the effect of high-pressure synthetic conditions on the microstructure, we have carried out SEM morphological studies on samples of two Pr-doped $R_2Ba_4Cu_7O_{14+\delta}$ phases. Shown in Fig. 7a,b are the SEM micrographs with 2000 \times magnification for $(Ho_{0.3}Pr_{0.7})_2Ba_4Cu_7O_{14+\delta}$ and $(Gd_{0.6}Pr_{0.4})_2Ba_4Cu_7O_{14+\delta}$ phases, respectively. In Fig. 7a bar-like and granular grains of irregular morphology were observed for the Pr-doped Ho247 phase. Step growth of the bar-like grains was also clearly observed, indicating the pseudo-laminar nature of the crystal structure of R247 phases. On the other hand, granular grains with diameter ranging from 1–2 to 10 microns were clearly observed in

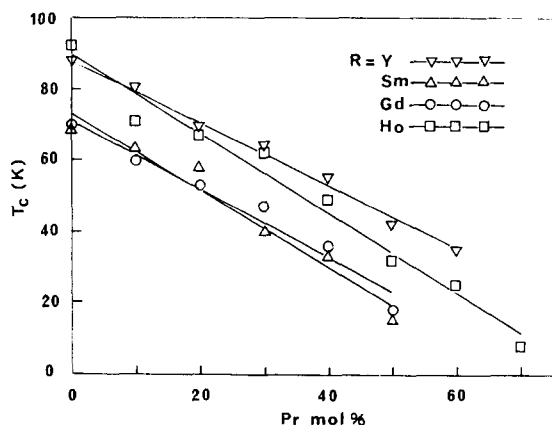


Fig. 6. T_c (determined from Meissner effect) as a function of Pr content (x) for the $(R_{1-x}Pr_x)_2Ba_4Cu_7O_{14+\delta}$ samples with R = Y, Sm, Gd and Ho, respectively.

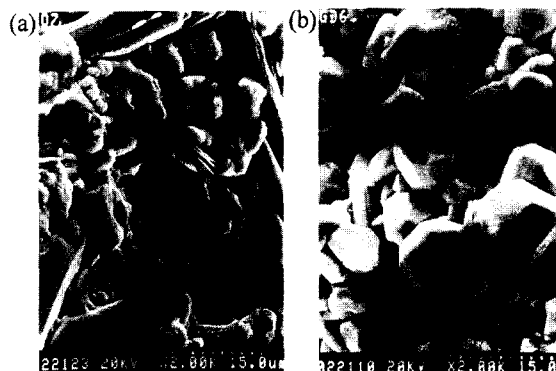


Fig. 7. The SEM micrographs (2000 \times) for (a) $(Ho_{0.3}Pr_{0.7})_2Ba_4Cu_7O_{14+\delta}$ and (b) $(Gd_{0.6}Pr_{0.4})_2Ba_4Cu_7O_{14+\delta}$.

Fig. 7b for the Pr-doped Gd247 phase. The difference in morphology for the two samples investigated was not clear and whether it is related to the content of Pr dopant requires further investigations.

4. Conclusions

Three series of Pr-doped R247 cuprates have been synthesized using high-pressure techniques. The substitution limits of Pr for R were determined to be 0.6, 0.5 and 0.7 for R = Gd, Sm and Ho, respectively, as indicated by XRD data. With increasing Pr dopant content both T_c and the crystallographic orthorhombicity of the Pr-doped R247 phases were found to decrease monotonically, whereas the cell dimensions were found to expand steadily. The variation of T_c was found to be strongly correlated to the dopant content as well as the oxygen content for the Pr-doped Ho247 series. The $|dT_c/dx|$ coefficient was determined to be 50.4, 48.5 and 55.5 for the three Pr-doped R247 series with R = Sm, Gd and Ho, respectively, and no R^{3+} -size dependence of $|dT_c/dx|$ was observed.

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