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Evolution of the complexity of the domain structure in boracites

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In this paper we analyze time series with chaotic dynamics from a communication system. The analysis is performed with the orthogonal wavelet transform, which gives us information about of energy distribution in the different wavelet levels from the time series. Furthermore, It is established the useful region as a function of the amplitude and frequency values of the information signal to be transmitted.

Keywords: Fractal structure; domain wall dynamics; phase transitions; ferroic materials.

Investigamos por medio de microscopía óptica de polarización la evolución de la estructura de dominios en muestras de compuestos ferroicos magnetoeléctricos llamados boracitas, particularmente en boracitas Cobalto-Cloro. La evolución de la complejidad de la distribución de paredes de dominio es caracterizada y cuantificada por medio de un análisis multifractal realizado en fotografías digitales de alta definición, tomadas a diferentes temperaturas de ciclos calentamiento-enfriamiento.

Descriptores: Estructura fractal; dinámica de dominios; transiciones de fase; materiales ferroicos.

PACS: 77.80bj; 77.80Dj; 77.84.-s; 77.90.+k; 78.20.Fm

1. Introduction

The importance of natural and synthetic boracites in the field of solid state physics has been widely recognized. This is due to the great potential of applicability and the rich phenomenology shown by these materials when they are subject to different physical conditions. For instance, some members of this family of compounds contain paramagnetic metal ions, that leads these boracites to exhibit simultaneously ferromagnetic, ferroelectric and ferroelastic behavior in the same phase [1]. Synthetic boracites have been prepared by four basic techniques: sintering flux methods [2], vapor transport methods [3], pressure mechanistic type method [4], and hydrothermal type methods [5], however, up to date, the most successful method to prepare single crystals of halogen boracites, has been the vapor transport method developed by Schmid [3].

Ferroic domain dynamics has been studied for past decades because of its importance to understand the microscopic causes of some phenomena such as multi-domain formation, stability of domain structure, and pattern formation, as well as the related aspects of technological applicability in multi-functional devices such as, ferroelectric random access memories, actuators and sensors [6].

It is well known that the domain structure determines many of the characteristics and physical properties of the ferroic systems, and that this structure is strongly affected by external factors such as temperature, applied fields etc., as well as the preparation conditions of the samples and its composition. It has been shown that in systems that present domain structure, it is possible to describe the structure and some physical properties by means of statistical tools such as scaling relations, distribution functions and correlation functions [7,8]. Physically, the relevance of having a knowledge of the domain wall dynamics in ferroic materials, is due to the fact that domain walls are high energy regions, in which these systems store energy. Once reached a critical value in the stock of energy, a phase transformation becomes possible. In this sense the domain wall dynamics drive the physical behavior of the system.

Traditionally the domain structure of boracites has been examined by polarized light microscopy (PLM) [1], both in transmitted and reflected modes; this is a simple, non-destructive, easily available technique which can be applied to as-grown crystals, after the elementary operation of polishing at least one facet of the crystal. Therefore, this could be the most direct method to reveal and to study the static domain structure of some ferroic materials [9].

Cobalt chlorine boracite, $Co_3B_7O_{13}Cl$ (hereafter Co-Cl) is a multiferroic compound that undergoes three successive phase transitions: (i) from a cubic ($\bar{4}3$ m) paraelectric phase to an orthorhombic(mm2) ferroelectric/ferroelastic at 350°C, (ii) to a monoclinic (m) ferroelectric/ferroelastic at 265°C, and (iii) to a rhombohedral (3 m) ferroelectric/ferroelastic phase at 195°C [10].

The aim of this work is to describe quantitatively the evolution of the complexity of the domain structure in Co-Cl boracites as a function of the temperature of the sample. Particularly we wish to characterize, by means of a multifractal analysis, the domain dynamics at different temperatures. The multifractal analysis consists of the generation of the singularity and mass exponent spectrums.

2. Fractal dimension as a measure of complexity

Many natural objects are the result of iterative processes which replicate themselves at different scales of observation.

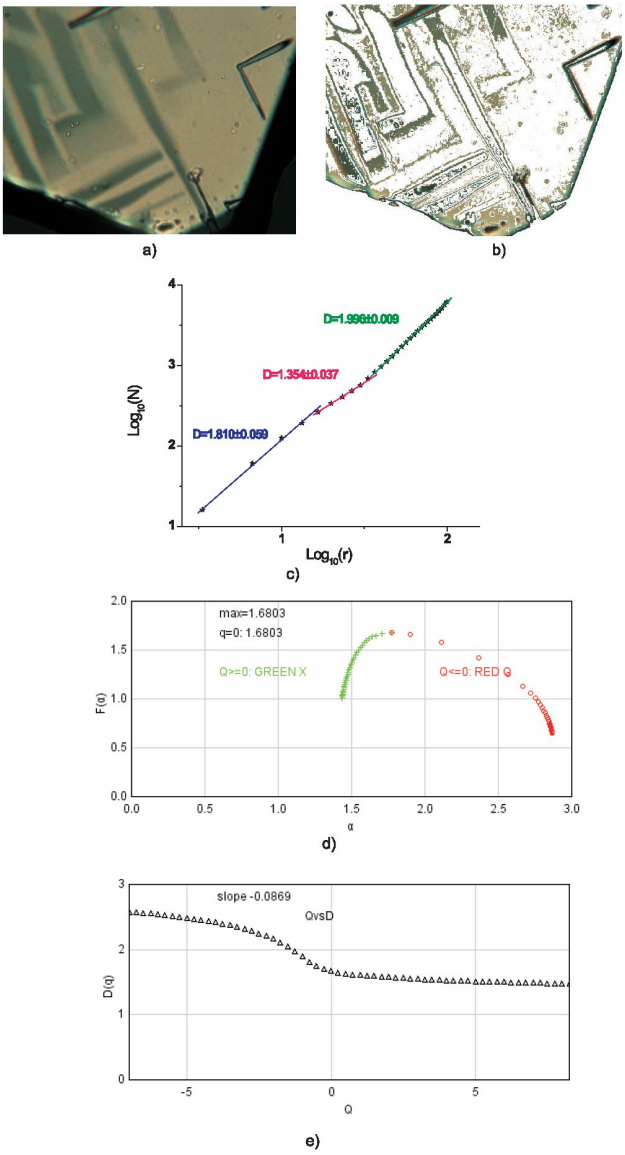

FIGURE 1. Cobalt bromine boracite: a) Microphotograph at 197°C, b) domain wall structure, c) graph of $\log_{10} N_w$ *vs* $\log_{10} r$, d) graph of the singularity spectrum $f(\alpha)$ and e) graph of the generalized dimensions $D(q)$.

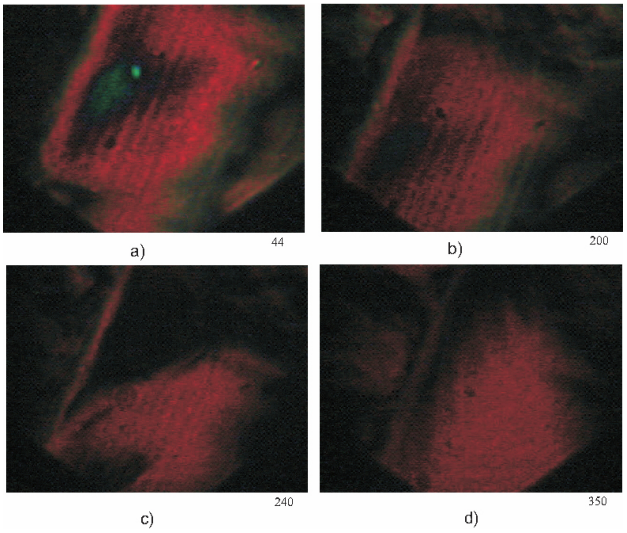

FIGURE 2. Microphotographs of the domain structure of cobalt chlorine boracites, on the first heating process at a) 44°C, b) 200°C, c) 240°C and d) 350°C.

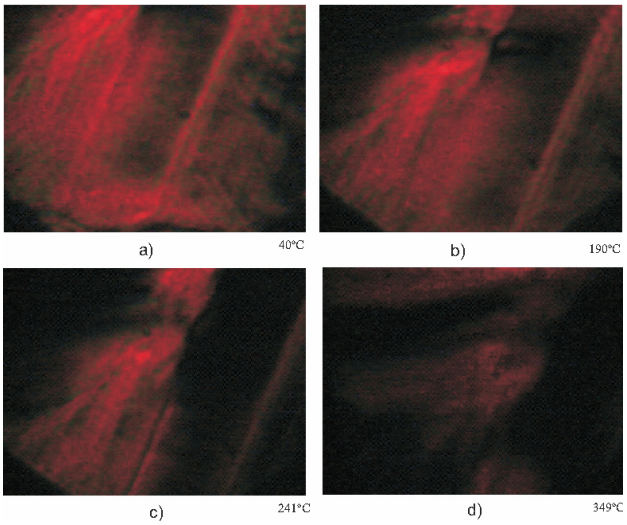

FIGURE 3. Microphotographs of the domain structure of cobalt chlorine boracites, on the second heating process at a) 40°C, b) 190°C, c) 241°C and d) 349°C.

Fractal objects and processes are therefore said to display self-similar properties. Mandelbrot (1982) developed fractal geometry as a tool to model the complexity in this kind of systems [11].

There are various definitions of quantities that conventionally attempt to quantify the complexity of an object. For instance, there exist various definitions of the fractal dimension and several different methods to calculate this for a given pattern. One of the most common methods to calculate the fractal dimension of a complex object is the box counting method. In this work, we focus our attention on two different, and complementary, techniques: 1) the box counting method; that gives a measure of the complexity called the box counting fractal dimension D_B, defined as follows,

$$D_B = -\lim \left[\frac{\log N_\varepsilon}{\log \varepsilon} \right]. \qquad (1)$$

This quantity is obtained as a ratio of the rate of increment in the detail of observation, to the rate of increment of spatial scale (ε). Using this technique, we perform the multifractal analysis that consist in generating the graphs of $f(\alpha)$ *Vs* α and $D(q)$ *vs* q, these quantities form the typical multifractal spectra.

The multifractal formalism used in this paper is based on a method proposed by Chhabra and Jensen [12,13] for determining the singularity spectrum $f(\alpha)$ directly from experimental data, without first calculating the generalized dimensions D_q and applying the usual Legendre transforms. According to this method the singularity spectrum is defined by:

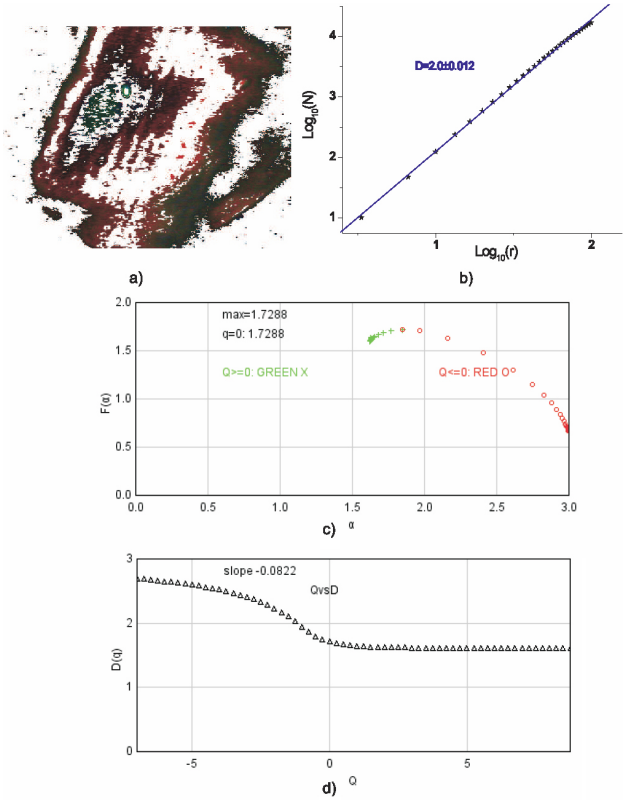

FIGURE 4. Multifractal analysis of the sample of cobalt-chlorine boracite at 44°C, during the first heating process: a) domain wall structure, b) graph of $\log_{10} N_w$ *vs* $\log_{10} r$, c) graph of the singularity spectrum $f(\alpha)$ and d) graph of the generalized dimensions $D(q)$.

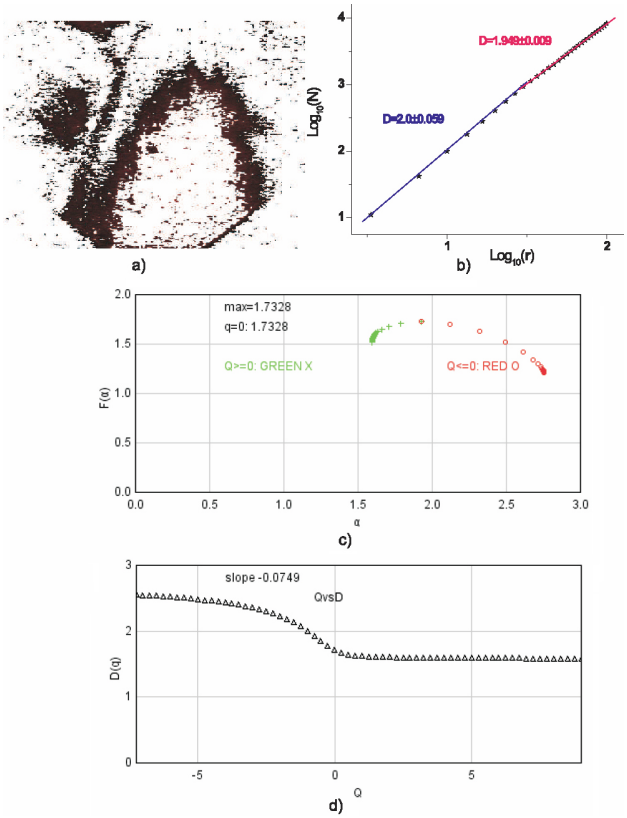

FIGURE 5. Multifractal analysis of the sample of cobalt-chlorine boracite at 350°C, during the first heating process: a) domain wall structure, b) graph of $\log_{10} N_w$ *vs* $\log_{10} r$, c) graph of the singularity spectrum $f(\alpha)$ and d) graph of the generalized dimensions $D(q)$.

$$f(\alpha_q) = \frac{\sum \mu \ln \mu_i}{\ln \varepsilon}, \tag{2}$$

where,

$$\mu_i = \frac{P_i^q}{\sum P_i^q}, \tag{3}$$

and

$$\alpha = \frac{\sum \mu \ln P_i}{\ln \varepsilon}. \tag{4}$$

Here μ is the mean number of pixels contained in the i^{th} box with certain size and position, and P_i is the probability of finding the pixels at that i^{th} box.

If the graph of $f(\alpha)$ is humped, the object is considered multifractal. If the graph converges , the object is considered mono or non-fractal. The graph of $D(q)$ *vs* q is decreasing for multifractals, but non-decreasing for mono or non-fractals. The mass exponent function τ reveals the degree of multifractality and nonlinearity of a pattern, and must be a straight line for a mono or non-fractal objects. The generalized dimension $D(q)$ statistically describes how mass varies with ε (box size) in an image. A multifractal system is a generalization of a fractal system in which a single fractal dimension is not enough to describe its dynamics; instead, a discrete or a continuous spectrum of exponents is needed. 2) The second way we use to characterize the domain wall structure is a variation of the box counting method, it consists in the statistical evaluation of the ratio between the rate of increasing of the mass (in this case pixels belonging to the domain walls) to the rate of the increasing of the space. This is obtained by drawing at different sites a set of equally separated concentric circles and counting the average number of pixels contained in each of them. In a log-log graph, if a straight line fits well the data, the slope of this line is the so called mass fractal dimension, therefore, this is defined by the scaling relation.

$$N_w \approx r_m^D, \tag{5}$$

below we will show that this is an useful tool, that complements the quantification of the changes in the complexity of the domain wall structure caused by temperature changes.

We begin the analysis of the domain wall structure by obtaining the mass fractal dimension or dimensions of the structure of the domain walls of a Co-Cl boracite at different temperatures. Then we perform a multifractal analysis.

For the sake of comparison and to illustrate the method, we show the photograph of a sample of a Cobalt Bromine boracite (Fig. 1a). In a previous work we demonstrated that

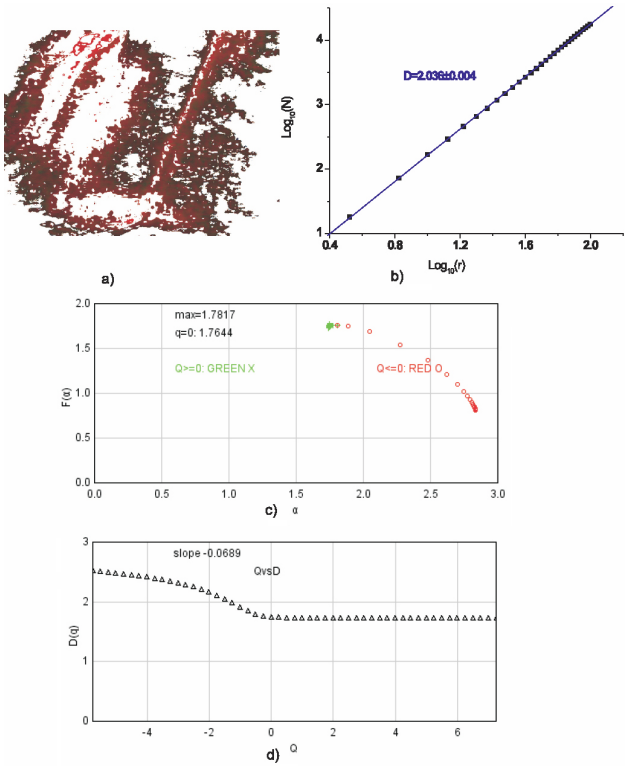

FIGURE 6. Multifractal analysis of the sample of cobalt-chlorine boracite at 40°C, during the second heating process: a) domain wall structure, b) graph of $\log_{10} N_w$ *vs* $\log_{10} r$, c) graph of the singularity spectrum $f(\alpha)$ and d) graph of the generalized dimensions $D(q)$.

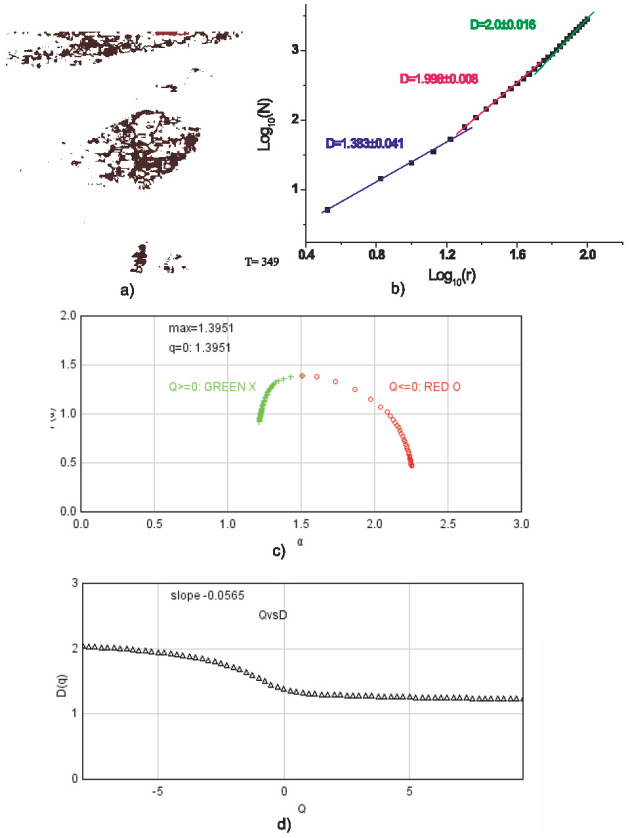

FIGURE 7. Multifractal analysis of the sample of cobalt-chlorine boracite at 349°C, during the second heating process: a) domain wall structure, b) graph of $\log_{10} N_w$ *vs* $\log_{10} r$, c) graph of the singularity spectrum $f(\alpha)$ and d) graph of the generalized dimensions $D(q)$.

in this material coexist three different values of mass fractal dimension [14]. Moreover, we have shown that the evaluation of the mass fractal dimension and the radial distribution function is enough to characterize these samples. We have shown that they clearly exhibit two kinds of memory in their domain structure. In the present study, we investigate samples whose domain wall structure requires a deeper analysis specify their multifractal spectra. In Fig. 1 we show a stage of the second heating process of a sample of cobalt-bromine boracite (a), its domain wall structure (b), three straight segments whose slopes are the respective mass fractal dimension (c), and the plots characterizing their multifractal spectra; $f(\alpha)$ versus α (d) and D_q versus q (e). In this way, by performing a multifractal analysis on series of digital photographs, taken at different temperatures and several heating-cooling cycles, we are able to quantify the evolution of the complexity of the the domain wall structure.

3. Experimental results and discusion

Our cobalt-chlorine boracite crystal under study was grown by chemical vapor transport. Platelets of different thickness (40 to 50 μm) were cut parallel to $(111)_c$ and were finely polished with diamond paste (0.25-1 μm). The study of the dynamics of the domain walls was made in situ, using an optical polarizing microscope (Zeiss Universal) in the transmission mode. The sample temperature was changed using a heating stage (Leitz 1350), and we inserted a λ-plate (550 nm) between the sample and the analyzer to reach a higher contrast in the domain structure. The evolution of the process was recorded by a digital video camera coupled to the microscope; from this film, digital pictures were then obtained at different stages. In Fig. 2 and Fig. 3 we present, at four different stages, the sequential rearrangement of domains caused by the increasing temperature, for the first and the second heating processes, respectively.

To quantify the complex characteristics of the domain structure of the samples of Co-Cl boracites, we used the photographs taken from the digital video and perform a high contrast treatment to extract the domain wall structure, this pattern is then converted to a binary (black and white) image. To obtain the different values of the fractal dimension we proceed as follows: we take the image of the domain wall structure, we choose a point and draw a set of equally separated concentric circles, then we count the number of pixels contained in each circle. This quantity is proportional to the area covered by the domain walls. This procedure is repeated on several different sites of the structure in order to take the average of the number of pixels for the corresponding radii. Fig. 4a and Fig. 5a present the domain wall structure at the

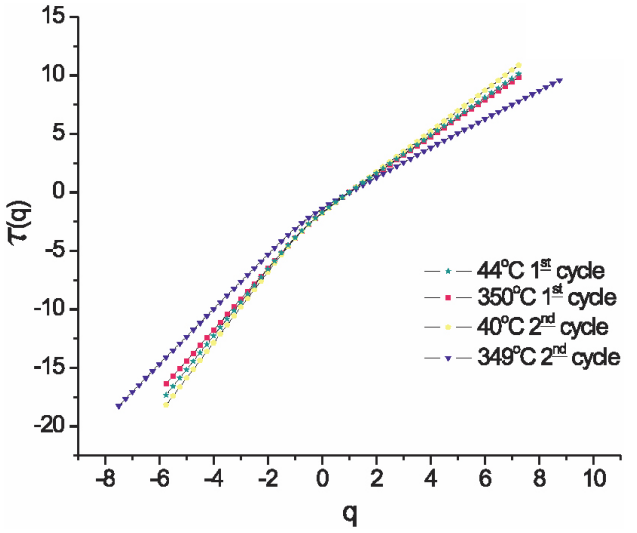

FIGURE 8. Mass exponent function $\tau(q)$ corresponding to the sample at 44°C and 350°C during the first heating process and at 40°C and 349°C during the second heating process.

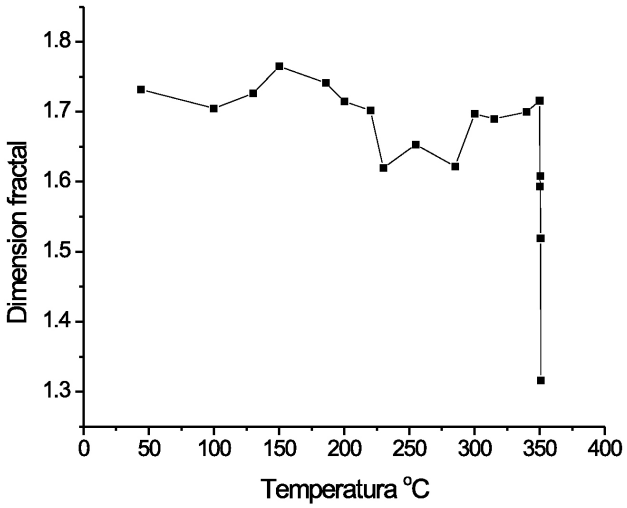

FIGURE 9. Evolution of the fractal dimension as function of temperature for the sample during the first heating process.

the beginning of the heating process and just before the third phase transition (ferroelectric-paraelectric), for the first heating process. In Fig. 4b and Fig. 5b, we have depicted the graph of $\log_{10} N_w$ *vs* $\log_{10} r_i$, for the two stages respectively.

The slope of the straight segments is the fractal dimension, which describes the scaling of the average number of pixels with radial distance r. The fractal dimension has only one value when starting the heating process, and two different values near the paraelectric phase. The graph of $f(\alpha)$ is convergent, and the graph $D(q)$ is not decreasing for the structure of Fig. 4. On the other hand, for the structure shown in Fig. 5, the graph of $f(\alpha)$ is not clearly convergent, and the graph of $D(q)$ is decreasing. This means that this structure is non-fractal at the beginning of the heating process, and evolves to a structure that exhibits some multifractal characteristics.

In Fig. 6 and 7 we present the analysis of two different stages of the second heating process. In Fig. 6a appears the domain wall structure at 40°C. Figure 6b shows the graph of $\log_{10} N_w$ *vs* $\log_{10} r_i$. In this graph it is observed that the structure has only one value of the fractal dimension, D=2. On the other hand, the graph of $f(\alpha)$ is convergent and the graph of $D(q)$ is not decreasing. This results tell us that the structure in that stage is non fractal. In contrast we have the domain wall structure at 349°C. One observes in Fig. 7b, that this structure presents three different values of the fractal dimension. This is corroborated with the corresponding curves of $f(\alpha)$ and $D(q)$, where the graph of $f(\alpha)$ is humped, and the graph of $D(q)$ is decreasing. This graphs make evident a multifractal behavior.

The mass exponent spectrum $\tau(q)$ corresponding to each one of the stages is shown in Fig. 8. In the latter we can observe that the curves of $\tau(q)$ corresponding to the sample at 44°C and 40°C match better to a straight line compared to the curves corresponding to the sample at 350°C and 349°C which exhibit a concave behavior.

In Fig. 9 we show a graph that in some way summarizes the results shown in the previous graphs. In Fig. 9 we depicted the evolution of the fractal dimension, the maximum value of the singularity spectrum, as a function of temperature during the first heating process. In this graph one can observe that the three structural transitions undergone by the sample in this temperature interval, produce some effect in the fractal dimension value. Note the slight decrement in the fractal dimension around the temperatures 195°C, 265°C and the large decrement around the fundamental transition at 350°C.

A detailed analysis of the evolution of the complexity in terms of the fractal dimension would require firstly, a study of the entire sample, and secondly, the analysis of a larger number of photographs, mainly for temperatures around the temperature of the transitions. However, this task is out of the scope of this work.

4. Summary and Remarks

The evolution of the complexity of the domain wall structure of cobalt bromine boracites was studied by a multifractal analysis performed on digital pictures taken at different stages along different heating-cooling cycles. We observe strong changes in the structure of the walls and our analysis shows that the multifractal characteristics change dynamically with temperature. At the beginning of each one of the heating processes, the sample exhibits a domain wall structure with an unique value of the mass fractal dimension (D=2). This value is representative of a non-fractal pattern, which means that the structure along that stage is ordered or homogeneous. Near the paraelectric phase transition there occurs a change in the characteristics of the wall structure, appearing different values of the mass fractal dimension and producing a definite multifractal spectra. These results tell us that the domain structure at that stage is more complex or non homogenous. From these, we can conclude that the sample

evolves with increasing temperature from a non-fractal structure to a multifractal structure. The changes in the structure of the domains exhibits a scaling behavior and make it possible to describe the evolution, not only of the complexity, but the energetic state of the sample. Additionally, the procedure and results of this analysis make possible to investigate in boracites different features, such as the memory of the domain wall structure (persistence of the structure after several heating-cooling cycles), and the energetic state of the sample, this latter, estimating by using the scaling relations of the spatial distribution of the walls.

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1. A.G. Castellanos-Guzman, M. Trujillo-Torrez, and M. Czank, *Materials Science and Engineering B* **120** (2005) 59.
2. R.J. Nelmes, *J. Phys. C. Solid State Phys.* **7** (1974) 3840.
3. H. Schmid, *J. Phys. Chem Solids* **26** (1965) 973.
4. M. Delfino, G.M. Loiacono, and P.S. Gentile, *Inorg. Chim. Acta* **43** (1980) 59.
5. C. Fouassier, A. Levasseur, J.C. Joubert, J. Muller, and P. Hagenmuller, *Zeitschrift fuer Anorg. Chem.* **375** (1970) 202.
6. J.Y. Jo, S.M. Yang, T.H. Kim, H.N. Lee, J.-G. Yoon, S. Park, Y. Jo, M.H. Jung, and T.W. Noh, *Phys.Rev.Lett.* **102** (2009) 045701.
7. J.L. Carrillo, F. Donado, and M.E. Mendoza, *Phys. Rev. E* **68** (2003) 061509.
8. R. Moctezuma, M.E. Mendoza, and J.L. Carrillo, *J. Mag. Mag. Mat.* **320** (2008) 186.
9. H. Schmid, in: N. Setter (Ed.), *Ferroelectric Ceramics* (Monte Verit'a, Birkh'ausen Verlag, Basel, 1992). pp. 107.
10. M.E. Mendoza, J.P. Rivera, and H. Schmid, *Jap. J. Appl. Phys.* **24** (1985) 1057.
11. C. Ricotta, *Ecological Modelling* **125** (2000) 254.
12. A. Chhabra and R.V. Jensen, *Phys. Rev. Lett.* **62** (1989) 1327.
13. A.B. Chhabra, Ch. Meneveau, R.V. Jensen, and K.R. Sreenivasan, *Phys. Rev. A* **40** (1989) 5284.
14. R.E. Moctezuma, J.L. Carrillo, and M.E. Mendoza, *Ferroelectrics* (in press).
15. P. Toledano, H. Schmid, M. Clin, and J.P. Rivera, *Phys. Rev. B* **32** (1985) 6006.
16. M.E. Mendoza, H. Schmid, and J.P. Rivera, *Ferroelectrics* **55** (1984) 227.