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Changes in structure and electrical properties of NaNbO_3 induced by Mn dopant

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Abstract. The electric permittivity of ceramic NaNbO_3 : x Mn ($x = 0$ –1 wt.%) was measured in the range 20–500 °C. The Mn dopant induces an additional anomaly in the $\epsilon(T)$. The temperature of the maxima in $\epsilon(T)$ is shifted under applied axial pressure. The x-ray test proved that the anomalies in $\epsilon(T)$ are related to the structural phase transitions.

1. Introduction

There is a series of structural phase transitions in NaNbO_3 [1–3]. Several other phases can be induced by doping or electric field [4, 5]. There is an antiferroelectric (AFE) and a ferroelastic phase (called phase P) with the orthorhombic structure (*Pbma*) at room temperature. Transition to the next antiferroelectric orthorhombic (*Pnmm*) phase (called R) occurs at 360 °C. This is connected with the main maximum in the electric permittivity [6–9].

It was recorded that either non-stoichiometry [10] or hydrostatic pressure [11] influenced the P–R phase transition. It was known from the literature that the temperature of the P–R phase transition could be shifted toward lower temperatures with various doping, e.g. with Ta, K or Mn ions. Another effect was the appearance of a new phase if the concentration of a dopant was high enough [4, 12, 13].

In the case of doping with Mn, a new anomaly in the electric permittivity was generated near 400 °C for quite low content of the doped ions in NaNbO_3 . Moreover, weak polar properties induced by the Mn dopant were detected below this anomaly [13]. It has not been stated yet whether this new maximum is related to a structural phase transition. The expected interaction between the ferroelasticity, antiferroelectric order and dopant ions may lead to complicated patterns of the crystal structure [14, 15].

The main purpose of this paper is to examine the influence of light Mn doping on the electric permittivity in the vicinity of the P–R and the induced phase transitions and also to investigate the dependence of electric permittivity on axial pressure in this range of temperature. The other aim is to determine whether the induced changes in the electric permittivity are related to a structural phase transition.

2. Experimental details

Ceramic samples of NaNbO_3 doped by various amount of Mn were sintered according to the procedure described in our earlier paper [13]. Mn oxide was added to stoichiometric

NaNbO_3 to obtain Mn content equal to 0.0, 0.1, 0.2, ..., 0.9, 1.0 wt.%. With increasing Mn content, the colour of the samples varied from light yellow to brown.

The x-ray test was performed on powdered samples using the modified DRON-1.5 spectrometer coupled with an IBM PC. Filtered Cu K_α radiation was used. Lattice parameters were calculated from (200) and (222) multiplets.

Electric permittivity was measured with a Tesla BM 595 capacitance meter within the temperature range 20–500 °C, at a constant rate of temperature change of 1.5 K min^{-1} . The measuring frequency was equal to 400 Hz, 2 kHz and 20 kHz. The measurement cycle, on cooling and heating, was repeated three times. Samples of thickness $d = 0.5$ mm and surface electrode area $s = 2 \times 2$ mm² were prepared for the electric measurements.

The sample doped by 0.5 wt.% of Mn was treated additionally, before the subsequent cycles of $\epsilon(T)$ measurement, using ultrasound in an alcohol bath at room temperature for 15 min. Then, the electric permittivity was recorded on heating and cooling. The next step was to check whether the effects caused by the ultrasound were irreversible. This irreversibility was tested by leading of the sample into the neighbouring phases. Therefore, the same sample was cooled, using liquid nitrogen, below the next-lowest-temperature phase transition and $\epsilon(T)$ was recorded. Then again the sample was treated with ultrasound and the $\epsilon(T)$ dependence was measured. The last measurement was performed after no ultrasound treatment but the irreversibility could again be checked because the sample had been transformed to the next-highest-temperature phase R during the former cycle of $\epsilon(T)$ measurement (heating up to 500 °C).

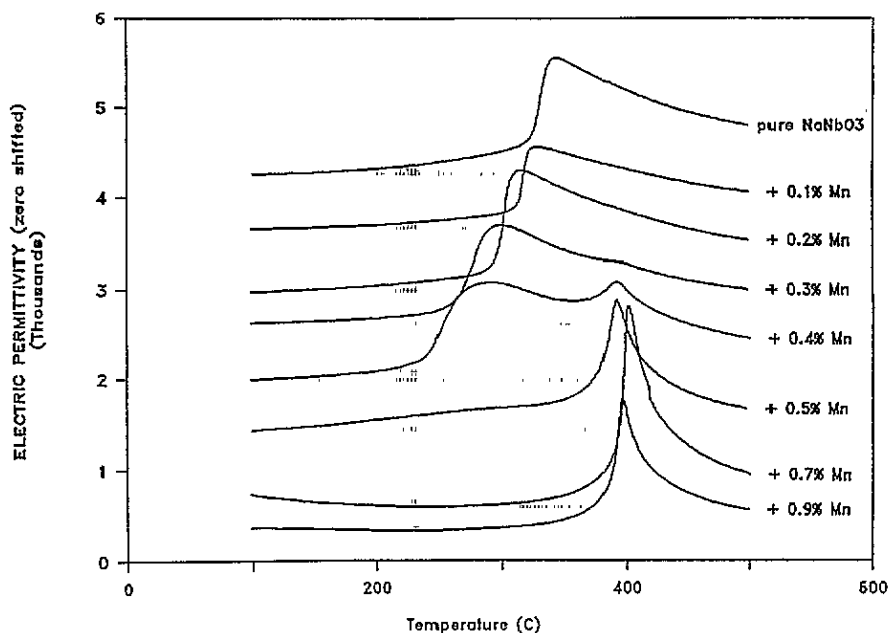


Figure 1. The electric permittivity against the temperature recorded on cooling. The amount of Mn dopant in the samples of NaNbO_3 : x wt.% is marked. The 'zero' level in the ϵ scale is shifted.

Samples with $s = 1$ mm² and $d = 3.8$ mm were prepared for measurements of the electric permittivity under axial compression. The sample holder was constructed to apply

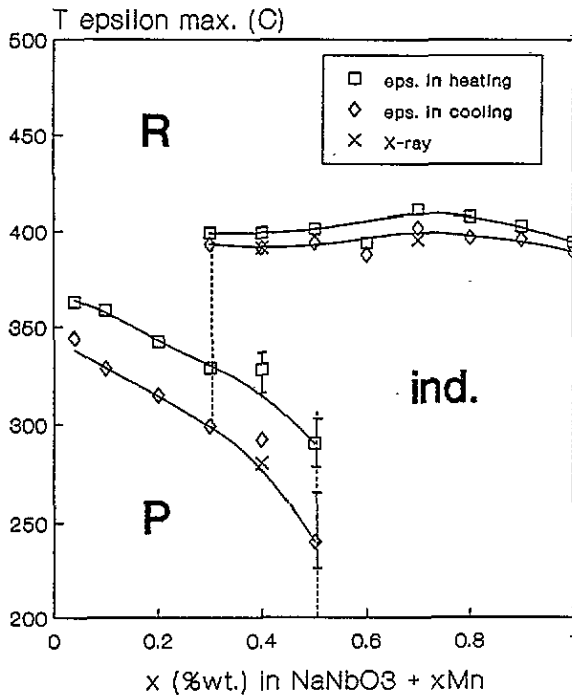


Figure 2. The phase diagram obtained from temperatures $T_{\epsilon_{\max}}$ of maxima in the $\epsilon(T)$ anomaly against Mn content (in wt.%). The temperature hysteresis is visible. Also shown are points (\times) added from the x-ray test data shown in figures 8 and 9 that denote the temperatures of appearance of the phases monoclinic 1 and monoclinic 2 for 0.4 wt.% of Mn and the temperature of transition to the phase monoclinic 2 for 0.7 wt.% of Mn.

axial pressure with the use of a lever and a weight, similarly to the standard procedure in the literature [16]. Axial pressure was applied within the range of 100 bar. The electric permittivity was measured under constant pressure at frequency 20 kHz in three subsequent cycles of cooling and heating.

It should be mentioned that the rod sample, demanded for the axial pressure experiment, does not obey the conditions needed to determine properly the value of the electric permittivity. However, $\epsilon(T)$ dependences obtained for both types of shape (rods and plates) of these ceramic samples coincide, which thus allows to compare these two series of data. In any case, specific values of parameters were not evaluated from the $\epsilon(T)$ data obtained for the rod samples.

3. Results

The dependences of the electric permittivity ϵ on temperature obtained for frequency $f = 20$ kHz are shown in figure 1. The values of $\epsilon(T)$ measured for lower frequencies are substantially similar but higher. It is apparent that the dependences of electric permittivity ϵ on temperature are influenced by the Mn dopant. The anomaly related to the AFE phase transition, existing at 360 °C in pure NaNbO_3 [6], is shifted down and reduced. A new anomaly appears at ~ 400 °C in the samples doped by Mn. This anomaly is clearly visible

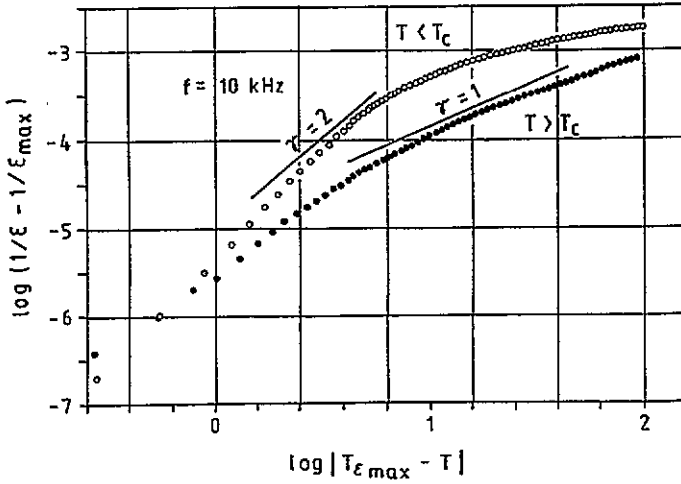


Figure 3. The reciprocal permittivity against the temperature on a log-log scale. Experimental points: \circ , temperature range below $T_{\epsilon_{\max}}$; \bullet , temperature range above $T_{\epsilon_{\max}}$. The full lines denote the slopes for $\gamma = 1$ or 2 in the Curie-Weiss law. The non-linear run of the experimental points shows that the Curie-Weiss law cannot be fitted.

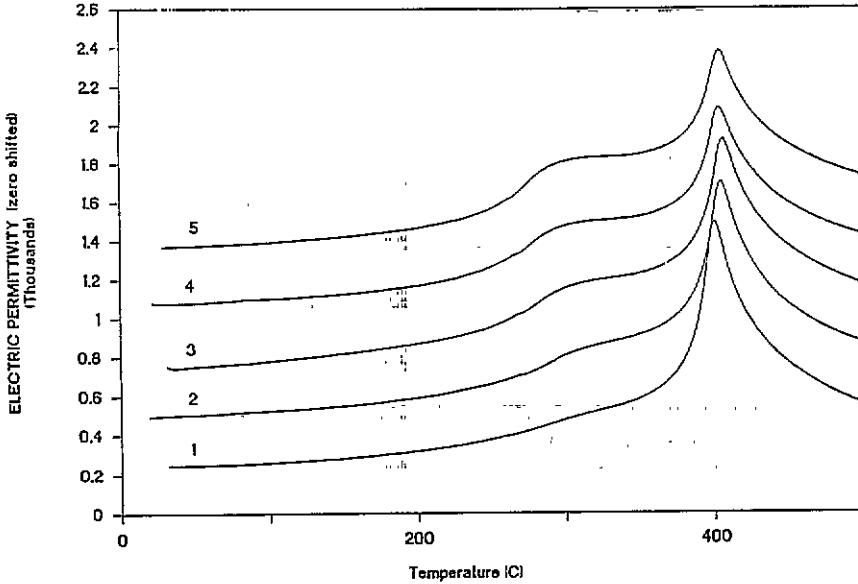


Figure 4. The electric permittivity against the temperature for the same sample of NaNbO_3 : 0.5 wt.% Mn recorded on heating ($f = 20$ kHz). The 'zero' level in the ϵ scale is shifted (by 300 for each subsequent curve). The runs were recorded after initial heating and cooling as follows: 1, sample not treated with ultrasound before the measurement cycle of heating and cooling; 2, sample after ultrasound bath in alcohol for 15 min at room temperature; 3, sample cooled down in liquid N_2 before the $\epsilon(T)$ measurement; 4, sample after ultrasound bath as for 2; 5, sample not treated with ultrasound after the previous cycle (4). The runs 3 and 5 allow us to check the irreversibility of effects caused by the ultrasound.

for the samples containing more than 0.2 wt.% of Mn. The new anomaly is dominant when the Mn content is higher than 0.5 wt.%.

The phase diagram obtained from $\epsilon(T)$ measurement performed on the samples with various Mn contents is presented in figure 2. The temperature of the maximal value of the electric permittivity has been recognized as the temperature of the phase transition. The two anomalies in $\epsilon(T)$ and thus two phase transitions are observed for samples with 0.3, 0.4 and 0.5 wt.% of Mn dopant.

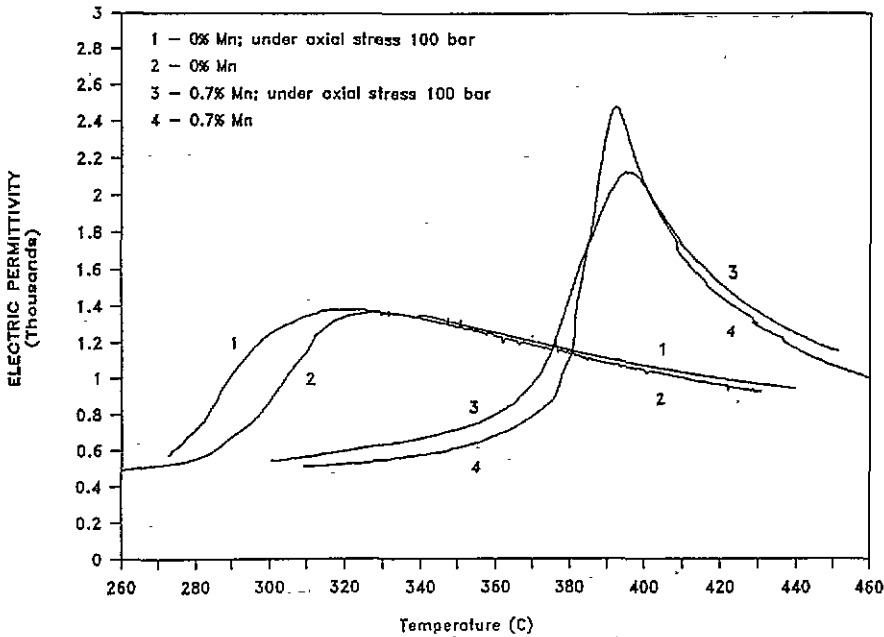


Figure 5. The electric permittivity against the temperature (recorded on cooling with or without axial stress, $f = 20$ kHz): 1, NaNbO_3 , $\sigma = 100$ bar; 2, NaNbO_3 , $\sigma = 0$ bar; 3, $\text{NaNbO}_3:0.07$ wt.% Mn, $\sigma = 100$ bar; 4, $\text{NaNbO}_3:0.7$ wt.% Mn, $\sigma = 0$ bar.

The new anomaly of $\epsilon(T)$ appearing near 400°C does not show Curie-Weiss type dependence on temperature [13]. The plot of reciprocal permittivity versus temperature (presented for the sample with 0.7 wt.% of Mn) shows that this non-linear dependence cannot be fitted with a simple function

$$\epsilon^{-1} \simeq A(T - T_{\epsilon_{\max}})^\gamma \quad (1)$$

with $1 \leq \gamma \leq 2$ (figure 3).

An additional insight into the properties of the NaNbO_3 crystal influenced by the Mn dopant was obtained when the sample was mechanically treated. The sample containing 0.5 wt.% of Mn, with both anomalies existing in $\epsilon(T)$, was treated with an ultrasound bath at room temperature. The results are shown in figure 4. The ultrasound caused a relative increase in the anomaly connected to the AFE phase transition (around 300°C) and a decrease in the new anomaly induced near 400°C (figure 4, curves 2 and 4). This effect was not reversed after the transformations to the next phases. The proportion between the

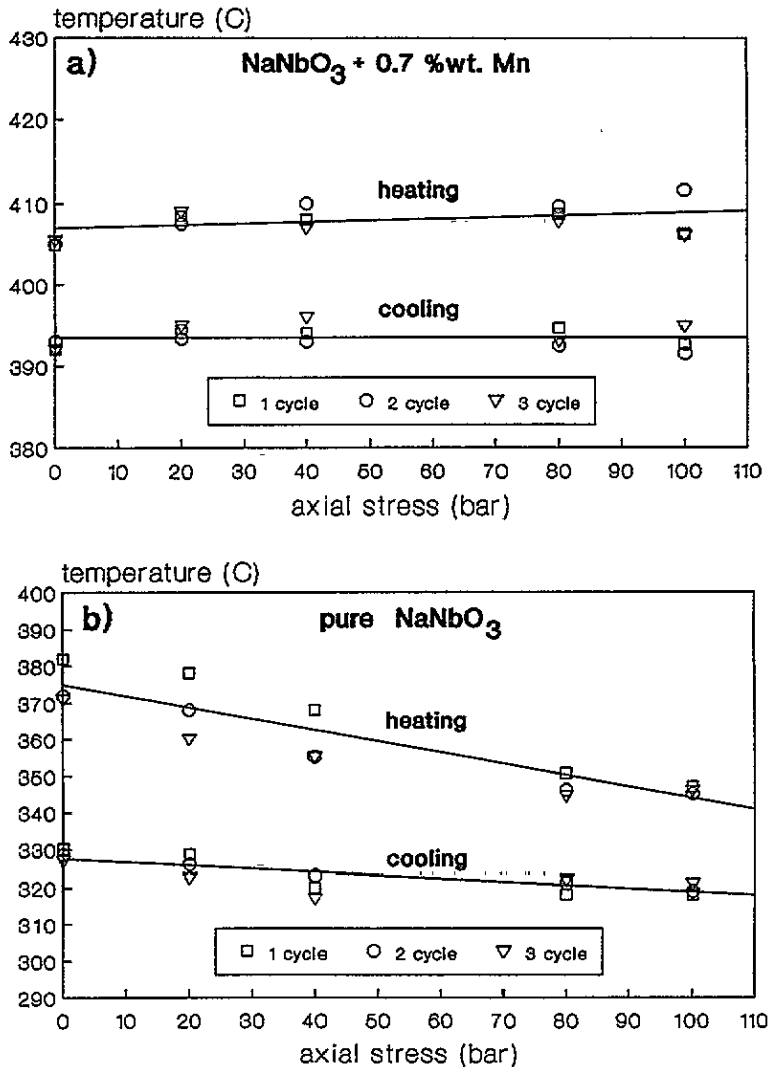


Figure 6. The phase diagrams for (a) doped NaNbO_3 : 0.7 wt.% of Mn and (b) undoped NaNbO_3 . The temperature of the maximal value in $\epsilon(T)$ is plotted against applied axial compression σ . The data were obtained at constant stress during three successive cycles of cooling and heating.

two anomalies concerned was not changed (figure 4, curve 3) after cooling the sample in liquid N_2 below the next-lowest-temperature phase transition [2, 17]. This relative change in the proportion between the two anomalies was not reversed either after keeping the sample in the next phase P without ultrasound treatment at room temperature (figure 4, curve 5). This suggests that such a treatment stabilizes mechanically the phase existing in the pure NaNbO_3 and not that induced by Mn dopant.

The axial pressure effect on the electric permittivity in the range of the two anomalies was investigated on the two ceramic samples. The first one was the sample of NaNbO_3 :0.7 wt.% of Mn for which the new anomaly induced with Mn dopant was the sharpest (see figure 1). the other one was the sample of undoped NaNbO_3 for which the anomaly is connected to the AFE phase transition. Under applied axial stress, the AFE

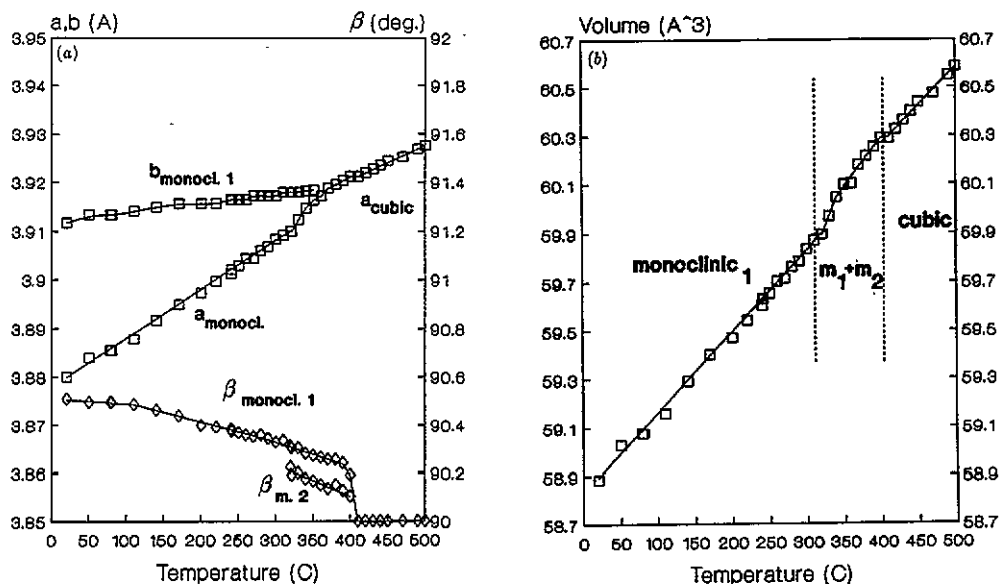


Figure 7. $\text{NaNbO}_3:0.2 \text{ wt.}\% \text{ Mn}$: the pseudoperovskite cell parameters (a) and the volume of the cell (b) against the temperature.

anomaly was shifted toward lower temperatures. The anomaly induced by Mn dopant was rounded and weakly shifted toward higher temperatures (figure 5).

The phase diagram obtained for these two samples is shown in figure 6. Particular values of $T_{\varepsilon_{\text{max}}}$ (related to maximal values of the electric permittivity) measured at constant pressure and obtained in the three successive cycles of cooling and heating can be regarded as fluctuating with decreasing tendency. The anomaly connected to the phase transition in the undoped NaNbO_3 is affected more strongly (figure 6(b)) than the anomaly induced with Mn dopant (figure 6(a)).

The temperature dependences of the parameters of the pseudoperovskite cell were measured to determine the phase transitions connected with the above described anomalies in the electric permittivity. Three samples of NaNbO_3 doped with 0.2, 0.4 and 0.7 wt.% of Mn were chosen for investigation.

There are traces of an additional orthorhombic phase with the monoclinic distortion of the pseudoperovskite cell observed for the sample doped with 0.2 wt.% of Mn (figure 7). This is visible as a coexistence of phases with two different distortions, monoclinic 1 and 2 (the phase with distortion 1 is known in pure NaNbO_3 as phase P [18]). The occurrence of two angles β_1 and β_2 ($\neq 90^\circ$) and the deviation from linearity in the plot of cell volume versus temperature prove the phase coexistence.

When the Mn content is higher the induced phase may be distinguished clearly and the temperature range of its existence increases. It is visible in the phase diagram obtained for the sample of $\text{NaNbO}_3:0.4 \text{ wt.}\% \text{ Mn}$. The phase induced with Mn dopant occurs in the range 220–390°C and only this phase exists in the range 290–390°C (figure 8). There are two different angles β_1 and β_2 not equal to 90° and also two different lattice parameters b_1 and b_2 , which characterize the two monoclinic distortions. It is apparent also from figure 8

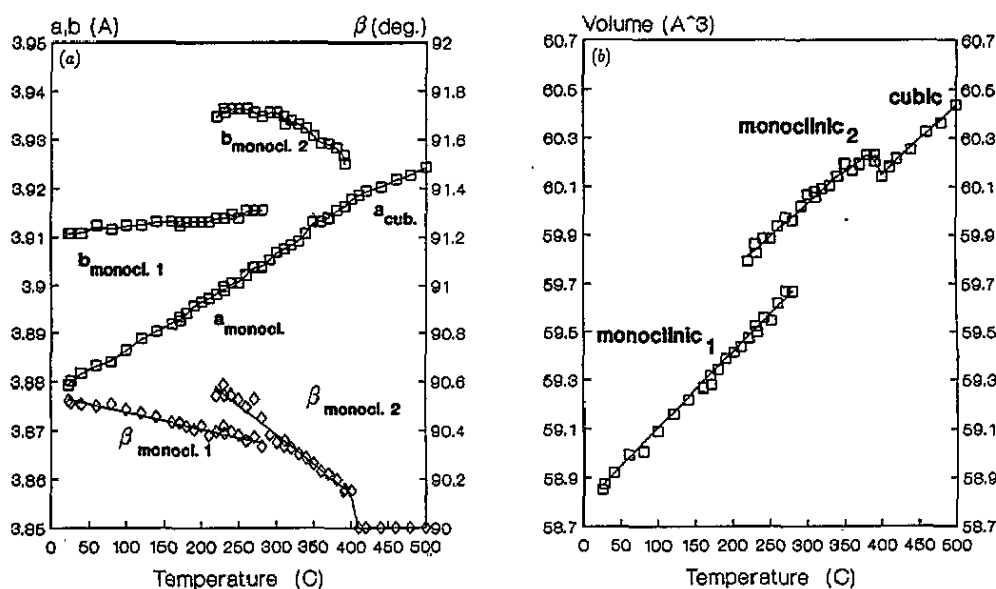


Figure 8. $\text{NaNbO}_3:0.4 \text{ wt.}\% \text{ Mn}$: the pseudoperovskite cell parameters (a) and the volume of the cell (b) against the temperature.

that the transition between the parent phase P (existing in the pure NaNbO_3) and the induced phase occurs with a non-continuous change in the volume of the pseudoperovskite cell.

The results obtained for the sample of $\text{NaNbO}_3:0.7 \text{ wt.}\%$ of Mn are shown in figure 9. There is a phase transition (at 395 °C) to the induced phase only. The phase with monoclinic 1 distortion was not observed.

The temperatures of appearance of the phases (monoclinic 1 and monoclinic 2 in the sample doped by 0.4 wt.% of Mn, monoclinic 2 for the sample containing 0.7 wt.% of Mn) are marked in figure 2, for comparison with the data obtained from the electric permittivity measurements.

4. Discussion

The x-ray test proves that the Mn dopant induces the new phase. This phase differs from phase P in the parameters of the monoclinic distortion. The increase in the volume of the phase monoclinic 2 in comparison with the volume of the phase monoclinic 1 suggests ferroelectric order. Such a correlation is observed in the other perovskites [19–22]. Phases with ferroelectric order are induced in NaNbO_3 by K dopant. There are the phases called Q (space group Pm) occurring approximately from room temperature to 260 or 200 °C and the G (space group $P2mm$) above phase Q up to 400 °C when the K ion content is 0.6–15 mol% [4]. When the values of the parameters obtained for the monoclinic 2 phase induced by Mn (figures 7–9) are compared to the parameters of the Q and G phases [1, 4] one can deduce that these phases are different. However, the Q and G phases are reported to be ferroelectric, which seems to be in conflict with the weak polar properties observed for the phase induced

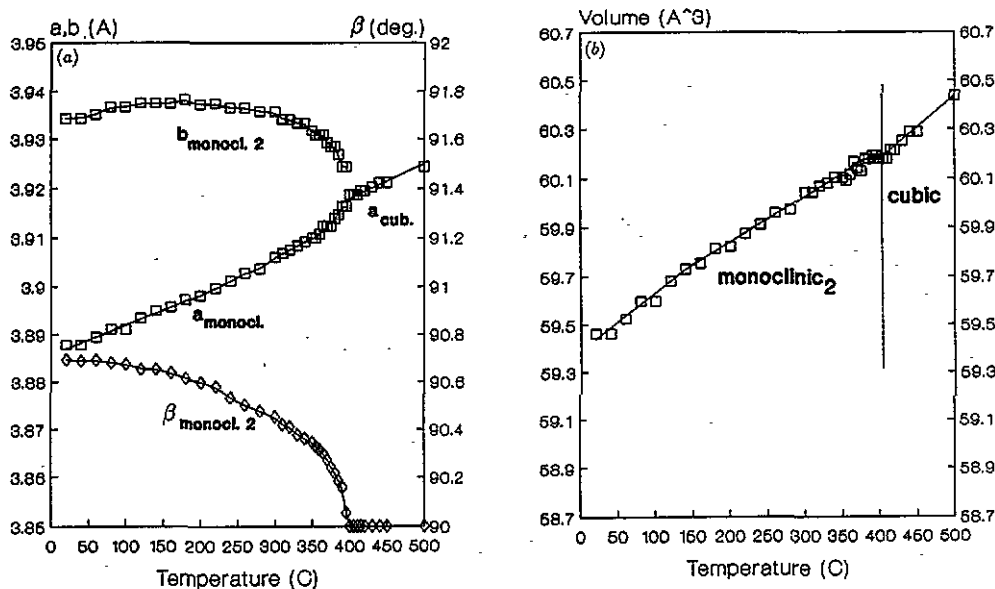


Figure 9. $\text{NaNbO}_3:0.7 \text{ wt.}\% \text{ Mn}$: the pseudoperovskite cell parameters (a) and the volume of the cell (b) against the temperature.

by Mn [13]. Moreover, the observation performed on the ceramic samples of $\text{NaNbO}_3:\text{Mn}$ did not show saturation of the D - E hysteresis loop [17]. The loop was not observed either for undoped NaNbO_3 samples under hydrostatic pressure [11].

There is a correlation between the observed anomalies in the electric permittivity and the range of appearance of the phases verified with the x-ray test (figure 2). The broad anomaly in $\epsilon(T)$ (in the temperature range 220–300 °C, see figure 1) is related to the coexistence of the two phases (figure 8). The anomaly induced by the Mn dopant (figure 1) is related to the appearance of the phase with monoclinic 2 distortion at ~ 400 °C (figures 8 and 9).

The axial compression caused the decrease of the transition temperature to the ferroelectric and antiferroelectric phase P (figure 6(b)). The transition to the induced phase is much less sensitive to the applied axial pressure (figure 6(a)). It has been observed that the induced phase is mechanically metastable and can, partially, change into phase P under ultrasound treatment (figure 4). Moreover, the anomaly in $\epsilon(T)$ connected with the transition to the induced phase is not described by the simple Curie-Weiss law and cannot be fitted with γ values from the range 1–2 (figure 3). Such a complicated behaviour indicates that the coupling between strain and electric polarization should be considered while these phase transitions in NaNbO_3 are investigated.

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