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PHASE TRANSITION OF $CaFeO_{2.5}$ AT HIGH TEMPERATURE

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Résumé

Les nombreuses études menées sur la structure de $CaFeO_{2.5}$ montrent que le matériau subit une série de transformations en fonction de la température. La première apparaît autour de 700 K et indique l'évolution du matériau de la phase magnétique à une phase paramagnétique. À environ 970 K la structure de $CaFeO_{2.5}$ change de la structure rhomboédrique à une structure centrée. Enfin vers 1180 K, il subit la transition vers une structure qui a été décrite comme structure modulée incommensurable. Nous avons observé le comportement du matériau au-delà de cette température par dilatométrie, DSC et TGA. Les tests effectués sur un monocristal de $CaFeO_{2.5}$ confirment les changements déjà observés. Pour la première fois il apparait une anomalie dilatométrique (confirmée par DSC et TGA) à 1310 K. Cette anomalie est observée uniquement dans la direction cristallographique b, et doit être probablement due à une transformation correspondante du matériau.

Mots clés: Dilatométrie, DSC , TGA

Abstract

The numerous studies conducted on the structure of $CaFeO_{2.5}$ showed that the material undergoes a series of transformations based on temperature. The first one appears around 700 K and indicates the evolution of the phase-magnetic material to a paramagnetic phase. At about 970 K the structure of $CaFeO_{2.5}$ changes from rhombohedral to centered structure. Finally, around 1180 K it undergoes the transition to a structure that has been described as incommensurate modulated structure. We have observed the behavior of the material beyond this temperature by dilatometry, DSC and TGA. The tests conducted on a single crystal $CaFeO_{2.5}$ confirm the changes already observed.For the first time there was a dilatometric anomaly (confirmed by DSC and TGA) at 1310 K. This anomaly appears only in the crystallographic direction b which should probably be a commensurate transformation of the material.

Keywords: Dilatometry, DSC , TGA

ملخص

العديد من الدراسات التي أجريت على بنية $CaFeO_{2.5}$ أظهرت أن هذه المادة تخضع لسلسلة من التحولات تبعا لتغيرات درجة الحرارة.أول تحول يظهر في حدود 700 K ويشير إلى تحول المادة من الحالة المغناطيسية إلى الحالة البارامغناطيسية. في حدود 970K تتغير بنية $CaFeO_{2.5}$ يتغير من منشور سداسي إلى بنية ممركزة. التحول الأخير يكون عند 1180 K ويشير إلى انتقال البنية من البنية الممركزة إلى ما وصف ببنية منظمة غير محددة. قمنا بدراسة تحولات هذه المادة في مجال من الحرارة يتجاوز 1180 K باستعمال تقنية dilatometry، DSC و TGA. التجارب التي أجريت على $CaFeO_{2.5}$ وحيد البلورة أكدت التغييرات التي نشرت من قبل. لأول مرة لاحظنا بوضوح بروز شذوذ يظهر حوالي1310 K بتقنية dilatometry (أكدنا ذلك باستعمال DSC و TGA).هذا الوضع الشاذ لوحظ فقط في الاتجاه البلوري b، ويري البنية للمادة.

الكلمات المفتاحية: dilatometry ، DSC و TGA.

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Introduction

The interest of many studies on solid solutions series $Ca_2(Fe_{1-x}Al_x)_2O_5$ (under normal pressure and temperature x varies from x = 0 to x = 0.7 by Taylor -1997 [1]) is due to Ca_2FeAlO_5 (x=0.5) compound which is one of the four basic constituents of Portland cement (calcite); and secondly the fact that these compounds exhibit attractive properties in ionic conduction for use as oxygen membranes or as solid electrolytes in fuel cells (SOFCs); or finally in a broader context for understanding diffusion phenomena of oxygen at low temperature [2].

Much work on the structure of these compounds has been made. Bertaut [3] in 1959 in a study on dicalcium ferrite and brownmillerite was the first given data on $Ca_2Fe_2O_5$ structure which was confirmed later by Smith [4]. $Ca_2Fe_2O_5$ (compound with pure iron member; i.e. x=0) is an oxide with brownmillerite structure. This oxide called srebrodolskite own orthorhombic structure with the following parameters a = 5.4, b = 14.8 and c = 5.6 Å. The structure consists of a superposition of alternating layers of octahedra and tetrahedral (fig. 1).

The compound $Ca_2Fe_2O_{5-\delta}$ (δ expressing the stoichiometry) is almost stoichiometric in ambient oxygen pressure in the range 300-1270 K (the non-stoichiometry δ not exceeding ± 0.02) [5]. The transition of $Ca_2Fe_2O_5$ from brownmillerite to perovskite structure requires the cleavage of the bond Ca-O and a rearrangement of atoms in the compound, and then it can give $CaFeO_3$. Speculating reasonably that the energy needed for this failure is so high that the cleavage is difficult.Thus, the author concludes that the transformation of $Ca_2Fe_2O_5$ in anion-deficient perovskite-type $CaFeO_3$ is possible at high pressure oxygen [6]. Woodward et al. [7] synthesized $CaFeO_3$ in these conditions using $CaFeO_{2.5}$ as base material and $KClO_4$ as oxygen source. This is not the case of $SrFeO_{2.5}$ similar product that is beginning to take oxygen at 900 K, while $CaFeO_{2.5}$ is stoichiometric relative to its amount of oxygen until at least 1300 K [2].

Magnetic measurements based on the ^{57}Fe Mossbauer spectroscopy and neutron diffraction [8] showed that $CaFeO_{2.5}$ is antiferromagnetic with Neel temperature around 703 K.

$CaFeO_{2.5}$ undergoes a transformation from the orthorhombic to a centered structure at about 970 K. Berastegui et al. [9] and Redhammer et al. [10] have showed that this transformation can be described in space group *Imma* with a disorder of the chains of tetrahedra instead of the expected structure and suggested type *I2mb* characterized by a single orientation of tetrahedra.

Other workers Lambert et al. [11] Abakumov et al. [12-14] used a model in superspace (3+1) dimensions to explain that tetrahedral chains in brownmillerite structures are subject to an order giving a commensurate structure characterized by two types of symmetry of tetrahedral chains (L and R) in the sequence ...LRLR... where the L and R chains alternate along the c axis in the same layer. Fukuda et al. [15] (2002) and Redhammer [10] (2004) reported that $CaFeO_{2.5}$ may make adjustments to the high temperature phase.

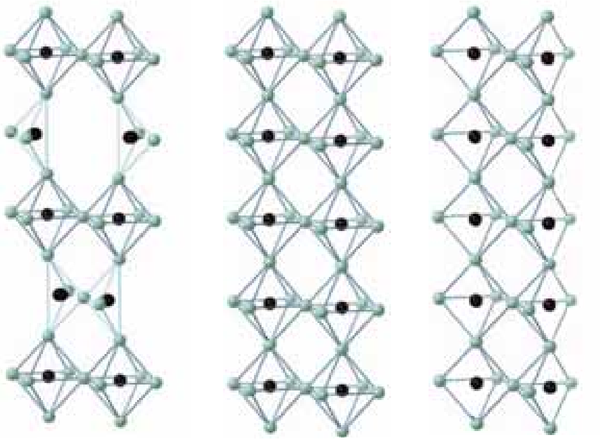

Fig. 1: Schematic structures of Brownmillerite(a), perovskite (b) and O_2-defect perovskite (c)
(*Captions are in open spaces*
and has been omitted for clarity)

In conducting the work of X-ray diffraction at high temperature on single crystals, Krüger et al., [15] (2005) have found that $CaFeO_{2.5}$ present at 1100 K an incommensurate modulated structure adopting the super-space group *Imma*(00γ)s00 with γ = 0588(2). More recently, Lazic et al [16] (2008) has found that a structurally similar compound $CaAlO_{2.5}$ is also subject to a transformation of the same type and at the same temperature range (1100 K).

We wanted to observe the structural behavior of the compound $CaFeO_{2.5}$ beyond this temperature by studying the material by various thermodynamic techniques including dilatometry, DSC and TGA up to 1473 K.

We have used single-crystal $CaFeO_{2.5}$ in the form of rod of 5.2 mm diameter. It was obtained after different stages of mechanical and thermal treatments, and finally crystallization in an image furnace. The crystal orientation was determined by the technique of neutron diffraction. The crystal was cut using a machine with diamond disc immersed in a coolant. We cut samples by side perpendicular to the three crystallographic directions a, b and c.

EXPERIMENTAL

For dilatometry, we have used a NETZSH DIL 402C dilatometer with a heating rate and cooling to 5 K / min in the temperature range 300-1473 K.

The thermal expansion tests were performed according to the three cristallographic directions a, b and c. For each sample, it was conducted 02 cycles dilatometer heating and cooling. The test parameters were identical for all trials to learn the same speed, with a constant force of alumina pushbutton and a resolution of 8 nm.

The DSC tests were performed using a device NETZSH STA 409 PC/PG coupled to a TG analyser. The analysis conditions were the same as dilatometry, namely a constant rate of heating and cooling to 5 K / min and at the same temperature range. DSC/TGA essays were conducted on a sample heating and cooling.

RESULTS ET DISCUSSION

Direct dilatometric curves ($\Delta L/L_0$ vs. K) along the three crystallographic directions a, b and c showed some dilatometric anomalies. Some anomalies are not very intense. They appear neater in dilatometric derived curves.

Following increased temperatures, a first expansion of the crystalline network in the 3 directions appears in the range 670-740 K (Fig. 2). This anomaly corresponds to a phase transition of magnetic material which has been already observed by various authors around 700 K [17, 18].

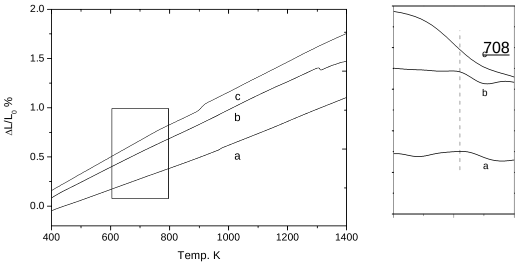

Fig.2: Direct dilatometric curves ($\Delta L/L_0$ vs. K) in the 3 crystallographic directions a, b and c and derivate curves betwee 600 and 800 K

At 948-1010 K, $CaFeO_{2.5}$ is subject to a 2nd dilatometric anomaly more pronounced in the 3 directions a, b and c (Fig. 3). Redhammer et al [10] observed an expansion on the same material at 997 K and attributed it to a centered phase transition of the structure. Similarly, Shaula et al. [5] showed that the network of the orthorhombic calcite iron undergoes a transformation of the original structure (Space group *Pnma*) to a centered structure at 950-1000 K.

Notice that intensity of this expansion follows the same course and will gradually increase according to b, then a, and finally c-axis. This behavior is comparable to that other workers have obtained with different techniques as X-ray diffraction [5, 9].

Furthermore, the transition appears in heating and cooling with the same intensity and a slight hysteresis in temperature (fig. 4), reflecting a 1st order transition. We conclude that this dilatometric anomaly is attributable to the transition phase in question, i.e. transition from rhombohedric to a body-centered structure.

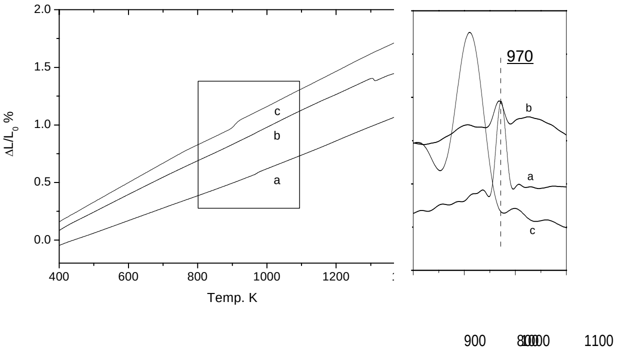

Fig.3: Direct dilatometric curves ($\Delta L/L_0$ vs. K) in the 3 crystallographic directions a, b and c and derivate curves between 800 and 1100 K

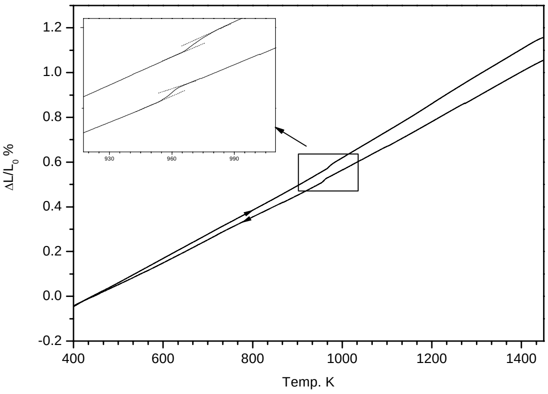

Fig. 4: Direct dilatometric curves on heating and cooling in crystallographic direction a.
(Same behavior is observed in direction b and c)

Beyond this temperature, curves show a series of dilatometric anomalies, the following is common to the 3 crystallographic directions lies in the temperature range defined between 1120 and 1245 K (fig. 5). While curves show contraction of the sample in the directions a, in b and c directions the result is an expansion. This transition is probably the same as that observed by Krüger [15] (2005) at 1100 K which is attributed to a modulated incommensurate transition of $CaFeO_{2.5}$.

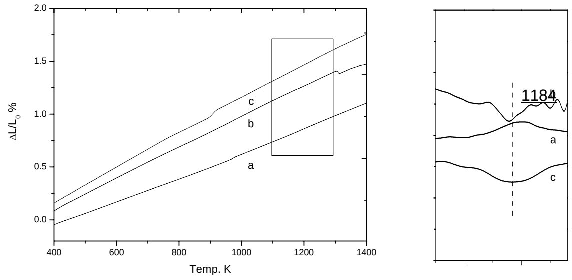

Fig.5: Direct dilatometric curves ($\Delta L/L_0$ vs. K) in the 3 crystallographic directions a, b and c and derivative curves between 1050 and 1280 K

At 1278 K begins a sharp clear contraction only in b direction (Fig. 6). The maximum is at 1308 K, and it is fully completed at 1338 K. This abnormality is not reversible and does not appear in cooling (Fig. 7). The second cycle of heating of the same dilatometer sample shows that this contraction is still present (Fig. 8).

Beyond this temperature, in the same cristallographic direction b, the sample is still undergoing a contraction followed immediately by a slight expansion and finally a last contraction before the onset of the liquid phase.

This particular behavior of $CaFeO_{2.5}$ is observed for the first time and only in one crystallographic direction due to the particular structure of $CaFeO_{2.5}$ [18, 19]. Structurally, $CaFeO_{2.5}$ differs from other similar products mainly in the extension of the b axis, which axis is the stacking of octahedral and tetrahedral layers.

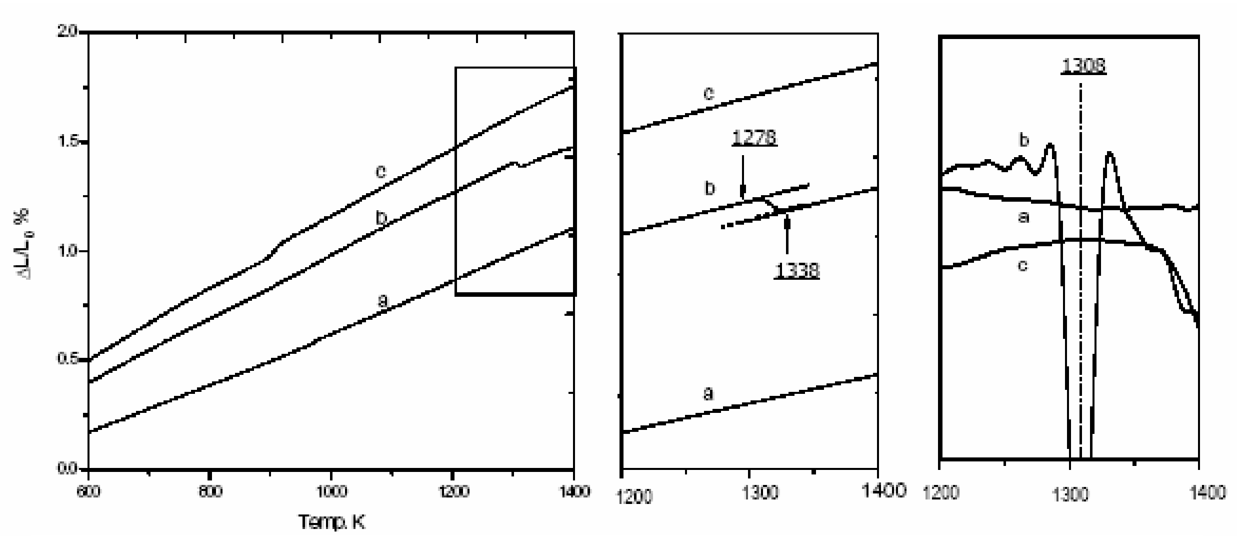

Fig. 6: Direct dilatometric curves ($\Delta L/L_0$) in the 3 crystallographic directions a, b and c and derivative curves between 1200 and 1400 K *(contraction observed in b direction does not appear in the 2 other directions a and c)*

The fact that this transformation does not appear in cooling indicates clearly that it is a of 2nd order transition phase which is probably due to the passage from incommensurate to a commensurate phase. On the other hand, examination of the DSC curve shows a slight endothermic peak around this temperature and confirms the transformation of a 2nd order.

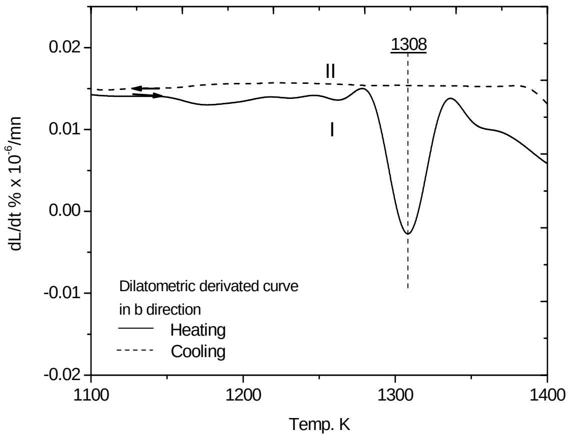

Fig. 7 : Dilatometric derivative curves on heating and cooling along b direction
(I heating – II cooling)

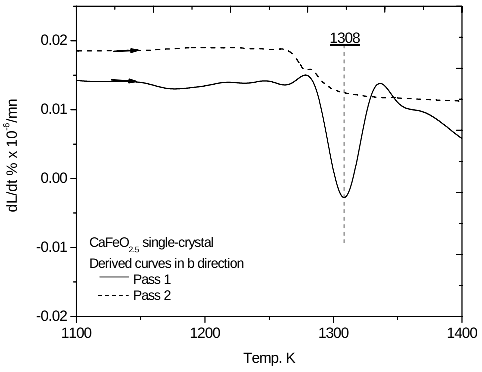

Fig. 8 : Dilatometric derivative curves on heating along b direction
(cycle 1 and 2 on the same sample)

For the comparative study by different techniques used, both DSC and TG curves confirm the presence of different processing as observed in dilatometry.

TG curve (Fig. 9) shows 2 peaks already observed by Woerman et al. [20] (1968), practically at the same temperatures (respectively 742 and 984 K). They correspond respectively to the magnetic transition and the transition from the rhombohedral structure to a centered body structure of $CaFeO_{2.5}$. A 3rd peak appears around 1064 K and 1382 K appears to confirm the sharp contraction in dilatometer only in the b direction to the same temperature. Similarly, the DSC curve (Fig. 10) shows a small peak at nearly the same temperature and also confirms the anomaly mentioned above.

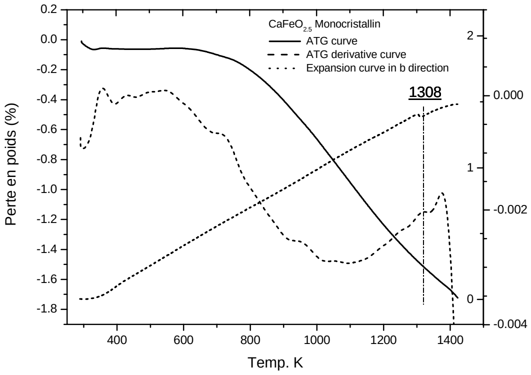

Fig. 9 TG curve and its derivate combined with expansion curve in b direction of $CaFeO_{2.5}$

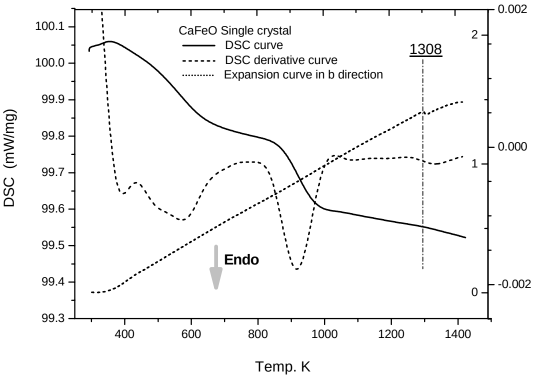

Fig. 10 DSC curve and its derivate combined with expansion curve in b direction of $CaFeO_{2.5}$

CONCLUSION

In this study, we have found the phase transitions already cited in the literature and whose transition temperatures are in agreement. The first appears at 670-740 K and is attributed to the magnetic phase transition of the material. The second is characterized by an expansion of the network with a higher amplitude in the direction a of the crystal lattice appears to 948-1010 K where the structure become centered.

We have also found a third anomaly around 913-1045 K. This anomaly is characterized by an expansion in the direction a, whereas in the b and c direction it leads to a contraction.

For the first time, we have found a sizeable contraction of the network and only in the crystallographic direction b appearing in the range 1278-1338 K (peak at 1308 K) which probably corresponds to a commensurate transition of $CaFeO_{2.5}$.

These abnormalities are confirmed by DSC/TG tests. Peaks showing the same onset temperature phases are already described and particularly the anomaly appearing only in b direction.

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