PS10.08.17 NEUTRON STUDY OF THE STRUCTURE AND CHEMICAL STABILITY OF $(Y_{1-x}Ca_x)(Ba_{2-x}La_x)Cu_3O_{7-d}$.

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It has been shown recently that appropriate amounts ($x \approx 0.4$) of cation substitutions in the title compound make it remarkably corrosion resistant and retain its Tc above 80K. An orthorhombic to tetragonal transition also occurs at x = 0.4. We have made a comparative structural study of three samples (x = 0.0 , 0.2 and 0.4) with Tc values of 93K, 80K and 79K respectively. Influence of cation substitution on the structural parameters as deduced by neutron Rietveld analysis is reflected in Table below:

Sample	x = 0.0	x = 0.2	x = 0.4
Sp.Group	Pmmm	Pmmm	P4/mmm
a (Å)	3.8190(9)	3.8192(8)	3.8480(6)
b (Å)	3.8826(9)	3.8773(8)	3.8480(6)
c (Å)	11.6892(35)	11.6590(29)	11.6575(35)
O-content	6.97	6.95	7.00
Cu(2) Valence	2.17	2.18	2.18
Cu(1)-O(4) (Å)	1.895(7)	1.885(6)	1.855(8)
Cu(2)-O(4) (Å)	2.245(9)	2.271(7)	2.299(9)
$\angle$O(2)-Cu(2)-O(2)	163.0°	165.1°	167.4°
Ba-O (avg) (Å)	2.862	2.856	2.841

La^{3+} is observed to substitute at Ba^{2+} site and Ca^{2+}, at Y^{3+} site. As x goes up, the bridging oxygen O(4) moves away from Cu(2) towards Cu(1), thus decreasing the puckering of CuO_2 sheets. This could be the cause of improved chemical stability.

PS10.08.18 RIETVELD ANALYSIS OF Al INCLUDING TDS TERMS.

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In the X-ray Rietveld analysis the optimized B-thermal factors are often physically unrealistic, generally smaller than the corresponding ones obtained with single crystal analysis. This could be due to the inadequate analytical description of the background scattering together with the great flexibility (in the fitting procedure) of the used Bragg peak profile functions (pseudo-Voigt or Pearson VII) that may overestimate the peak areas, especially at wide 2θ Bragg angles. In order to obtain more accurate B-factors we have included in the Rietveld refinement of a powder sample of Al the main TDS correction terms starting from our procedure (P.Riello, J. Appl. Cryst. 28, 1995, 115) that is suited to describe, on physical basis, the global background scattering, $Y^{bk}(s_i)$, at the i-th s step, with $s=2sin\theta/\lambda$. Now we have expressed $Y^{bk}(s_i)$ as follows:

$$Y^{bk}(s_i) = K^{inc} Y^{inc}(s_i) + K^{TDS} Y^{TDS}(s_i) + Y^{air}(s_i) ,$$

where K^{inc} is the scale factor for the incoherent independent scattering, $Y^{inc}(s_i)$, and K^{TDS} is the scale factor for the TDS terms, these two factors being related to each other as well as to the Bragg scale factor by means of specific equations obtained according to Warren's theory (B.E.Warren: X-ray Diffraction, Addison-Wesley, 1969, p. 193); $Y^{air}(s_i)$ is the air scattering contribution; $Y^{TDS}(s_i)$ is the TDS contribution based on the theoretical approach developed by Borie (Acta Cryst., 14, 1961, 566): it contains a sum of peaked terms (centered at the hkl Bragg reflection maxima, s_{hkl}) given by: $\sum_{hkl} j(hkl) [1/(s_i s_{hkl})] ln (g_m/| s_i - s_{hkl}|)$, where $j(hkl)$ is a multiplicity factor and g_m is given by $(3/\pi)^{1/3}/a_o$, with a_o the edge of the fcc unit cell of Al; these functions have been suitably truncated according to J.P.Urban (Acta Cryst. A31, 1975, 95) in order to avoid the singularity when $s_i = s_{hkl}$.

The so performed Rietveld refinement has given a B_{Al} factor of 0.86(1)Å^2, and the following agreement indices: $R_{wp}= 0.141$, $R_{exp}=0.071$, $R_{Bragg}= 0.054$. Using the routine polynomial background we have instead obtained the following values: $B_{Al}= 0.35(1)$Å^2, $R_{wp}= 0.156$, $R_{Bragg}= 0.065$.

PS10.08.19 X-RAY RIETVELD ANALYSIS OF THE 6H SOLID SOLUTION $BaTi_{1-x}Fe_xO_{3-z}$.

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$BaTiO_3$ is stabilised in the 6-layer hexagonal structure by the addition of iron at x ~ 0.05 in $BaTi_{1-x}Fe_xO_{3-z}$. This structure is stable to a composition with x ~ 0.85. Specimens equilibrated at 1250 - 1270°C followed by step cooling to 750°C show a maximum in the plot of the cell parameter c versus x (Vanderah, Loezos & Roth, 1996).

Rietveld analysis of x-ray powder patterns of nine compositions spanning this series revealed interesting details of the structure and chemistry of these specimens. The use of a variable counting time data collection strategy (Madsen and Hill, 1994) was found to give more consistent refined structural parameters, particularly thermal parameters and site occupancies.

With increasing iron content of the solid solution phases, progressively poorer fits to the powder patterns were obtained for the step-cooled samples. This led to studies on the effect of quenching and low temperature annealing on the bulk structure properties, the results of which will be reported.

T.A. Vanderah, J.M. Loezos and R.S. Roth, J. Solid State Chem. (1996) (in press)
I.C. Madsen and R.J. Hill, J.Appl. Cryst. (1994), 27, 385-392

PS10.08.21 MODELLING DISLOCATION-INDUCED LINE BROADENING IN RIETVELD REFINEMENTS USING A VOIGT FUNCTION.

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The theory of dislocation-induced X-ray or neutron diffraction peak broadening developed by Krivoglaz et al. [1] and Wilkens [2] has been adapted for Rietveld refinement of powder profiles. Information on both the slip system and the dislocation density in the crystallites is evaluated from a the shape of the profile via a Voigt function fit.

The integral breadth of the dislocation-broadened peaks is related to the dislocation structure of the crystal by $\beta = \rho\chi f(M)tan^2\theta$ [2], where ρ is the dislocation density, χ is the orientation factor [3], $f(M)$ is a dimensionless function of M, $M = r \rho^{1/2}$ is a dislocation interaction parameter [2], where r denotes the outer cutoff radius of the dislocation strain field.

We incorporated this theory into Rietveld refinement by using a Voigt function, with integral breadth $\beta_V = \beta_G/\Omega(iy)$, to fit the theoretical profile of a dislocation-broadened peak, with various values of M [2]. Here Ω is the complex error function, $y = \beta_L/\pi^{1/2}\beta_G$ is the peak shape parameter, and β_L and β_G are the integral breadths of the Lorentzian and Gaussian components. This yielded a numerical relationship between the parameters y and M, which were then incorporated into the Lorentzian and Gaussian half-widths. Hence, for a given form of χ, both M and ρ can be determined by a refinement. We will discuss the application of this treatment to structure refinements and dislocation analyses of neutron diffraction patterns of $LaNi_5$ and Pd deuterides.

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