FACULTAD DE INGENIERÍA

REVISTA DE LA FACULTAD DE INGENIERIA
www.revistaingenieria.uda.cl

30 (2014) 21-25

REACTIVE MILLING IN THE SYSTEM BI_2O_3-FE_2O_3, AND THE RIETVELD REFINEMENT OF THE CRYSTALLIZED PHASES OBTAINED BY CONTINUOUS HEATING

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ABSTRACT

The synthesis and characterization of the crystallized phases obtained from an amorphous precursor is reported in the system Bi_2O_3-Fe_2O_3 in order to get the multiferroic compound $BiFeO_3$. To diminish the thermal treatment time to obtain bulk samples, the reactive milling was chose as a synthesis form. It was found that the crystallized products were nanostructured, and it was suggested a metaequilibrium equation, $Bi_{25}FeO_{39} + 12Fe_2O_3 \leftrightarrow 25BiFeO_3$, that states the evolution of the phases over 500ºC. It could be said that with a temperature increasing the perovskite $BiFeO_3$ phase is stabilized, furthermore using a Differential Scanning Calorimetry the Curie temperature of 844ºC was determined.

Keywords: Reactive milling, Multiferroics, Amorphous, Crystallization, Rietveld analysis.

1. INTRODUCTION

The possibility of mixing in one compound at least 2 ferroic properties (ferroelectricity, ferromagnetism and ferroelasticity) [1] represents a great potential, not only from the technological point of view, but also from the fundamental science sight. This property could be seen in the mulitferroic materials, in which the electric field control, allows the magnetic or stress fields management [2], then these materials can offer the potential for revolutionary device designs in the spintronic and microelectronic fields, as they are at the heart of multifunctionality. The $BiFeO_3$ compound, with a rombohedrally distorted simple perovskite structure [3], shows antiferrogmanetism below the 370ºC, and ferroelectricity below the 820-850ºC range [4], for this reason the $BiFeO_3$ compound is one of the most representative of this singular group.

In this article the synthesis of the powder sample using reactive milling or mechanical activation [5], is used in order to generate a precursor capable of crystallized in the perovskite structure of the $BiFeO_3$ right through a continuous heating increase. Due to the difficulty in the obtaining bulk samples of high purity for this compound, this method of synthesis was chose because it resulted more useful than other techniques less stable [6] and hence can be used to diminish the sintering times to obtain compact samples. Although, the Fe^{+3} incorporation to the structure, and considering that the milling process (not in equilibrium synthesis method) allows the possible stabilization of solids solutions related to the polymorphous metastable γ-Bi_2O_3 [7], it is expected that the energy delivered to the reagents in the milling process will be enough to ensure the complete mixture at an atomic level, making possible the stability of the perovskite phase.

The Rietveld method for X-rays diffraction patterns analysis [8], has positioned since its origin as a powerful characterization tool [9], and it is used in this paper, not only to determine the reticular structure of the phases, but also to establish the compositional analysis of the samples. It is also used to determine the crystallites size of the phases (often equaled to the grain size in the powder milling technology [10]).

2. EXPERIMENTAL

Powder samples in the system Bi_2O_3-Fe_2O_3 were prepared using high-energy reactive milling assisted by continuous heating. Analytical grade reagents Bi_2O_3 (Baker 99.94%), and Fe_2O_3 (Riedel de Häen 99.99%) were mixed carefully using 1:1 stoichiometry in order to obtain 6 g. The milling was carried out in a Spex8000 high energy mixer mill with a WC vial and balls, with a 3.5:1 ball to powder ratio. The grinding experiment was made under dry conditions at room temperature. After 96 hours of treatment, 100 mg of resulting powder was withdrew, with the purpose of applying differential scanning calorimetry in the TA Instruments SDT-2960 equipment. Through this technique, and after heating the sample until 900ºC, the stability range was determined. Then, an equal mass samples were put under a continuous heating with a 20ºC/min rate until 380ºC, 450ºC, 600ºC y 800ºC. Following this an air quenching process was performed in every samples. The structural characterization was obtained using X ray diffraction in the Shimadzu XRD-6000 equipment, with Cu anode in the Bragg-Brentano geometry. The powder pattern analysis was executed using structural Rietveld refinement utilizing the Fullprof Suite software [11], and cell models taking from the literature [3,12,13,14].

3. RESULTS AND DISCUSSIONS

It can be seen in the Figure 1 that the original mixed powder after a 96 hours milling, turns into an amorphous precursor.

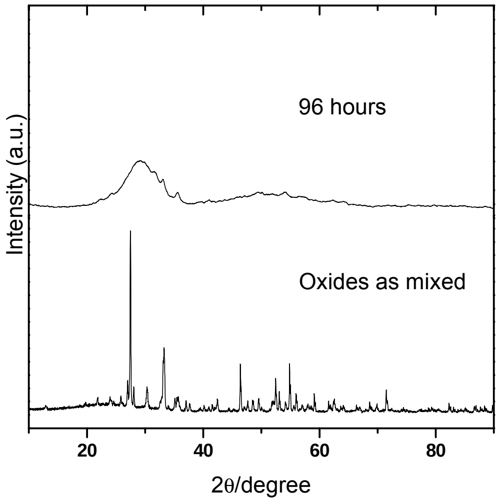

Figure 1. 96 hours milling effect into original powder

The resulting precursor is the starting point of the crystallization process. The thermal evolution is shown in the Figure 2.

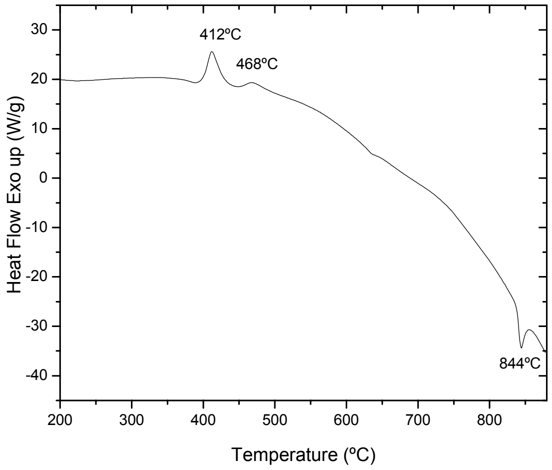

Figure 2. Powder sample's thermal evolution

Two exothermal peaks occurs at 412ºC and 468ºC, can be related with the crystallization process. On the other side, the endothermal low occurs at 844ºC which is the Curie temperature (ferroelectric-paraelectric transition) considering the Fisher`s work [4], the reversibility, and zero mass lost of a series thermal cycles near to this temperature in which the sample was put as it is shown in the Figure 3. The mass lost phenomenon could be associated to high volatilization Bi_2O_3 or their solid solutions over 750ºC [15].

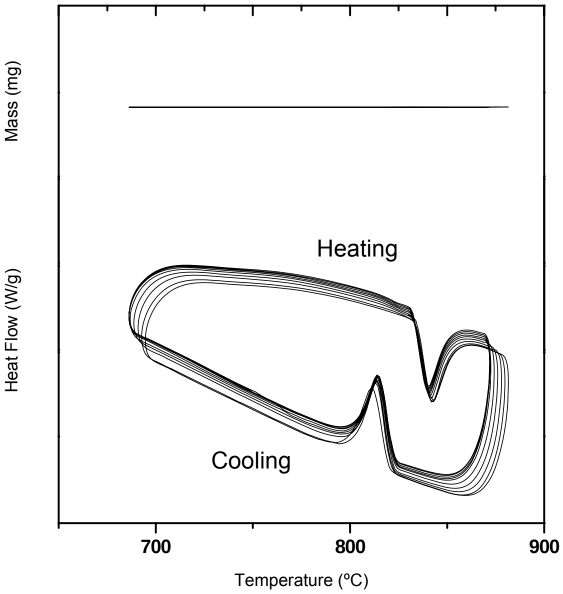

Figure 3. Thermal cycles near to 844ºC

The Bi_2O_3, Fe_2O_3, $Bi_{25}FeO_{39}$ y $BiFeO_3$ compounds were identified comparing the equipment database with the diffraction patterns obtained, and also considering the evolution with the temperature treatment. The Figure 4 shows this phenomenon.

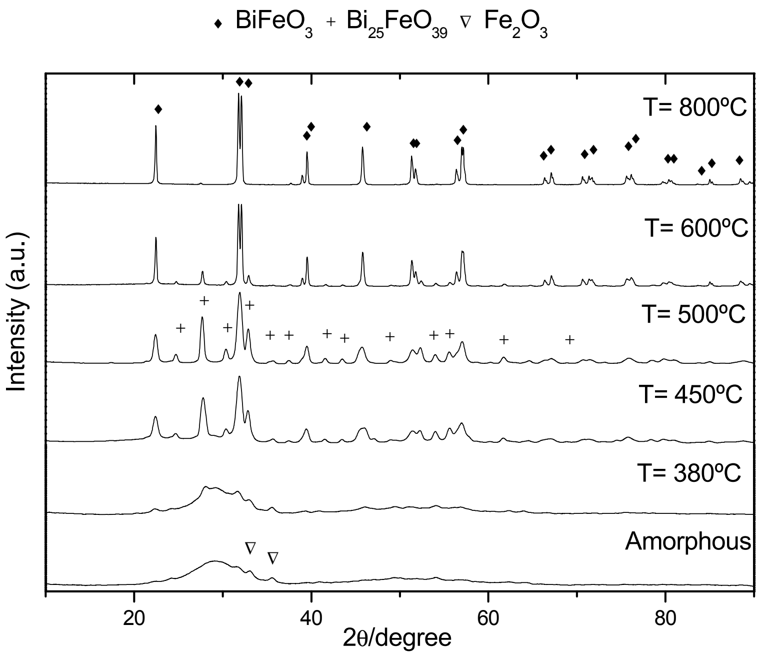

Figure 4. Diffraction patterns of the samples at different temperaturas

The structural refinement carried out using the Rietveld analysis can be seen in the Table 1.

Table 1 Rietveld refinement results at different treatment temperatures.

TT (ºC)	Phases	% (p/p)	R_{Bragg}	GOF	Vol. (Å^3)	ρ (g/cm^3)	Crystallite (Å)
380	Amorphous	100.00					
450	$BiFeO_3$	67.15	3.04	2.10	375.2	8.31	140.4
	$Bi_{25}FeO_{39}$	20.13	10.9		1064	9.21	582.2
	Bi_2O_3	5.250	11.1		338.5	9.15	2704
	Fe_2O_3	7.470	14.4		301.9	5.27	2657
500	$BiFeO_3$	56.36	3.60	1.90	374.3	8.33	335.4
	$Bi_{25}FeO_{39}$	33.47	4.77		1060	9.25	526.2
	Fe_2O_3	10.17	11.1		301.2	5.28	484.5
600	$BiFeO_3$	83.47	5.16	2.20	373.9	8.34	625.3
	$Bi_{25}FeO_{39}$	12.98	7.28		1056	9.28	559.7
	Fe_2O_3	3.55	21.4		302.0	5.27	371.4
800	$BiFeO_3$	100.00	5.58	2.90	373.7	8.34	970.5

R_{Bragg} and GOF are the statistic parameters responsible of the Rietveld adjust quality

The amorphous phase persists until 402ºC, here the first crystallization process carried out. Bi_2O_3 and Fe_2O_3 are present as unreacted phases together with $Bi_{25}FeO_{39}$ and $BiFeO_3$. Over 500ºC, when the second crystallization process happened, Bi_2O_3 has reacted completely and the powder patterns shown Fe_2O_3, $Bi_{25}FeO_{39}$ and $BiFeO_3$.

The evolution of the powders considering the phases percentages over 500ºC, is determined by the following reaction:

$Bi_{25}FeO_{39} + 12Fe_2O_3 \leftrightarrow 25BiFeO_3$

With the increasing of the temperature this reaction moves into the product phase, and over the 800ºC only $BiFeO_3$ can be obtained. As a remark, the continuous heating, and the consequent quenching do not permit the perovskite decomposition into $Bi_{25}FeO_{39}$ and $Bi_2Fe_4O_9$, as it occurs using other synthesis techniques [16]. Moreover, the eutectic and peritectic decomposition showed at the Morozov's work [15] not made it, maybe the high reactivity reached with grinding technique stabilizes perovskite $BiFeO_3$ to respect other phases.

The R_{Bragg} and GOF values were acceptable considering that the phases resulting are nanocrystalline [17] (crystallite size below 1000Å=100nm for $BiFeO_3$).

4. CONCLUSION

The reactive milling allows the synthesis of an amorphous precursor that crystallizes after set continuous temperature in the perovskite phase of the $BiFeO_3$ (pure and stable over 800ºC). It was found that this phase is nanostructured although the high treatment temperature, this due to a powder's high reactivity reached in milling process that diminishes time of thermal treatment. In addition it was determined the Curie temperature of 844ºC for $BiFeO_3$ in agree with the literature.

5. ACKNOWLEDGEMENTS

P. Lara acknowledges to his colleagues Mauricio Salas, Rodrigo Romero and Ricardo Tapia without their help the milling experiments had not been possible.

6. REFERENCES

K. Aizu, Physical Review B. 2(3), 754, (1970)

G. A. Smolenskii and I. E. Chupis, Sov. Phys. Usp. 25(7), 475, (1982)

C. Michel et al, Solid State Communications 7, 701 (1969)

P. Fisher et al., J. Phys. C. Solid St. Phys., 13, 1931, (1980)

V.V. Boldyrev, Russian Chemical Reviews 75(3), 177, (2006)

J.K. Kim et al., Materials Letters 59, 4006, (2005)

M. Valant, D.Suvorov, Chem. Mater. 14(8), 3471, (2002)

H.M. Rietveld, J. Appl. Cryst. 2, 65, (1969)

H.M. Rietveld in The Rieveld Method, R.A. Young ed., IUCr Oxford University Press, Oxford, 1993, pp. 39-42.

C. Suryanarayana Mechanical Alloying and Milling, Marcel Dekker, New York, 2004.

J. Rodríguez-Carvajal, Fullprof Suite for Windows, http://www.ill.eu/sites/fullprof

S.K. Blower, C. Greaves, Acta Cryst. C 44, 587, (1988)

K. Kelm, W. Mader, Z. Anorg. Allg. Chem. 631, 2383, (2005)

N. Rangavittal, T.N. Guru Row, C.N.R. Rao, European Journal of Solid State Inorganic Chemistry 31, 409 (1994)

M.I. Morozov, N.A. Lomanova, V.V. Gusarov, Russian Journal of General Chemistry 73(11), 1676, (2003)

T.T. Carvalho, P.B. Tavares Materials Letters 62, 3984, (2008)

G. Dercz et al., Rev.Adv.Mater.Sci. 18, 764, (2008)