JOURNAL OF SOLID STATE CHEMISTRY 102, 492–500 (1993)

Superconducting and Nonsuperconducting Ca-Free Single Crystals of $Pb_2Sr_2RCu_3O_8$ (R = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Y): Effect of Cation Vacancies and the Metal/Insulator Transition

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Received April 27, 1992; accepted May 15, 1992

Ca-free single crystal and polycrystalline samples of $Pb_2Sr_2RCu_3O_8$ have been prepared by a PbO/NaCl flux growth method and a fast solid state reaction, respectively. The electronic character of the single crystals of this series can be roughly categorized into three groups: insulating (no carrier doping in the CuO_2 planes) for R = La, Ce, Pr, and Nd, semiconducting for R = Sm, Eu, Gd, and Tb, and poorly metallic for R = Dy, Ho, and Y. Crystals with R = Eu to Ho are found to be superconducting with the exception of Tb. The metallic character in these crystals is likely promoted by a cation vacancy at the rare-earth sites which has been established by crystal structural and chemical analyses. The anomalous behavior of the Tb crystals may originate from a lower dopant level as inferred from the structure determination or possibly from the presence of Tb^{4+}. The fact that metallic behavior is observed in nonstoichiometric polycrystalline samples and not in stoichiometric ones seems consistent with the cation vacancy carrier doping mechanism. © 1993 Academic Press, Inc.

I. Introduction

A widely accepted point of view regarding the origin of superconductivity in copper oxides is that a critical concentration of charge carriers on the two-dimensional CuO_2 planes is necessary. The mobile carriers can be created via several mechanisms: (1) chemical substitution of di-, or quadrivalent elements for trivalent elements in the p-type or n-type high-temperature superconductors, respectively; (2) anion vacancies which can be depleted or produced by adjusting the oxygen content in the copper oxides through various annealing procedures; (3) cation vacancies on the noncopper sites; (4) interstitial oxygen, detected in the bismuth 2212 phase (*1*); and (5) an internal redox reaction such as $2Tl^{3+} + Cu^{2+} \rightarrow Tl^{3+} + Tl^{+} + Cu^{3+}$ (or the so-called self-doping mechanism) in the thallium cuprates (*2*). Among them, only mechanisms 1 and 2 are well established. Mechanism 3 is controversial since cation vacancies have been reported only in the 2212 and 2201 phases of the bismuth and thallium cuprates (*3, 4*).

Studies of the lead cuprate superconductors, which are related to the Tl and Bi cuprates, have focused on mechanisms 1 and 2. $Pb_2Sr_2YCu_3O_8$—the so-called prototype 2213 lead cuprate—has been concluded to be a nonsuperconducting insulator (*5–7*) rather than a metal as suggested by band

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0022-4596/93 $5.00

structure calculations (*8*). An attempt to make this compound superconducting via various oxygen annealing procedures was unsuccessful because the holes created by oxygen addition are not transferred to the CuO_2 layers but oxidize the Pb^{II} and Cu^{I} ions in the rocksalt-like PbO–CuO_{δ}–PbO blocks instead (*9*, *10*). The presence of superconductivity in Ca-free compounds is controversial. Superconductivity had been reported in $Pb_2Sr_2RCu_3O_8$ crystals by Cava *et al.* (*5*) but with variable values of T_c (10 ~ 70 K) and poor reproducibility. A $Pb_2Sr_{2.24}Nd_{0.76}Cu_3O_8$ crystal, characterized by Hayri *et al.* (*7*), was nonsuperconducting. Subsequently, Prasad *et al.* (*11*) observed small superconducting volume fractions ranging from 1 to 10% in polycrystalline samples of $Pb_2Sr_2RCu_3O_{8+\delta}$ (R = rare-earth elements, except La and Ce).

We have synthesized a series of $Pb_2Sr_2RCu_3O_8$ (R = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Y) single crystals using a PbO/NaCl flux method (*12*) and determined their crystal structures by single crystal X-ray diffraction (*13*). This Ca-free $Pb_2Sr_2RCu_3O_8$ single crystal series has been found to be a fascinating system for several reasons: (i) it has a rich substitution chemistry, the R sites in the 2213 phase can be substituted with Y, rare-earths or mixed occupation between these elements and Ca, and all of the Sr can also be replaced by Ba (*14*) and nearly one-third of the Cu by Ni (*15*); (ii) the structural similarity with other high-T_c copper oxide systems, such as the thallium, bismuth cuprates, and the well-studied $Ba_2YCu_3O_{6+\delta}$ enables a comparison of their physical properties; (iii) the electronic properties of the materials can be controlled by varying the size of the rare-earth constituent which is useful for studies of metallic, insulating, and superconducting behavior in the same type of crystal lattice; and (iv) the materials are relatively easy to prepare in single crystal form. In this paper we provide details of the growth of Ca-free $Pb_2Sr_2RCu_3O_8$ single crystals for R = La to Ho and Y, and a more complete set of electrical and midinfrared optical reflectance data on these crystals. Further evidence for the presence of an R-site vacancy carrier doping mechanism for R = Eu to Ho and Y is presented, supplementing that in the accompanying paper (*13*). T_c up to 75 K in crystals with small and medium size rare-earths is established by direct current (dc) resistivity and magnetic flux exclusion measurements. The suppression of superconductivity in the Tb crystals is discussed. Stoichiometric polycrystalline samples of $Pb_2Sr_2RCu_3O_8$ and nonstoichiometric $Pb_2Sr_2Y_{1-x}Cu_3O_8$ have also been prepared for comparison with the single crystals.

II. Experimental

Crystal growth involved weighing out stoichiometric amounts of PbO, R_2O_3 (R = La, Ce,[1] Pr,[1] Nd, Sm, Eu, Gd, Tb,[1] Dy, Ho, and Y), CuO, and prefired $SrCuO_2$, loading them into platinum crucibles, and combining this mixture (PSRCO) with PbO and NaCl flux in a molar ratio of PSRCO : PbO : NaCl = 1 : 2 : 30 for a total of about 28 g for each run. A vertical tube furnace employing a flow of N_2 gas was used. The samples were heated rapidly to a maximum temperature (T_{max}), soaked for 1–2 hr, then cooled at a rate of 5°C/hr to 770°C under the N_2, followed by furnace-cooling to room temperature. The crystals were separated nondestructively from the melt using methanol and an ultrasonic bath as described in our previous report (*16*). Postannealing of the as-grown crystals at 600°C under a N_2 atmosphere for 40 hr was found to improve the superconducting properties of the crys-

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[1] CeO_2, Pr_6O_{11}, and Tb_4O_7 were used in the cases of R = Ce, Pr, and Tb, respectively.

TABLE I

MAXIMUM TEMPERATURES (T_{max}) FOR THE CRYSTAL GROWTH OF CA-FREE $Pb_2Sr_2RCu_3O_8$ (R = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, AND Y) AND COMMENTS ON CRYSTAL QUALITY AND SIZE

R	T_{max}(°C)	Comments
La	1015	Small, extremely thin-plates (a few μm)
Ce	985	Small, a few large, plate-like crystals
Pr	1040	Plate-like crystals
Nd	1040	Large, thick crystals
Sm	1010	Crystals up to ~4 × 4 × 1 mm^3 were obtained
Eu	1000	Fairly large, thick crystals of good quality
Gd	1020	Large, thick crystals (~1 × 1 × 0.5 mm^3)
Tb	1040	Small, a few large, plate-like crystals
Dy	1030	Crystals of good quality
Ho	1040	Crystals formed but of poor quality
Y	1030	Medium sized crystals (~0.5 × 0.5 × 0.2 mm^3)

tals. Table I summarizes the synthetic temperatures and comments on crystal quality and size. Both stoichiometric and nonstoichiometric polycrystalline samples of $Pb_2Sr_2RCu_3O_8$ (R = La, Ce,[1] Pr,[1] Nd, Sm, Eu, Gd, Tb,[1] Dy, Ho, and Y) were prepared using a fast solid state synthesis technique. Appropriate amounts of PbO, R_2O_3, CuO, and $SrCuO_2$ were carefully weighed, well ground, and pelletized. Pt boats were used to hold the pellets which were left in the cold zone of a quartz-tube furnace under N_2 or air for about 20 min before being pushed into the hot zone with a maximum temperature (T_{max}). After a 1- to 12-hr reaction period, the samples were quenched to room temperature by pulling the quartz tube out of the furnace under the same atmosphere. Most samples prepared by this method are single phase (see Table II for the quality of samples). The lattice parameters of polycrystals, whether prepared as such or from crushed single crystal fragments, were determined from powder X-ray diffraction analysis using a Hägg–Guinier camera with Cu $K\alpha_1$ radiation and a bent graphite crystal as monochromator, while for some of the single crystals the analysis was performed using a Siemens $P3$ single crystal X-ray diffractometer, and the results are given in Table III.

Chemical analysis on the Ca-free $Pb_2Sr_2RCu_3O_8$ (R = Pr, Sm, Eu, Tb, and Dy) single crystals using inductively coupled plasma/mass spectroscopy (ICP/MS) has been described in Ref. (*13*). The chemical composition of a $Pb_2Sr_2Y_{1-x}Cu_3O_{8-y}$ crystal was deduced from electron probe microanalysis (EPMA). The crystal was cold-mounted in an epoxy resin and polished to obtain a clean surface. A point analysis mode was employed with probe voltage and current of 20 kV and 30 μA, respectively. The measurement was performed by selecting randomly four locations on the polished surface. The X-ray intensities for all of the constituent elements in the crystal were accurately calibrated using corresponding standards: crocoite for Pb, celestite for Sr, anorthite for Ca, cuprite for Cu, and yttrium metal for Y.

Direct current resistivity and magnetic flux exclusion measurements of the

TABLE II

MAXIMUM TEMPERATURES (T_{max}) FOR THE SYNTHESIS OF CA-FREE $Pb_2Sr_2RCu_3O_8$ (R = RARE-EARTH ELEMENT OR Y) POLYCRYSTALLINE SAMPLES AND COMMENTS ON SAMPLE QUALITY. MOST OF THE POLYCRYSTALLINE SAMPLES WERE PREPARED IN AIR, EXCEPT FOR THOSE MARKED WITH A *, WHICH WERE PREPARED UNDER N_2

R	T_{max}(°C)	Comments
La	860*	Almost single phase
Ce	840*	Almost single phase
Pr	890	Single phase
Nd	870	Single phase
Sm	870	Single phase
Eu	870	Single phase
Gd	900	Single phase
Tb	830*	Single phase
Dy	900	Single phase
Ho	910	Single phase
Er	860	Almost single phase
Tm	860*	Very small amount of impurity
Yb	860*	Very small amount of impurity
Lu	860*	Small amount of impurity present
Y	880	Single phase

TABLE III

Lattice Parameters for Single Crystal and Polycrystalline Samples of Ca-Free $Pb_2Sr_2RCu_3O_8$ Deduced from High-Resolution Guinier Powder X-Ray Diffraction or Single Crystal X-Ray Diffraction for Those Marked with a *. The Orthorhombic Lattice Parameters for Those Polycrystals with R = Pr, Nd, and Tb Have Been Given Here Due to Negligible Differences ($\leq 3\sigma$) between Those Parameters Refined in Monoclinic and Orthorhombic Symmetries

	Single crystals			Polycrystals		
R	a(Å)	b(Å)	c(Å)	a(Å)	b(Å)	c(Å)
La	5.460(1)	5.505(1)	15.876(3)*		—	
Pr	5.456(2)	5.481(2)	15.804(5)*	5.377(1)	5.430(1)	15.798(2)
Nd	5.443(2)	5.468(2)	15.774(3)*	5.441(1)	5.474(1)	15.779(3)
Sm	5.432(2)	5.479(2)	15.772(3)	5.444(2)	5.468(1)	15.776(4)
Eu	5.421(1)	5.459(1)	15.758(2)	5.414(1)	5.455(1)	15.740(3)
Gd	5.394(2)	5.421(1)	15.789(3)	5.410(1)	5.444(2)	15.741(2)
Tb	5.407(1)	5.446(1)	15.742(2)*	5.406(1)	5.444(1)	15.733(2)
Dy	5.398(1)	5.432(2)	15.773(3)	5.402(1)	5.438(1)	15.724(3)
Er		—		5.387(1)	5.427(1)	15.702(2)
Tm		—		5.380(1)	5.420(1)	15.702(2)
Yb		—		5.376(1)	5.417(1)	15.702(2)
Y	5.389(1)	5.420(1)	15.750(2)	5.391(1)	5.430(1)	15.728(2)

$Pb_2Sr_2RCu_3O_8$ crystals and powders were carried out using a standard four-probe technique in the van der Pauw configuration (*17*) and a Quantum Design SQUID magnetometer, respectively, while midinfrared reflectance measurements were made using a BOMEM/Spectra-Tech infrared microscope.

III. Results and Discussion

1. Metal/Insulator Transition

Recently, the discovery of a transition from insulating to metallic and superconducting character in selected Ca-free $Pb_2Sr_2RCu_3O_8$ crystals as the size of the rare-earth ion decreases has been presented (*18*). Here more extensive dc resistivity measurements show that the crystals with large rare-earth elements (R = La, Ce, Pr, and Nd) are insulators, those with small Rs (i.e., Dy, Ho, and Y) are metallic, and the medium size rare-earths (R = Sm, Eu, Gd, and Tb) are near the metal–insulator (M–I) transition (see Figs. 1a and 1b). An insulating/superconducting transition, starting from R = Eu, happens near the M–I transition. Magnetic flux exclusion measurements show a sharp diamagnetic transition for the crystals with R = Y, but not so sharp a transition for the crystals with other rare-earths (i.e., Eu, Gd, Dy, and Ho). For example, an onset T_c of 75 K for $Pb_2Sr_2Dy_{1-x}Cu_3O_8$ crystal has been shown in Fig. 2 with a hump at low temperature which might be caused by the magnetization of the f electrons of Dy^{3+}. Optical measurements of these crystals suggest that the Ca-free crystal series can be roughly divided into three groups in terms of the carrier-doping levels: an insulating group for R = La, Ce, Pr, and Nd with basically no hole-doping, a lightly doped group with R = Sm, Eu, Gd and Tb, and a poorly metallic group which includes those crystals with small Rs (Dy, Ho, and Y). This can be seen from Fig. 3 which shows the midinfrared reflectance of these crystals. Ce, Pr, and Nd show a low

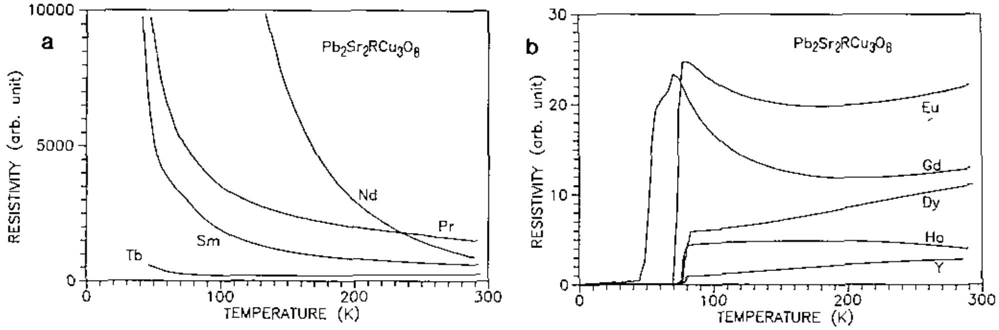

FIG. 1. Direct current resistivity measurements of the $Pb_2Sr_2RCu_3O_8$ single crystal series showing that (a) the crystals with R = Pr, Nd, Sm, and Tb are insulating, and (b) those with R = Eu, Gd, Dy, Ho, and Y are increasingly more metallic and superconducting.

and essentially flat and featureless reflectance in the midinfrared which is characteristic of an insulator, while that of Dy, Ho, and Y increases monotonically with decreasing frequency in this region and approaches 70% near 1000 cm^{-1}, more typical of a poor metal. The midinfrared reflectance of the lightly doped materials (Sm, Eu, Gd, and Tb) is intermediate between that of these other two groups. The small slope suggests the presence of a plasma edge associated with a small number of carriers. Figure 4 summarizes the trends observed in the electronic character of the $Pb_2Sr_2RCu_3O_8$ crystals as the ionic radius of R decreases. Note that the results for Tb are anomalous in one respect. Although the optical measurement indicates a comparable carrier concentration to the other lightly doped members, resistivity of one crystal behaves like that of a semiconductor, decreasing as the temperature is raised, while another one exhibits a temperature-induced metal/insulator transition (see Fig. 5). Neither crystal shows any evidence for a superconducting transition.

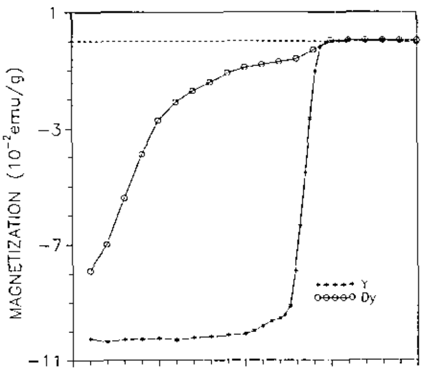

FIG. 2. The temperature dependence of the zero-field cooled (ZFC) magnetization of $Pb_2Sr_2RCu_3O_8$ single crystals with R = Y and Dy.

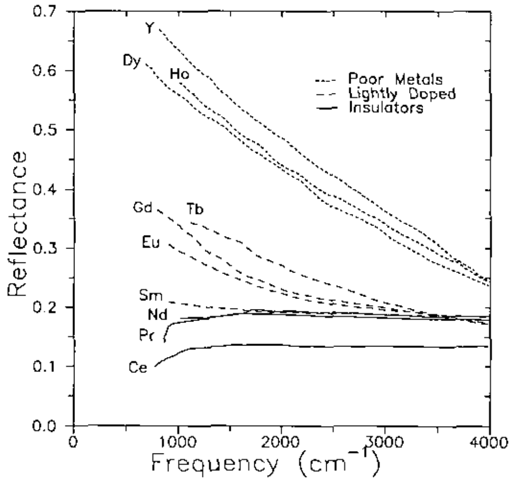

FIG. 3. Midinfrared reflectance of the $Pb_2Sr_2RCu_3O_8$ single crystals showing that the series can be divided into three groups as indicated in the legend.

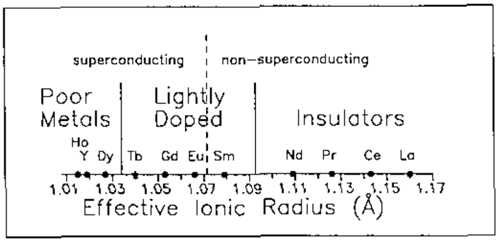

FIG. 4. Summary of the trends in the electronic character of the Ca-free $Pb_2Sr_2RCu_3O_8$ crystals as a function of effective ionic radius.

TABLE IV

CHEMICAL FORMULAE OF SELECTED $Pb_2Sr_2RCu_3O_8$ SINGLE CRYSTALS WITH R = La, Pr, Nd, Sm, Eu, Tb, Dy, AND Y AS DETERMINED BY STRUCTURE REFINEMENT OF SINGLE CRYSTAL X-RAY DIFFRACTION AND CHEMICAL ANALYSES (ICP/MS AND EPMA) (*13*)

R	Refined formulas	ICP/MS and EPMA
La	$Pb_2Sr_2LaCu_3O_8$	—
Pr	$Pb_2Sr_2PrCu_3O_8$	$Pb_{2.14(4)}Sr_{1.94(4)}Pr_{1.07(2)}Cu_{3.00}O_y$
Nd	$Pb_2Sr_2NdCu_3O_8$	—
Sm	—	$Pb_{2.05(4)}Sr_{1.93(4)}Sm_{1.15(5)}Cu_{3.00}O_y$
Eu	$Pb_2Sr_2Eu_{0.906(7)}Cu_3O_8$	$Pb_{1.79(4)}Sr_{2.03(4)}Eu_{0.89(2)}Cu_{3.00}O_y$
Tb	$Pb_2Sr_2Tb_{0.956(3)}Cu_3O_8$	$Pb_{2.39(5)}Sr_{1.89(4)}Tb_{0.91(2)}Cu_{3.00}O_y$
Dy	$Pb_2Sr_2Dy_{0.911(8)}Cu_3O_8$	$Pb_{2.12(4)}Sr_{1.98(4)}Dy_{0.95(2)}Cu_{3.00}O_y$
Y	—	$Pb_{2.00(6)}Sr_{2.08(3)}Y_{0.87(2)}Cu_{3.01(5)}O_y$

2. *Evidence for a Cation Vacancy Carrier-Doping Mechanism*

Appearance of bulk superconductivity in those Ca-free $Pb_2Sr_2RCu_3O_8$ crystals with medium or small size rare-earths is similar to the Tl and Bi cuprates in the aspect that there is no apparent chemical doping. But neither interstitial oxygen such as in the Bi cuprates (*1*) nor an internal redox reaction as proposed in the Tl system (*2*) has been found in the Ca-free 2213 crystals. Crystal structure refinement by single crystal X-ray diffraction on several representative $Pb_2Sr_2RCu_3O_8$ crystals showed that the nonsuperconducting crystals are stoichiometric (i.e., R = La, Pr, and Nd), while the superconducting crystals have about 9% electron density deficiencies at the rare-earth sites (i.e., $Pb_2Sr_2Eu_{0.906(7)}Cu_3O_8$ and $Pb_2Sr_2Dy_{0.911(8)}Cu_3O_8$) which are caused by cation vacancies rather than Sr substitution (*13*). The results of ICP/MS (*13*) and EPMA on selected crystals show chemical compositions consistent with those refined from single crystal X-ray diffraction and thus confirm the presence of cation vacancies in those crystals with medium and small rare-earths, while preserving the R-site stoichiometry of those with large rare-earths (see Table IV). These cation vacancies may function as zero-valence ions, or as centers of negative charge since local charge neutrality has to be satisfied. These negative charges will be compensated by the oxidation of some neighboring cations, i.e., Cu^{2+}, and thus hole carriers will be created in the CuO_2 planes.

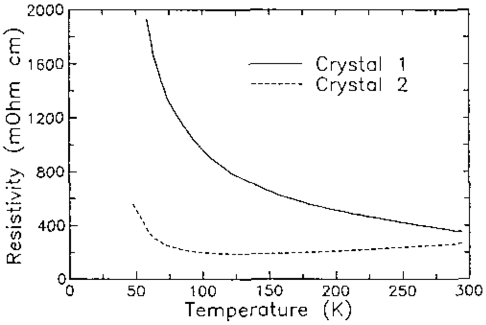

FIG. 5. Direct current resistivity measurements of the two $Pb_2Sr_2TbCu_3O_8$ crystals show that crystal 1 is insulating while crystal 2 shows metallic behavior at higher temperatures and becomes insulating for temperatures lower than 100 K.

Further evidence for the cation vacancy carrier-doping mechanism can be found from our studies of the polycrystalline samples where all of the carefully prepared stoichiometric polycrystalline $Pb_2Sr_2RCu_3O_8$ (R = lanthanides or Y) material shows no sign of superconductivity down to 5 K in magnetic flux exclusion measurements while the nonstoichiometric $Pb_2Sr_2Y_{1-x}Cu_3O_8$ (x = 0.1 and 0.2) samples are superconducting (see Fig. 6). Guinier powder

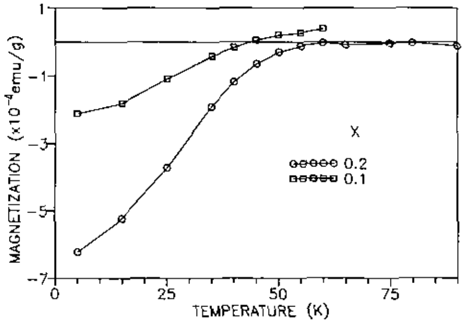

FIG. 6. Temperature dependence of the ZFC magnetization for two $Pb_2Sr_2Y_{1-x}Cu_3O_8$ (x = 0.1 and 0.2) polycrystalline samples showing a maximum superconducting transition near 60 K for x = 0.2.

X-ray diffraction indicated that the samples with x = 0.1 and 0.2 were single phase within a detection limit of ~2%. The maximum onset T_c of 60 K for x = 0.2 is comparable to the result for single crystals. The small diamagnetic signals of the powder samples imply small superconducting volumes (a few percent), similar to the results reported by Prasad *et al.* (*11*).

The existence of cation vacancies in the Ca-free $Pb_2Sr_2RCu_3O_8$ single crystals also has an effect on their lattice parameters. Figures 7a and 7b show plots of the lattice parameters of single crystal and polycrystalline samples versus the effective ionic radius of the rare-earth. Here the lengths of the *a*- and *b*-axes of both single crystals and polycrystals increase linearly as the size of the rare-earth in these compounds increases. No significant difference in the *a*- or *b*-axes has been observed between these two sample forms, except for those of R = Pr polycrystal which are anomalously short, the reason for which is presently under investigation. Accordingly, the length of the *c*-axis for stoichiometric single crystals (R = Pr, Nd, and Sm) and polycrystals is also proportional to the rare-earth size, while those nonstoichiometric single crystals (R = Eu, Gd, Dy, and Y) clearly have longer *c*-axes than their corresponding polycrystals (see Fig. 7b). This *c*-axis elongation is likely traceable to the presence of R-site vacancies. A cation vacancy will appear as an effective negative charge and will thus repel the oxide ions in the surrounding cage. Sites with cation vacancies will thus have a larger effective size than normal sites. That the expansion takes place primarily along the *c*-axis likely reflects the fact that the *ab* plane dimensions are determined mainly by the requirements of the CuO_2 network. A smaller difference between the *c*-axis of the R = Tb single crystals and polycrystals seems to be consistent with the smaller vacancy concentration (~4.5%) in comparison to those of R = Eu and Dy (~9%) found from the structure refinement.

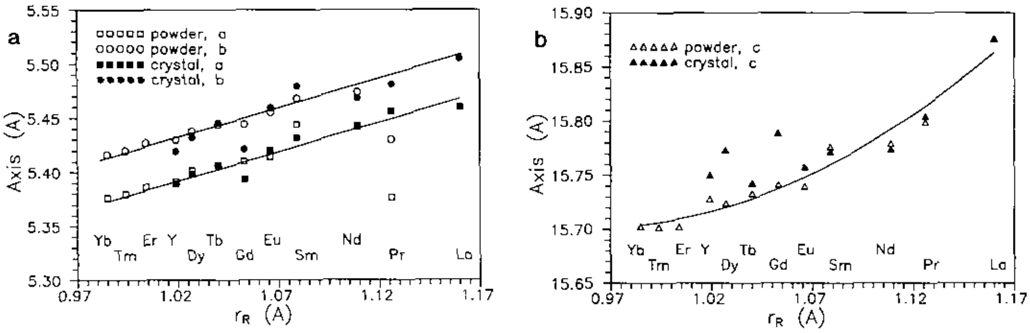

FIG. 7. A comparison of the lattice parameters (a) *a*, *b*, and (b) *c* between the Ca-free $Pb_2Sr_2RCu_3O_8$ single crystal and polycrystalline samples.

3. *Hole Concentration in* $Pb_2Sr_2RCu_3O_8$

According to the electrical neutrality principle, the hole concentration, or formal oxidation state (p) per plane copper of high-T_c copper oxide superconductors, can be calculated by summing the different formal charges of the metal and oxygen ions. For example, the maximum T_c of 93 K in the $Ba_2YCu_3O_{6+\delta}$ compound corresponds to a hole concentration (p) from 2.15 to 2.20 (*19*). $Pb_2Sr_2YCu_3O_{8+\delta}$ is structurally similar to $Ba_2YCu_3O_{6+\delta}$ except that the oxygen-deficient Cu^I layers in the latter are sandwiched by two PbO layers in the former. The reduced forms of both compounds, if stoichiometric, are found to be antiferromagnetic insulators (*6*, *20*). Despite these similarities, they are quite different in other aspects. For example, superconductivity has been observed in fully oxidized $Ba_2YCu_3O_{6+\delta}$, but not in oxidized $Pb_2Sr_2YCu_3O_{8+\delta}$. Oxygen annealing can enhance the δ-value of the latter (*6*) from 0 to 1.9 which is much larger than the δ range (from 0 to 1.0) in $Ba_2YCu_3O_{6+\delta}$. As pointed out by Cava (*9*), the holes created by adding a certain amount of oxygen seem to be absorbed by oxidized lead and copper ions in the rocksalt-like blocks without being transferred to the conducting CuO_2 planes. In that sense, the rocksalt-like block in the title compounds acts like a *buffer* which manipulates the carriers doped or depleted by various annealing procedures. Thus for the Ca-free $Pb_2Sr_2R_{1-x}Cu_3O_8$ crystals studied here, the hole concentration, p, may be calculated in a straightforward manner, $p = 2 + 3x/2$, assuming eight oxygens per formula unit. For R = Eu, Dy, and Y with $x \approx 0.09$, $p \approx 2.14$ which is not inconsistent with a T_c near 75 K assuming the same systematics as found for $Ba_2YCu_3O_{6+\delta}$ (*19*) and $Bi_2Sr_2CaCu_2O_{8+\delta}$ (*21*). For R = Tb, if the x value of 0.045 from the structure refinement is taken, $p = 2.07$. Again, assuming that these holes reside in the CuO_2 planes, then one would expect $T_c \approx 40$ K. From Fig. 1, the R = Tb phase is the only one in the rare-earth series with an atomic number greater than Sm which does not exhibit superconductivity and is also the only small rare earth for which a stable tetra-positive state is known. As mentioned previously Tb_4O_7, which contains Tb^{4+}, was used as one of the starting materials for crystal growth. This tempts us to make the assumption that some Tb^{4+} is present at the R sites which could absorb holes and lower the p value below the critical threshold for superconductivity. However, the crystallographic evidence for Tb^{4+} is ambiguous at best (*13*). The question of the presence of Tb^{4+} in these crystals cannot be decided on the basis of the present information. It is of course also possible that different p vs T_c systematics than those of $Ba_2YCu_3O_{6+\delta}$ pertain in this system and that the smaller apparent doping for R = Tb lies below the critical threshold for superconductivity.

A final problem concerns the actual oxygen content of the crystals which can give rise to errors in the p values calculated in the manner stated. Attempts to determine accurate oxygen contents by conventional thermal gravimetric analysis (TGA) gave inconsistent results due in part to the small sample size, the observed presence of PbO flux particles on crystal surfaces and in cracks, and, probably, the volatility of lead as addressed by Gallagher *et al.* (*22*). Useful information can be obtained from the crystal structure refinements in which the oxygen thermal and occupational parameters were refined (*13*). No significant differences are seen in the thermal parameters of the R = Eu, Tb, and Dy phases, which show R-site vacancies, and those of R = La, Pr, and Nd, which show no such vacancies. In all cases the oxygen sites refined to full occupation to within experimental error. From a crystal chemical point of view, an oxygen stoichiometry less than eight per formula unit is also unacceptable because it means that some of the Cu^{I} ions in the rocksalt-like blocks are coordinated by only one oxygen.

IV. Conclusions

The growth of $Pb_2Sr_2RCu_3O_8$ single crystals via the PbO/NaCl flux technique described here should allow further exploration of the physical properties of this fascinating crystal series. The electronic properties of these crystals can be altered by varying the size of the rare-earth constituent. A trend from insulating to metallic and superconducting characters has been observed in dc resistivity, magnetization, and optical measurements. Stoichiometric single crystals and polycrystalline samples are insulating. Metallic and superconducting behavior in the Ca-free Pb-2213 phase is observed only in nonstoichiometric crystals or polycrystalline samples which indicates that the carrier-doping mechanism giving rise to superconductivity in these samples is a cation vacancy at the rare-earth sites. Only the compound with R = Tb deviates from this trend which may be due to the lower cation vacancy doping level or the presence of some Tb^{4+}.

Acknowledgments

The authors acknowledge M. Maric, B. Zvan, N. Imanaka, and Nichia Chemical Industries Ltd. for assistance in sample preparation, physical property measurements, and ICP/MS analysis, respectively. This work was supported by the Ontario Centre for Materials Research (OCMR) and by the Natural Sciences and Engineering Research Council of Canada (NSERC).

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