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Crystal Growth of Ln_2NiO_4 (Ln = La, Pr, Nd) by Skull Melting*

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Growth of large single crystals of quasi-two-dimensional Ln_2NiO_4 (Ln = La, Pr, Nd) has been accomplished using the radio frequency technique of skull melting under controlled oxygen partial pressures. No evidence of intergrowth of other phases such as $Ln_3Ni_2O_7$ or higher homologs was observed. Determination of the Ni^{3+} content indicates that the crystals are cation deficient. © 1984 Academic Press, Inc.

Introduction

Oxides of the quasi-two-dimensional K_2NiF_4 structure (*1*) or related structures have been receiving considerable attention in recent years due to a growing interest in their magnetic, transport, and structural properties. The high degree of anisotropy manifested in these properties requires single crystals of suitable size for orientation, characterization, and measurements.

Among the many oxides in this group, those of the type Ln_2NiO_4 (Ln = La, Pr, Nd) (*2, 3*) are of particular interest due to the existence of a gradual semiconductor–metal transition in two dimensions near 550 K (*4, 5*) as well as the possible existence of 2-D antiferromagnetic order (*5–7*).

The Ln–O and Ni–O bond distances are near the limit of stability of the K_2NiF_4 structure (*8, 9*) and result in distortions which become increasingly severe as the size of the lanthanide ion is decreased. Single crystals are therefore desirable for investigation of the structural relationships between the tetragonal K_2NiF_4 and these distorted structures.

Since little is known about the liquidus or subsolidus stability ranges over which these materials are stable, the choice of a method of crystal growth and appropriate atmosphere is difficult. The existence of the Ruddlesden–Popper phases (*10*), $LnO(LnNiO_3)_n$ where n = 2, 3, 4, poses an additional problem because of the possible intergrowth of phases (*11, 12*), and demands particularly careful control of the growth atmosphere.

In this paper we report the application of the skull-melting technique to the growth of the oxides La_2NiO_4, Pr_2NiO_4, and Nd_2NiO_4 under controlled oxygen partial pressures.

Experimental

The general principles of the skull-melting technique have been the subject of a

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number of extensive reviews (*13–17*). Since heating is achieved by radio frequency induction in a water-cooled crucible, the melt is always contained within a sintered shell of the same composition, and contamination is thereby avoided. This method also permits the use of any atmosphere desired for the crystal growth.

A schematic view of the skull-melting apparatus is depicted in Fig. 1. There is no intrinsic limitation on the size of the skull crucible, which is ultimately dictated by the density and available mass of starting material. For loads of less than 1100 g, a crucible 6 cm in diameter and 8 cm in height was utilized, whereas larger loads were accommodated in a crucible of 8.5 cm diameter and 10 cm height.

The Ln_2NiO_4 compounds were prepared by solid–solid reaction of Ln_2O_3 and NiO. The nickel content of 99.999% NiO was analyzed gravimetrically by precipitation of nickel dimethylglyoxime to determine the extent of nonstoichiometry. Dehydration of 99.99% La_2O_3 and 99.9% Nd_2O_3 was accomplished by heating in air at 1000°C in a nickel crucible, followed by cooling under vacuum. The extent of nonstoichiometry of 99.9% Pr_2O_3 was determined by iodimetric titration of Pr^{4+} under a nitrogen atmosphere. The reaction describing the titration is

$$Pr_2O_{3+\delta} + 2\delta I^- + 2(3 + \delta)HCl \rightarrow 2Pr^{3+} + \delta I_2 + (3 + \delta)H_2O + 2(3 + \delta)Cl^-$$

where the amount of Pr^{4+} is represented by 2δ. Knowing δ, the extent of hydration of the $Pr_2O_{3+\delta}$ was then determined from the loss of mass incurred on heating in hydrogen at 900°C.

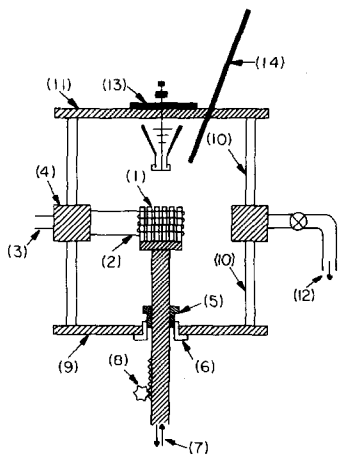

FIG. 1. Schematic diagram of the skull melter as used in controlled atmosphere experiments: (1) skull crucible; (2) work coil; (3) to RF generator; (4) 12-port vacuum collar; (5) vacuum quick connect coupling; (6) Teflon insulating flange; (7) water supply (in and out) for crucible; (8) motor-driven gear system for lowering the crucible; (9) base plate and supporting frame; (10) 18-in.-diam. × 12-in.-high Pyrex vacuum cylinders; (11) aluminum top plate; (12) to mechanical pump; (13) powder hopper; (14) ceramic poker. (Reproduced, with permission, from *J. Cryst. Growth* **61**, 223 (1983).)

Because of potential problems with reduction of NiO in the skull melter, stoichiometric proportions (corrected as described above) of NiO and Ln_2O_3 were prereacted to form polycrystalline Ln_2NiO_4 before loading. This step was carried out by grinding the oxide mixture and firing for 24–36 hr at 1200°C in a nickel crucible, followed by regrinding and refiring.

Since the room-temperature electrical conductivity of the Ln_2NiO_4 compounds is too low for direct coupling with the radio frequency field, a graphite susceptor (1–4 g), which ultimately burns off as CO_2, must be used to initiate heating. Larger susceptor masses are required for more oxidizing atmospheres because of the increased rate of burn-off.

Following evacuation, the chamber was back-filled with the desired mixture of O_2 and with an inert diluent (CO_2) using a Matheson R 7300 Series gas proportioner. A continuous flow of this gas mixture was then established at an initial rate of 10 liters/min.

The source of radio frequency was a Lepel High Frequency Labs 50-kW dual fre-

quency generator, which was operated in the range 2.6 to 2.9 MHz. As power was applied, the susceptor began to heat and then burn, heating the surrounding power sufficiently to cause it to couple directly to the applied field. Once the heating had spread throughout the charge, establishing a melt, material was slowly added from the powder hopper without loss of atmosphere control in order to produce the desired volume of melt. After the melt had equilibrated for about 1 hr, the rate of gas flow was reduced to 5 liters/min and the crucible was lowered from the stationary work coil at a rate of 15 mm/hr. This permits crystals to grow in a Bridgman-like manner, while maintaining equilibrium with the controlled atmosphere at all times, since the top surface remains molten. This type of growth produces columnar crystals in the boule core which are separated from plate-like crystals at the top of the boule by the zone of last freezing.

X-Ray powder patterns were recorded with a Norelco diffractometer using Cu$K\alpha$ radiation. High-resolution electron microscope investigations were carried out using a JEM 200CX electron microscope equipped with a side entry goniometer.

Characterization

Table I provides a summary of experimental conditions and results of all skull melter runs to date. The various regions of the boule can be appreciated in the cross-sectional view of the boule illustrated in Fig. 2a. The skull consists of the thin outer sintered shell which encloses two regions of sizeable single crystals, separated by a narrow band of polycrystalline material representing the zone of last freezing. Several single crystal specimens are shown in Fig. 2b.

Single crystal specimens (columnar) were selected from the boule core in each

TABLE I

CONDITIONS AND RESULTS OF ALL SKULL MELTER RUNS TO DATE

Ln	% O_2	Susceptor mass (g)	Mass of starting material (g)	Mass of boule (g)	% Ni^{3+}	Typical crystal size (mm)
La	4	1.7 + 5.7 + 9.0 + 5.5	1350	1260	—[b]	—
	20	1.3 + 1.3	575	490	10	1 × 1 × 3
	20	2.3	710	650	10	2 × 3 × 6
	20	1.0	1240	980	11	2 × 3 × 10
	100	1.9 + 1.7	700	630	21	—[e]
Pr	15	1.5	1100	345[a]		1 × 2 × 3
	25	3.4	1170	850	22	—[e]
	80	3.8	585	495	—[c]	—
Nd	20	3.3 + 3.8 + 4.7	770	730	—[b]	—
	80	3.8	585	495	—[d]	—
	80	3.0	1470	965		2 × 3 × 5
	90	4.3	1200	1160	18	4 × 4 × 5[f]
	100	1.2 + 2.0	1090	717	32	—[e]

[a] Skull crucible failed to lower, too little material melted.
[b] Reduced Ni^0, no crystals formed.
[c] Conditions too oxidizing, no useable crystals.
[d] Small amount of Ni^0 formed, probably due to overheating at the start of the run.
[e] Crystals contain many cracks.
[f] Crystals found only near the top of the boule.

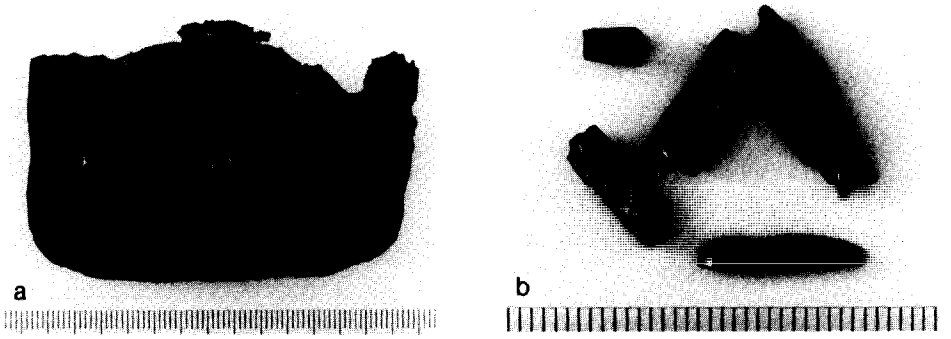

FIG. 2. (a) Cross-sectional view of a boule of La_2NiO_4. (b) Single crystals selected from the center of the boule. (Scales in millimeters.)

successful attempt, except in one case in which large (plate-like) single crystals of Nd_2NiO_4 were taken from the top of the boule. All crystals appeared black and highly lustrous. When the partial pressure of O_2 was excessive, as evidenced by a very large Ni^{3+} content (>20%) the crystals formed contained many cracks. All boules were stored in the absence of air (in vacuum desiccators or under mineral oil) after it was found that the polycrystalline regions disintegrated on contact with air for several days. No deterioration of the single crystals has been observed even after lengthy exposure to air.

Single crystal specimens from each useful boule were characterized by X-ray powder diffraction and found to be single phase within the limit of detection of this technique (2–5%). X-Ray Laue back-reflection photographs confirmed the single crystal nature of these specimens. The growth habit of the columnar crystals appears to favor the basal plane, leaving the *c* axis as the smallest dimension.

Samples were taken from the top and center of each of a number of the boules to determine the *Ln*/Ni ratio. After dissolution of samples in HCl, the resulting solutions were rendered basic with NH_4OH to precipitate $Ln(OH)_3$ selectively in the presence of Ni^{2+}. Upon separation, the metal content of each part was determined by titrating

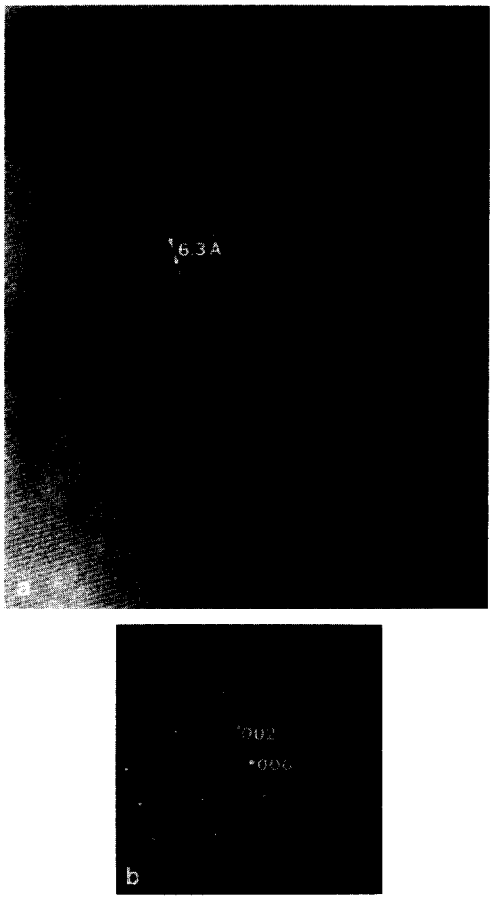

FIG. 3. La_2NiO_4 crystal: (a) Lattice image showing no evidence of intergrowth of $La_3Ni_2O_7$ or other phases along *c*. (b) Electron diffraction pattern of the same particle. The incident beam is in the [110] direction.

with a standard solution of EDTA. In each case, the *Ln*/Ni ratio was found to be 2.00 ± (0.01).

High-resolution electron microscopy revealed no other phases. Figure 3 shows a representative lattice image and diffraction pattern which illustrates the homogeneity of these crystals.

The extent of oxygen nonstoichiometry was determined by iodometric titration of Ni^{3+} under a nitrogen atmosphere. Results of these analyses are shown in Table I.

Polished sections taken from a boule of La_2NiO_4 prepared in air were examined by reflected polarized-light microscopy under oil immersion. The material was found to form a single phase throughout the top and center of the boule. La_2NiO_4 also exhibited

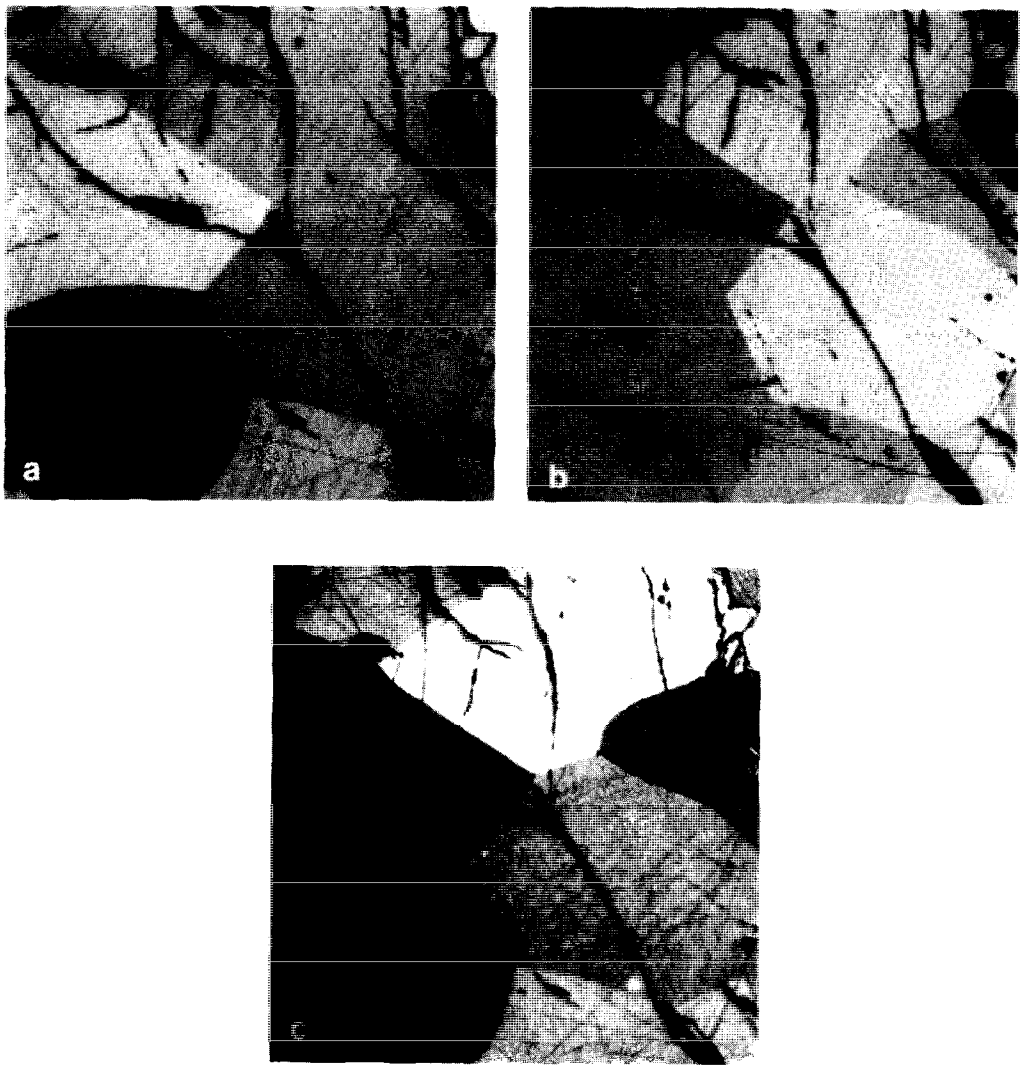

FIG. 4. (a) Plane polarized reflected light micrograph under oil immersion of pleochroic La_2NiO_4 grains at the bottom of the boule. (b) As above after 90° rotation of the stage. (c) Same image under crossed nicols.

strong pleochroism (pale yellow to gray–green) as illustrated in Fig. 4, which is consistent with the high degree of anisotropy in this structure.

Near the sides and bottom edges of the boule, some evidence of phase segregation was encountered, in the form of a narrow band of unreacted La_2O_3 and an intergrowth texture of NiO and La_2NiO_4 (see Fig. 5). NiO is readily identified through its isotropic behavior and bright-green internal reflections.

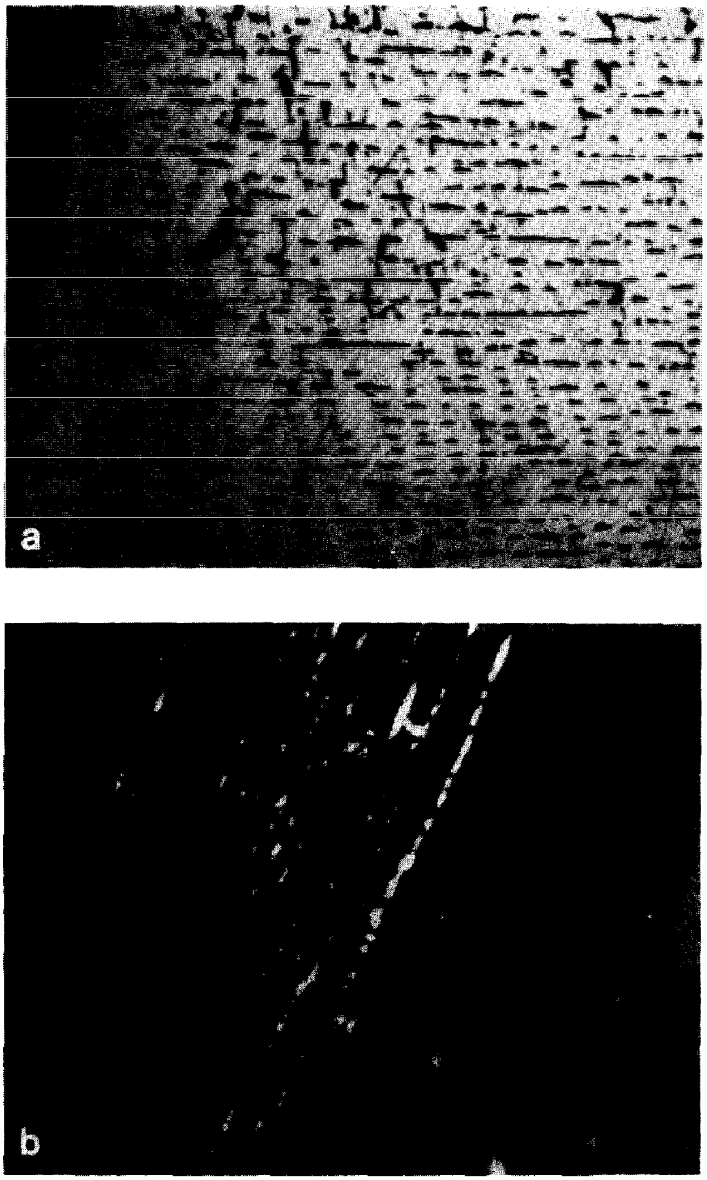

FIG. 5. Intergrowth texture of NiO (dark phase) in La_2NiO_4 (light phase) in the polycrystalline edge of the boule. (a) Plane polarized light. (b) Under crossed nicols, NiO exhibits bright-green internal reflections.

Discussion

A number of factors were found to be crucial to the successful growth of Ln_2NiO_4 crystals. The optimal oxygen partial pressure required in the skull-melting operation had to be determined by systematic variation, followed by characterization of the resultant boules. Factors which were found to be of importance for avoiding Ni^0 reduction include: (i) thorough prereaction of the starting material, (ii) optimizing the graphite susceptor size, and (iii) particularly, avoidance of overheating of the melt during the initial stages of melting (i.e., before the molten charge stabilizes).

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