Characterization of new solid solution phases in $(Y,Ca)(Cr,Co)O_3$ system

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New solid solution phases in the $(Y,Ca)(Cr,Co)O_3$ system have been synthesized and characterized by powder X-ray diffraction. The selected compositions in this system were prepared by the modified Pechini method. Powder-diffraction patterns were prepared.

I. INTRODUCTION

Since the arrival of the first solid oxide fuel cells (SOFC), there have been continuous efforts to improve the electrical and physicochemical properties of the cell electrodes and interconnects. The use of perovskite-type oxides as cathodes and interconnects in SOFCs has received much attention in the ceramic fuel cell development. Recently, $YCrO_3$ has been conceived (Weber *et al.*, 1987; Carini *et al.*, 1991) as an alternative interconnect material to $LaCrO_3$. $YCrO_3$ has the advantage of greater stability (less interaction with the other cell components and shows no hydration) in the fuel cell environments although it is less refractory than $LaCrO_3$. The search for interconnect materials that possess the chemical stability and electrical conductivity required in high-temperature SOFC (operating at about 1000 °C) applications has led us to investigate the substitutionally mixed $(Y,Ca)(Cr,Co)O_3$ system.

In the selected compositions of the $(Y,Ca)(Cr,Co)O_3$ system, Ca^{2+} ions substitutionally occupy the Y^{3+} sites [ionic radii (Shannon, 1976) for Y^{3+} and Ca^{2+} being 0.90 and 1.00 Å, respectively] while the Co^{3+} ions substitutionally occupy the Cr^{3+} sites [ionic radii (Shannon, 1976) for Cr^{3+} and Co^{3+} being 0.62 and 0.61 Å, respectively]. The effect of Co^{3+} substitution for Cr^{3+} in $YCrO_3$ on densification was studied as a function of Co^{3+} content and temperature (1400 °C) in air. The substitution of Co^{3+} ions for Cr^{3+} ions improved the sinterability by forming a transient liquid phase. The additional substitution of Ca^{2+} ions for Y^{3+} ions in $YCr_{1-y}Co_yO_3$ with $y=0.1$ and 0.2 further enhanced the sinterability. This is possibly due to the further decrease in the formation temperature of the liquid phase.

The primary difficulty of sintering $YCrO_3$- and $LaCrO_3$-based perovskites in air arises from the volatilization of Cr from the structure at temperatures in excess of 1400 °C, causing undesired porosity. This has been a general disadvantage for oxides that contain substantial quantities of Cr. In these oxide samples, densities greater than 90% of the theoretical could be achieved if the sintering atmospheres contained oxygen of activity near that specified by the Cr/Cr_2O_3 phase boundary (Halloran and Anderson, 1974). Higher oxygen activities result in essentially no densification due to the volatilization of higher valency oxides of Cr. This is inhibited by using reducing atmospheres during sintering. Typically, the densification of $LaCrO_3$- and $YCrO_3$-based perovskites involves temperatures as high as 1750 °C and oxygen activities in the 10^{-12}–10^{-9} atm range. Fabrication of these chromites, under such extreme conditions, becomes uneconomical in practical applications and detrimental to other cell components which may have to be cosintered with them. Thus it would be desirable to search for new avenues of processing of $YCrO_3$ at lower temperatures in an air atmosphere.

To our knowledge, there have been no published studies regarding the phase characterization with powder X-ray diffraction, sintering, and electrical properties of the $(Y,Ca)(Cr,Co)O_3$ system. Powder X-ray diffraction patterns for several solid solution phases have been prepared to complement comprehensive sintering and electrical conductivity studies (Basceri, 1994) in this system.

II. EXPERIMENT

Most of the time the mixed-cation oxide powders are not available commercially, and each research laboratory is required to produce its own powders for specific applications. Standard methods of physically mixing the oxides followed by calcining at high temperatures and subsequent ball milling are often not adequate in the purity, homogeneity, particle size, and morphology of the powders required by many advanced applications. As a result, a number of powder preparation techniques, such as sol gel, freeze drying, and various organometallic routes of synthesis have been developed. One of these processes, developed by Pechini (1967) in 1960s to prepare capacitor oxide compositions like titanates or niobates, has not received much attention as a versatile powder preparation technique. The Pechini approach has been modified and popularized by Eror and Anderson (1986), and Anderson *et al.*, (1987) who originally utilized the method to fabricate perovskite ceramics for high-temperature magnetohydrodynamic (MHD) electrode materi-

TABLE I. XRD experimental methods.

Radiation type, source: X-ray, Fe	λ value used: 1.936042 Å $K\alpha_1$
λ Discrim.: Diffracted beam, graphite mono	
λ Detector: Scintillation	
Instrument description:	
Div.: 1° Rec.: 0.3°	
Instrumental profile breadth: 0.10°2θ	Temp. (°C): 24±1
Specimen form:	
Side loaded powder, packed for 2θ's	
Range of 2θ from: 20°2θ to 90.0°2θ	Specimen motion: None
Internal/external 2θ std: Si (external)	
Lattice parameter of 2θ std: 5.4315 Å	
2θ error correction procedure: Linear interpolation from nearest 2θ's of std.	
Intensity meas. technique: Automated computer software (Rigaku DMAX-B), Peak heights	
Error (~): 5%	
Cell refinement method: Least-squares	Appleman and Evans (1973) TREOR (Werner, 1984)

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TABLE II. Crystal data; space group *Pmnb* (62), Z=4.

	Synthesis condition	*a*	*b*	*c*	*V*	D_X	M_{20}	F_{30}
$YCrO_3$	1400 °C, 2h, air	7.5318(6)	5.5211(4)	5.2408(4)	217.93(2)	5.757	85.37	73.56
$YCr_{0.9}Co_{0.1}O_3$	1400 °C, 10 h, air	7.5202(4)	5.5140(3)	5.2349(3)	217.07(2)	5.801	137.57	126.36
$YCr_{0.8}Co_{0.2}O_3$	1400 °C, 10 h, air	7.5043(4)	5.5039(3)	5.2252(3)	215.82(1)	5.856	159.00	124.28
$YCr_{0.7}Co_{0.3}O_3$	1400 °C, 10 h, air	7.4881(7)	5.4952(6)	5.2156(5)	214.62(2)	5.911	92.02	82.94
$Y_{0.9}Ca_{0.1}Cr_{0.9}Co_{0.1}O_3$	1400 °C, 10 h, air	7.5158(7)	5.4996(4)	5.2411(4)	216.63(2)	5.663	119.14	97.22
$Y_{0.9}Ca_{0.1}Cr_{0.8}Co_{0.2}O_3$	1400 °C, 10 h, air	7.4963(6)	5.4903(4)	5.2302(4)	215.26(2)	5.721	129.36	118.21

als in 1970s. Eror and Anderson (1986) claimed that the method is suitable for the preparation of a much wider range of oxides (over 100 different mixed-oxide compounds including $LaCrO_3$ and $BaTiO_3$ reported) than Pechini (1967) originally foresaw.

We used the modified Pechini method to synthesize the powders of the selected compositions in the $(Y,Ca)(Cr,Co)O_3$ system. This liquid-mix technique involves the ability of certain weak acids (alphapyroxy-carboxylic acids) to form polybasic acid chelates with various cations. These chelates can undergo polyestherification when heated in a polyhydroxyl alcohol to form a polymeric glass that would have the cations uniformly distributed throughout the batch. Thus the glassy phase retains homogeneity on the atomic scale and may be calcined at low temperatures to yield fine particulate oxides whose chemistry and stoichiometry can readily be regulated.

The cationic sources that have been successfully used in the modified Pechini method are carbonates, hydroxides, isopropoxides, and nitrates. The general reaction sequence that

TABLE III. X-ray powder data for $Y(Cr_{1-y}Co_y)O_3$, $y=0$–0.3.

	$YCrO_3$			$YCr_{0.9}Co_{0.1}O_3$			$YCr_{0.8}Co_{0.2}O_3$			$YCr_{0.7}Co_{0.3}O_3$		
hkl	2θ exp (°)	I/I_0	d_{exp} (Å)	2θ exp (°)	I/I_0	d_{exp} (Å)	2θ exp (°)	I/I_0	d_{exp} (Å)	2θ exp (°)	I/I_0	d_{exp} (Å)
101	26.01	2	4.302	26.05	2	4.295	26.10	2	4.287	26.15	2	4.279
011	29.51	6	3.801	29.54	6	3.797	29.60	6	3.790	29.64	5	3.785
200	29.79	6	3.766	29.83	5	3.761	29.90	5	3.752	29.96	4	3.745
111	33.16	19	3.392	33.19	23	3.389	33.26	22	3.382	33.30	22	3.378
020	41.07	19	2.760	41.11	17	2.7571	41.20	25	2.7513	41.25	21	2.748
211	42.44	100	2.674	42.49	100	2.6715	42.59	100	2.6655	42.66	100	2.661
002	43.36	22	2.620	43.41	20	2.6175	43.50	24	2.6123	43.59	23	2.607
120	43.87	10	2.591	43.92	11	2.5886	44.01	11	2.5835	44.08	12	2.580
012	48.35	1	2.364	48.33	1	2.3647	48.40	1	2.3615	48.51	1	2.3564
121	49.23	1	2.324	49.32	1	2.3201	49.41	1	2.3161	49.51	1	2.3118
301	...	...	...	...	...	...	...	...	...	50.93	4	2.2514
112	50.77	7	2.2580	50.81	8	2.2564	50.92	7	2.2518	51.00	8	2.2485
220	51.54	5	2.2266	51.61	7	2.2238	51.73	6	2.2189	51.81	5	2.2158
202	53.49	8	2.1511	53.55	9	2.1488	53.69	8	2.1436	53.78	9	2.1403
311	55.02	8	2.0957	55.12	9	2.0922	55.24	9	2.0880	55.36	9	2.0839
221	56.39	2	2.0488	56.45	3	2.0468	56.58	3	2.0425	56.68	3	2.0392
212	57.75	1	2.0046	57.85	1	2.0014	57.96	2	1.9980	58.08	2	1.9942
022	61.24	20	1.9005	61.31	19	1.8986	61.45	21	1.8947	61.54	20	1.8922
400	61.88	18	1.8828	61.97	18	1.8803	62.13	18	1.8760	62.26	16	1.8724
320	62.82	7	1.8574	62.92	7	1.8548	63.06	6	1.8511	63.20	7	1.8474
122	63.37	9	1.8430	63.46	12	1.8406	63.60	11	1.8370	63.73	11	1.8337
031	67.75	1	1.7367	67.86	2	1.7342	68.00	1	1.7311	68.12	2	1.7284
312	68.40	1	1.7222	68.49	2	1.7202	68.66	2	1.7165	68.84	1	1.7125
131	69.81	12	1.6917	69.90	16	1.6898	70.04	14	1.6869	70.19	16	1.6837
013	71.06	1	1.6658	71.16	1	1.6637	71.31	1	1.6607	71.47	1	1.6575
113	73.06	2	1.6263	73.17	3	1.6242	73.31	3	1.6215	73.48	3	1.6183
231	75.73	6	1.5771	75.87	8	1.5746	76.02	8	1.5720	76.19	8	1.5690
420	76.95	8	1.5559	77.10	9	1.5533	77.30	9	1.5499	77.47	8	1.5471
402	78.55	11	1.5292	78.69	11	1.5269	78.88	11	1.5238	79.07	9	1.5207
213	78.90	19	1.5235	79.03	19	1.5214	79.22	21	1.5183	79.39	21	1.5156
322	79.39	4	1.5156	79.55	4	1.5131	79.73	4	1.5102	79.88	4	1.5079
132	81.91	1	1.4768	...	...	...	...	...	...	...	...	...
023	81.95	1	1.4763	82.06	1	1.4746	82.26	1	1.4717	82.46	1	1.4687
303	84.95	1	1.4335	85.07	1	1.4319	85.70	7	1.4234	85.50	1	1.4261
331	85.34	7	1.4282	85.51	7	1.4259	...	...	...	85.92	7	1.4205
511	87.47	1	1.4002	87.62	1	1.3983	87.84	1	1.3955	88.10	1	1.3923
232	87.64	1	1.3981	...	...	...	...	...	...	...	...	...

curs during polymerization process is as follows: Certain hydroxycarboxylic acids, such as citric, lactic, tartaric, and glycolic acids, form polybasic acid chelates with metal ions. When compared to the majority of the acids, citric acid is more widely used in the processing of ceramic materials in routes involving the use of organic precursors. The addition of a polyhydroxyl alcohol, such as ethylene glycol, allows the formation of an organic ester with the acid chelate. Upon heating, polyestherification occurs throughout the liquid medium, resulting in a homogeneous solution of metal ions attached to an organic matrix. The solution is gradually heated to remove excess solvent, leaving an intermediate resinlike solid phase. The resin is then calcined to remove the organic material, while the remaining inorganic metal groups are chemically combined to form the desired stoichiometry of the phases of interest.

We have studied the following solid solution compositions in the $(Y,Ca)(Cr,Co)O_3$ system:

(1) $YCr_{1-y}Co_yO_3$ with $y=0.0$, 0.1, 0.2, and 0.3, and
(2) $Y_{0.9}Ca_{0.1}Cr_{1-y}Co_yO_3$ with $y=0.1$, 0.2.

Our starting chemicals were Y (99.9%, Aldrich, Inc.) and Ca (99.95%, Strem Chemicals) carbonates [$Y_2(CO_3)_3H_2O$ and $CaCO_3$] and Cr (>98%, Merck, Inc.) and Co (99%, Merck, Inc.) nitrates [$Cr(NO_3)_39H_2O$ and $Co(NO_3)_26H_2O$]. The desired compositions were prepared by dissolving the appropriate amounts of selected carbonates and nitrates in solutions of citric acid (Cryst. extra pure, Merck, Inc.), ethylene glycol (>99%, Merck, Inc.), and distilled water. The solutions were heated on a hot plate at about 90 °C until all of the carbonates and nitrates go into solution. The mixtures were stirred while heating until a clear solution is obtained. This was the most important step of the process as complete dissolution of the cations was necessary to ensure homogeneity and a strict control over stoichiometry. Upon heating to moderate temperatures (around 150–250 °C), polyestherification occurred in which a polymeric glass was formed. Most of the excess water was removed by evaporation. An amorphous, solid polymeric resin was obtained. Continued heating resulted in the decomposition of the polymer resin and charring at about 400 °C, forming a black, brittle mass. The solid was then ground in an agate mortar and transferred to an alumina crucible and calcined at 900 °C for 8 h, in air, to form crystallites of mixed-cation oxides. The resulting powders were milled in an agate mortar and subjected to X-ray diffraction to assure that they were single phase. The resultant powders were first uniaxially pressed (700 kg/cm^2) into pellets in steel dies, and then cold isostatically pressed at 1400 kg/cm^2 followed by firing at 1400 °C for 2–10 h in air. The sample pellets were allowed to cool to room temperature within the furnace.

The powder X-ray-diffraction patterns of finely ground samples were obtained using a Rigaku D-MAX/B powder diffractometer equipped with an incident-beam monochromator to produce Fe $K\alpha_1$ radiation. The X-ray-diffraction data were collected employing a step scan of 0.02 °2θ steps and 2-s counting time. The magnitude of the systematic machine errors (typically in the range of 0.0015 Å in d spacings) was determined by using an external standard (Si, >99.5%, Grade A10, Herrmann C. Starck, Inc.), and then a corresponding calibration was carried out on the actual d spacings of our raw powder X-ray-diffraction data. Least-squares refinements of data were performed by two separate cell refinement methods, namely Appleman and Evans (1973) and TREOR (Werner, 1984). The further details of the experimental procedures are summarized in Table I.

TABLE IV. X-ray powder data for $(Y_{0.9}Ca_{0.1})(Cr_{0.9}Co_{0.1})O_3$ and $(Y_{0.9}Ca_{0.1})(Cr_{0.8}Co_{0.2})O_3$.

	$(Y_{0.9}Ca_{0.1})(Cr_{0.9}Co_{0.1})O_3$			$(Y_{0.9}Ca_{0.1})(Cr_{0.8}Co_{0.2})O_3$		
hkl	2θ exp (°)	I/I_0	d_{exp} (Å)	2θ exp (°)	I/I_0	d_{exp} (Å)
101	26.02	2	4.300	26.09	2	4.289
011	29.56	5	3.795	29.62	5	3.787
200	29.86	4	3.757	29.93	4	3.749
111	33.21	21	3.387	33.29	21	3.379
020	41.23	23	2.749	41.30	26	2.7449
211	42.51	100	2.670	42.62	100	2.6637
002	43.37	31	2.620	43.47	28	2.6141
120	44.05	9	2.5813	44.14	11	2.5763
012	48.30	2	2.3661	48.40	2	2.3615
121	49.37	1	2.3179	49.50	1	2.3122
301	50.72	4	2.2601	50.85	4	2.2547
112	50.78	8	2.2576	50.91	7	2.2522
220	51.72	7	2.2193	51.82	6	2.2154
202	53.53	10	2.1496	53.67	8	2.1444
311	55.17	9	2.0905	55.31	11	2.0856
221	56.53	3	2.0442	56.67	3	2.0395
212	57.83	2	2.0021	57.96	2	1.9980
022	61.36	23	1.8972	61.49	27	1.8936
400	62.02	16	1.8790	62.19	16	1.8743
320	63.03	6	1.8519	63.17	6	1.8482
122	63.50	11	1.8396	63.65	13	1.8357
031	68.02	2	1.7307	68.17	2	1.7273
312	68.51	2	1.7198	68.66	2	1.7165
131	70.06	12	1.6864	70.21	16	1.6833
013	71.12	1	1.6645	...	...	...
113	73.09	3	1.6257	73.27	3	1.6222
231	76.02	6	1.5720	76.20	8	1.5688
420	77.21	9	1.5514	77.42	8	1.5479
402	78.69	11	1.5269	78.92	11	1.5231
213	78.97	31	1.5223	79.17	25	1.5191
322	79.60	4	1.5123	79.79	5	1.5093
331	85.68	7	1.4237	85.86	6	1.4213
511	...	...	...	87.99	1	1.3936
040	89.53	2	1.3746	89.71	2	1.3725

III. RESULTS AND DISCUSSION

The compositions we have studied in $(Y,Ca)(Cr,Co)O_3$ system have been characterized with powder X-ray diffraction. Table II reports the crystal data and Tables III and IV give the powder-diffraction patterns. The extent of grain coarsening and crystallization was monitored by microstructural examination in a scanning electron microscope (JEOL-JSM 6400). One typical microstructure showing the distribution of grain sizes and crystallization is depicted in Figure 1. The sample micrograph shows that the grain sizes of the $YCr_{0.8}Co_{0.2}O_3$ solid solution phase are in the range 4–9 μm, and it displays the attainment of the characteristic crystal habit among the grains, meaning that the recrystallization stage has been achieved during sintering at 1400 °C for 10 h.

The compositions investigated, starting with pure $YCrO_3$, involved doping the Cr^{3+} sites with Co^{3+}, and then simultaneous doping of Y^{3+} and Cr^{3+} sites with Ca^{2+} and

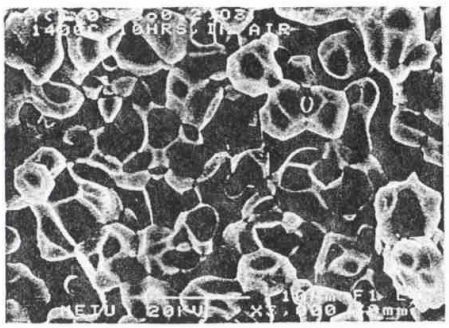

Figure 1. Scanning electron micrograph of the fracture surface of $YCr_{0.8}Co_{0.2}O_3$ sintered at 1400 °C for 10 h in air atmosphere.

Co^{3+}, respectively. The pattern we have obtained for pure $YCrO_3$ compares well with the already available PDF pattern (34-365) for this phase. In the powder X-ray-diffraction traces of Ca^{2+} and Co^{3+} codoped compositions ($Y_{0.9}Ca_{0.1}Cr_{0.9}Co_{0.1}O_3$ and $Y_{0.9}Ca_{0.1}Cr_{0.8}Co_{0.2}O_3$) a minor second phase was observed. Few small, broad peaks (with relative intensities less than 5 out of 100) of this second phase were identical in these two samples and they did not match with any of the existing PDF files including binary oxides of Y, Ca, Cr, and Co (PDF No.: 25-1200, 37-1497, 38-1479, 9-402, and 9-418), calcium and cobalt oxychromates (PDF No.: 8-458, 21-137, 30-239, 38-292, 38-294, 22-1084, and 24-236), calcium oxycobaltates (PDF No.: 37-668 and 37-669) and Ca-Y-O compounds (PDF No.: 19-265, 19-266, and 28-856). These extra peaks mean either that we have not reground and refired enough to achieve a homogeneous solid solution phase, that Cr oxides have volatilized, or that we have a nonstoichiometric solid solution phase that differs from the starting composition. It should be kept in mind that the reported compositions are only nominal, based on the stoichiometries of starting mixtures. Actual compositions may vary somewhat from those listed.

IV. SUMMARY

The compositions given in Table II were synthesized by the modified Pechini method. Powder X-ray-diffraction runs were performed on sintered and finely ground samples. Unit-cell parameters of solid solutions in the $(Y,Ca)(Cr,Co)O_3$ system have been determined and powder-diffraction data were prepared.

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Anderson, H. U., Pennell, M. J., and Guha, J. P. (1987). "Polymeric synthesis of lead magnesium niobate powders," Adv. Ceram. **21**, 91–98.

Appleman, D. E., and Evans, H. T. (1973). U.S. Geological Survey, Computer Contribution 20, U.S. National Technical Information Service, Document No. PB-216188.

Basceri, C. (1994). "Sintering and electrical properties of the calcium and cobalt doped yttrium chromite ceramics," M.Sc. thesis, METU, Ankara, Turkey.

Carini II, G. F., Anderson, H. U., Sparlin, D. M., and Nasrallah, M. M. (1991). "Electrical conductivity, Seebeck coefficient and defect chemistry of Ca-doped $YCrO_3$," Solid State Ionics **49**, 233–243.

Eror, N. G., and Anderson, H. U. (1986). "Polymeric precursor synthesis of ceramic materials," Mat. Res. Soc. Symp. Proc. **73**, 571–577.

Halloran, J. W., and Anderson, H. U. (1974). "Influence of O_2 partial pressure on initial sintering of alpha Cr_2O_3," J. Am. Ceram. Soc. **57**, 150.

Pechini, M. P. (1967). "Method of preparing lead and alkaline earth titanates and niobates and coating method using the same to form a capacitor," US Patent No. 3,330,697.

Shannon, R. D. (1976). "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," Acta Crystallogr. A **32**, 751–767.

Weber, W. J., Griffin, C. W., and Bates, J. L. (1987). "Effects of cation substitution on electrical and thermal transport properties of $YCrO_3$ and $LaCrO_3$," J. Am. Ceram. Soc. **70**, 265–270.

Werner, P. E. (1984). Trial and Error Program for Indexing of Unknown Powder Patterns, TREOR, University of Stockholm, Stockholm, Sweden.