Synthesis and characterization of \((\text{Nd}_{1-x}\text{Sr}_x)\text{CoO}_3, (0.10 < x < 0.50)\) system

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We report the formation of the solid solution series \((\text{Nd}_{1-x}\text{Sr}_x)\text{CoO}_3, (0.10 < x < 0.50)\), which has been prepared by the conventional solid-state reaction method. By X-ray powder diffraction, we observed that the system is isomorphous to the \(\text{NdCoO}_3\) compound [1]. We found that the reaction temperature for this system is \(860 \pm 3^\circ\text{C}\), lower than the one reported by other authors [2-4]. Further characterization studies by scanning electron microscopy and differential thermal analysis are described.

**Keywords:** Inorganic compounds; X-ray diffraction; scanning electron microscopy

Reportamos la formación de la serie de solución sólida del sistema \((\text{Nd}_{1-x}\text{Sr}_x)\text{CoO}_3, (0.10 < x < 0.50)\), el cual fue preparado por el método convencional de reacción en estado sólido. Por difracción de rayos X en polvos, observamos que el sistema es isomórfico al compuesto \(\text{NdCoO}_3\) [1]. Encontramos que la temperatura de reacción del sistema es \(860 \pm 3^\circ\text{C}\), menor que el reportado por otros autores [2-4]. Se describen los estudios realizados por microscopía electrónica de barrido y análisis térmico diferencial.

**Descripciónes:** Compuestos inorgánicos; difracción de rayos X; microscopía electrónica de barrido

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1. **Introduction**

In a group of oxides with perovskite structure it has been found analogies between several properties like electrical [2,3], optical [4] and magnetic [5-7]. This perovskites are candidate materials for various engineering applications [5]. From the viewpoint of history and their crystal structures, they have the general formula \(\text{ABO}_3\). Where \(A\) is a large ion in the center of a cubic environment and has a coordination number of twelve and \(B\) is a smaller ion, which occupies octahedral sites. It is debatable whether the oxygen coordination number is best regarded as two (linear), as six (a grossly squashed octahedron with two short and four long distances), or as fourteen (six cations and eight oxygens). No firm recommendation is made [6]. Particular interest in these materials was sparked off by the discovery that some perovskite materials possess a giant magnetoresistance. It was recently shown, that the manganite \(\text{LaMnO}_3\) [7] with distorted perovskite-type structure may also be lanthanum-deficient [5].

In this paper we report our recent results on the synthesis and characterization of \((\text{Nd}_{1-x}\text{Sr}_x)\text{CoO}_3\) system for \(0.10 < x < 0.50\), we have synthesized single-phase compositions in this range and characterized them by X-ray powder diffraction (XRD), differential thermal analysis (DTA) and scanning electron microscopy (SEM). Magnetic measurements will be reported elsewhere.

2. **Experimental part**

A series of single-phase polycrystalline samples of the general formula \((\text{Nd}_{1-x}\text{Sr}_x)\text{CoO}_3\) with \(x = 0.10, 0.20, 0.30, 0.40\) and 0.50 were prepared from stoichiometric mixture quantities of pre-dried \(\text{SrCO}_3\) (Sterm Chemical, 99%), \(\text{Nd}_2\text{O}_3\) (RE-acton, 99.99%) and \(\text{Co}_3\text{O}_4\) (Aldrich, 99.995%). Mixture totaling ca. 2 g were weighed out, mixed with an agata mortar and fired in high-density alumina crucibles in electronic muffle furnace. Firing schedules were typically of \(830^\circ\text{C}\) for few hours to drive off \(\text{CO}_2\). Samples were then removed from the crucibles ground and reheated at \(860^\circ\text{C}\) to allow solid state reaction continue, with regrinding each day, observing that melting does not occur. The intermediate regrindings were very important for the formation of homogeneous single-phase samples. Solid state reactions often required long times, at least several days, for equilibrium to be reached. It was found, that equilibration times of 8 days were required in order to attain equilibrium. The samples were cooled from high temperature in the furnace, over a period of 8–10 h. The resulting polycrystalline samples had grain sizes of 1–4 \(\mu\text{m}\) and were shown to be single phase by X-ray powder diffraction. These data for the \((\text{Nd}_{1-x}\text{Sr}_x)\text{CoO}_3, (0.10 < x < 0.50)\) sample series, were collected on a SIMENS D5000 automated powder diffractometer (Cu \(K\alpha\) radiation, \(\lambda = 1.5406\) \(\text{Å}\), graphite monochromator on the counter side and an auto-divergence-slit system), in the range \(2^\circ < 2\theta < 70^\circ\).

Possible phase transitions and the melting behavior of selected samples were studied using a TA Instruments (model 2910, with \(\Delta T = \pm 0.001^\circ\text{C}\)), thermal analysis instrument. The instrument was calibrated against standard reference samples. Approximately 2 mg of samples was used in each measurement. Data were recorded in air and ambient pressure.

Room-temperature electron microprobe analysis was carried out on a Leica-Cambridge, model Stereoscan 440, with
X-ray diffraction testing results of synthesized samples in \((\text{Nd}_{1-x}\text{Sr}_x)\text{CoO}_3, (0.10 < x < 0.50)\) showed that formation of the series of perovskite-type solid solution with cubic structure took place in the investigated region. Nevertheless, comparing the powder pattern of the \((\text{Nd}_{0.7}\text{Sr}_{0.3})\text{CoO}_3\) composition, it is observed that the diffractogram is isomorphous to the \(\text{NdCoO}_3\) compound [1], which has a cubic unit-cell (see Fig. 1). The diffraction data for all the samples were indexed using cubic unit-cell of the International Centre for Diffraction Data (ICDD) file 25–1064. We note that the lines in the \((\text{Nd}_{1-x}\text{Sr}_x)\text{CoO}_3\) diffractograms were shifted to high angles \((2\theta)\), due to the substitution of \(\text{Sr}\)-cation by \(\text{Nd}\)-cation. The variation of unit-cell constant with composition is shown in Fig. 2. The \(a\)-axis increases for \(x = 0.20\) and then decreases for the other \(x\)-values.

By a microstructural analysis for \(x = 0.10\) (Fig. 3) we observed two types of grains, the small ones (white color) that correspond to the \((\text{Nd}-\text{Sr})\)-\text{Co}-O system and the big ones (gray color) correspond to the reactive \(\text{Co}_3\text{O}_4\) (we can see more details by SEM analysis, than by XRD), and the black part corresponds to the holes in the polycrystalline powder. In Fig. 4, we show the SEM photomicrograph of \(x = 0.30\), here we can observe that the size of some grains increase by a factor of two, \(x = 0.404\) has a similar behavior. For \(x = 0.50\), the grain sizes decrease, we think that it is because we are very near to the solubility limit in the solid solution.
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The differential thermal analysis (DTA) data for \((\text{Nd}_{1-x}\text{Sr}_x)\text{CoO}_3\), \((0.10 < x < 0.50)\) samples show the melting temperature. For \(x = 0.10\) (see Fig. 5), we observed the first transition at 315.03°C, which correspond to intermolecular water or carbonates \([8]\), the second transition at 917.10°C correspond to the sample melting, and the last transitions corresponds to the reaction of the sample with the Pt container. For \(x = 0.20\) we also observed a transition at 309.72°C, and other at 920.37°C which is the melting temperature. For \(x = 0.30, 0.40,\) and 0.50 the samples melting occurs at 925.75°C (see Fig. 6), 930.25°C, and 929.59°C, respectively. In these compositions we did not observe the list transition that we detected in the samples with \(x = 0.10\) and 0.20. For all the \(x\)-values we do not observed the melting point at 895°C of Cobalt (II, III) oxide reactive. In order to explain the last two problems, it is necessary to use other characterization techniques.

4. Conclusion

We observed the formation of the solid solution in the \((\text{Nd}_{1-x}\text{Sr}_x)\text{CoO}_3\), \((0.10 < x < 0.50)\) system, synthesized in air at ambient pressure with a reaction temperature of \(860\pm3°C\). By X-ray powder diffraction we observed a single-phase, that is isomorphous to the \(\text{NdCoO}_3\) compound \([1]\), which has a cubic unit-cell. Here we obtained the solid solution series using different heat treatments reported by other authors \([2-4]\).

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1. International Centre for Diffraction Data (ICDD) file 25-1064.
8. A.M. Alario Franco, private communication.