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Structural investigation on $Ba_2CoGe_2O_7$ at room and low temperature

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Magnetic field induced ferroelectricity was recently found in $Ba_2CoGe_2O_7$ [1]. Induced by the magnetic transition below 6.7 K the electric polarisation along **a** direction in the cell with magnetic field applied along **c** and its smooth rotation with the magnetic field, rather than a sudden flip, is unique and cannot be explained by classical mechanisms applied in the other multiferroics. A novel spin-dependent hybridization mechanism with a metal-ligand hybridization modified by local spin configurations through spin-orbit coupling has been proposed [2]. There are only very few structural data about this compound in the literature [3,4] and to our knowledge no detailed structural investigation of $Ba_2CoGe_2O_7$ and it temperature dependence have been reported previously. From the available sources the P-42_1m group is suggested.

The crystal structure of $Ba_2CoGe_2O_7$ has been precisely determined by single crystal diffraction at three different temperatures. Room temperature as well as 90 K structure determinations were performed using x-ray synchrotron radiation. The structure measurement at 10 K was done by neutron diffraction to serve as a reference for the future investigation of the magnetic structure below transition temperature 6.7 K. The melilite type structure composed of tetrahedral layers built-up by CoO_4 and Ge_2O_7 groups separated by intermediate layers of large Ba cations has been confirmed. The symmetry of the **average** melilite structure is tetragonal with space group P-42_1m. The structural results show no significant changes with the temperature and the data for the all measured temperatures could be well refined within the P-42_1m space group. However the presence in the measured data of the reflexions violating the systematic extinctions for P_2_1_ symmetry (h,0,0) (0,k,0) (h and k odd) at all measured temperatures, clearly indicate that the true space group is different. The number of the new (prohibited in P-42_1m) reflections is not large enough to increase significantly the quality of refinement by lowering symmetry. However performing theoretical analysis of the possible isotropy subgroup of the parent group 113 (Int. Tables) P-42_1m [5] one obtains 6 possible true structures: 1) $P2_12_12$, 2) Cmm2, 3) P-4, 4) $P2_1$, 5) Cm, 6) P1, which are more consistent with the observed magnetoelectricity in the $Ba_2CoGe_2O_7$.

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Study of the transformation of boehmite into alumina by Rietveld method

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The transformation of boehmite into alumina involve a complex sequence of transitional phases of alumina: Boehmite/amorphous Al_2O_3 → γ-Al_2O_3 → δ-Al_2O_3 → θ-Al_2O_3 → α-Al_2O_3 . This transition depends strongly on the chemical routes of synthesis, atmospheric conditions, degree crystallinity, heating rate, impurities, moisture, alkalinity, thermal history of the material, etc. A wide variety of experimental and computational methods have been used to describe the structures of transition aluminas over the last half century. However, no definitive consensus has been reached on issues such as the arrangement of vacancies and so, the structures of transition aluminas are under certain amount of debate. The structures of these transition aluminas are traditionally considered to be based on a face-centered cubic (fcc) array of oxygen anions. The structural differences between these forms only involve the arrangement of aluminum cations in the interstices of an approximately cubic close-packed array of oxygen anions [1].

The aim of this paper is to study the conversion of boehmite into alumina, by means of the application of Rietveld refinement method to the X-ray diffraction patterns of samples obtained by thermal treatment of boehmite. Boehmite was synthesized by a hydrothermal method from an aluminium industry waste [2].

To study the microstructure evolution after heating at different temperatures, calcinations were performed at temperatures ranging from 1300 to 1500ºC during 2 or 7h and air or nitrogen atmosphere. Samples were also studied by TEM and SEM to determine the morphology of the different phases of alumina.

Preliminary results of the Rietveld refinement is summarized in Table I.

Table I

Alloy	Phase	a (nm)	b (nm)	c (nm)	β	Mass fraction
1300°C 7h air	α-Al_2O_3	0.4766		1.3008		63.3 %
	γ' -Al_2O_3	0.5642		2.3460		12.5%
	δ-Al_2O_3	0.5607		2.4911		2.7%
	θ-Al_2O_3	1.1790	0.2907	0.5618	103.78°	3.5%
	Amorph					18.0%
1400°C 7h nitrogen	α-Al_2O_3	0.4766		1.3007		55.3%
	γ' -Al_2O_3	0.5628		2.3444		16.8%
	δ-Al_2O_3	0.5651		2.4067		2.6%
	θ-Al_2O_3	1.1790	0.2907	0.5618	103.78°	5.4%
	Amorph					19.9%
1400°C 2h air	α-Al_2O_3	0.4765		1.3006		21.2%
	γ' -Al_2O_3	0.5624		2.3441		36.8%
	δ-Al_2O_3	0.5567		2.4848		12.0%
	θ-Al_2O_3	1.1838	0.2890	0.5608	103.57°	9.2%
	Amorph					20.8%
1400°C 7h air	α-Al_2O_3	0.4766		1.3009		81.5%
	δ-Al_2O_3	0.5651		2.4067		1.7%
	θ-Al_2O_3	1.1790	0.2907	0.5618	103.78°	0.7%
	Amorph					16.0%
1400°C 7h Air	α-Al_2O_3	0.4765		1.3006		35.3%
	γ' -Al_2O_3	0.5630		2.3414		25.9%
	δ-Al_2O_3	0.5565		2.4837		7.5%
	θ-Al_2O_3	1.1824	0.2895	0.5612	103.51°	5.4%
	Amorph					20.8%
1500°C 7h air	α-Al_2O_3	0.4766		1.3009		79.2%
	Amorph					19.8%

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