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## A Raman investigation of the ordered complex perovskite $\text{PbMg}_{0.5}\text{W}_{0.5}\text{O}_3$

A Kania<sup>†</sup>, E Jahfel<sup>‡</sup>, G E Kugel<sup>‡</sup>, K Roleder<sup>†</sup> and M Hafid<sup>‡§</sup>

<sup>†</sup> Institute of Physics, University of Silesia, ulica Uniwersytecka 4, 40007 Katowice, Poland

<sup>‡</sup> CLOES-MOPS, University of Metz and Supelec, 2 rue Edouard Belin, 57078 Metz, France

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**Abstract.** The complex perovskite  $\text{PbMg}_{0.5}\text{W}_{0.5}\text{O}_3$ , exhibiting a long-range B-site cation ordering, has been investigated by Raman scattering from 10 K up to 956 K. The Raman results are systematically treated, and analysed through the characteristic parameters of phonon peaks. The existence of an additional intermediate phase I between the low-temperature antiferroelectric phase A and the high-temperature paraelectric phase P has been demonstrated ( $T_{AI} \simeq 240$  K,  $T_{IP} = 312$  K). These results were compared with dielectric measurements. The disappearance of the first-order Raman structures near 1000 K in the paraelectric phase is discussed in terms of dynamic disorder in the Pb and O sublattices.

### 1. Introduction

The lead-based complex perovskites  $\text{Pb}(\text{B}'_{1-x}\text{B}''_x)\text{O}_3$  have attracted much attention for several years from the theoretical, experimental and applications points of view. According to the different degrees of order in the B-ion sublattice, they exhibit a great variety of physical properties and phase transitions [1–3]. They can be classified into three different groups:

- (i) a disordered group presenting a random cation distribution (or a coherence length below 2 nm);
- (ii) a group with short coherence length of order with a nanoscale between 2 and 50 nm; and
- (iii) a group with long coherence length of order above 100 nm.

The coherence length of the order has a strong influence on all physical properties as well as on the nature of the phase transitions. A short coherence length results in a relaxor behaviour as observed for  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  (PMN) (see, e.g., [4]). In contrast, compounds with long coherence lengths exhibit normal ferroelectric or antiferroelectric behaviour—for example,  $\text{PbYb}_{0.5}\text{Nb}_{0.5}\text{O}_3$  (PYN) [5]. In some specific materials, namely  $\text{PbSc}_{0.5}\text{Nb}_{0.5}\text{O}_3$  (PSN),  $\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$  (PST),  $\text{PbIn}_{0.5}\text{Nb}_{0.5}\text{O}_3$  (PIN), and  $\text{PbIn}_{0.5}\text{Ta}_{0.5}\text{O}_3$  (PIT), the degree of order can be easily changed by annealing at suitable high temperatures [2, 3, 6–8], which allows one to study the same system with different states of order. Only few papers concerning Raman scattering experiments have been devoted to this kind of complex perovskite [9–12]. One common feature observed in the paraelectric phase, even in the case of low degrees of order in the B-ion sublattice (PMN), is the occurrence of the first-order Raman spectra, which disappear at high enough temperatures [9–12].

§ On leave from the Faculty of Science, University of Kenitra, Morocco.

Raman measurements carried out for differently ordered PST and PIN crystals clearly showed the influence of the degree of order on the lattice dynamics characteristics [10, 12]. A decrease of the degree of order leads to broadening of the Raman lines, the disappearance of their eventual splitting, and increased diffuseness of evolution near the phase transition temperature.

It is already known that the first-order Raman lines active in the paraelectric phase disappear at high temperature, close to 1000 K. It has been suggested that the explanation of this phenomenon lies in the symmetry deviations in the oxygen sublattice [9, 12]. However, one cannot disregard the fact that the disappearance of Raman activity takes place in PIN and PST at temperatures at which the annealing procedures are usually being carried out.

In order to avoid any ambiguity connected with the transformation in the degree of order, we have chosen for the present Raman study a highly ordered complex perovskite: lead magnesium tungstate  $\text{PbMg}_{0.5}\text{W}_{0.5}\text{O}_3$  (PMW) [13–15]. The investigations have been performed in the temperature range from 10 K to 956 K.

PMW is known to be a completely ordered perovskite over the whole temperature range [15]. Thus, in this material the expected disappearance of Raman lines in the paraelectric phase should be unconnected with the B-ion-sublattice order–disorder transformation. PMW undergoes the following phase transformations: the first-order sharp phase transition from the cubic paraelectric phase (P) to the orthorhombic intermediate (I) phase at 312 K, and then to the orthorhombic antiferroelectric (A) phase of symmetry  $Pm\bar{c}n$  ( $Pnma$ ) at about 240 K [15, 16, 17]. Moreover, the combination of Raman and dielectric investigation was helpful in confirming the occurrence of the above-mentioned phase transitions.

## 2. Crystal growth

The PMW crystals were grown by the flux method. A  $\text{PbO-B}_2\text{O}_3\text{-PbF}_2$  mixture was used as the solvent, and the growing processes were carried out from 1300 to 1000 K with a cooling rate of about  $1.5 \text{ K h}^{-1}$ . Pt–Ir or Pt crucibles were used. Dark brown and light yellow crystals were obtained from Pt–Ir and Pt crucibles, respectively. In both cases crystals with a double-pyramid shape, and edges of up to 5 mm were grown. For dielectric and Raman scattering measurements the crystals were cut and polished in a cuboid shape with surfaces perpendicular to (100) directions. For the PMW grown in the pure Pt crucible, a higher value of the electric permittivity, and better resolution of the Raman spectra were observed, and thus the results for this type of crystal are presented in this report.

## 3. Raman scattering

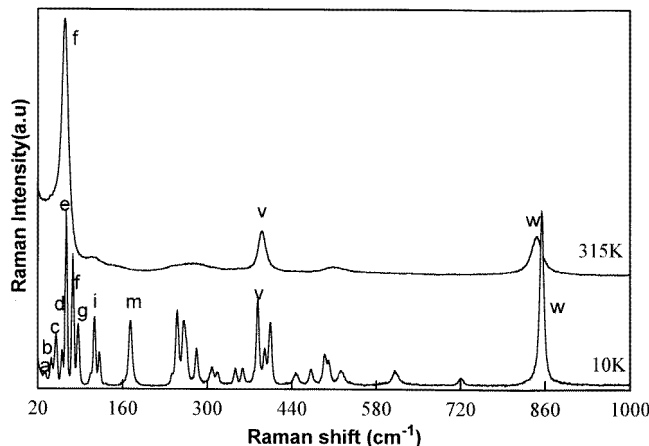
The Raman experiments were carried out for a  $90^\circ$  geometrical configuration from 10 K to 956 K with a Spex double monochromator, Model 1401, using a photon-counting system, and linked with a Datamate microprocessed spectrometer controller. A laser line of  $5145 \text{ \AA}$  and 200 mW power was used. The low-temperature spectra were recorded with the sample placed in an Air-Product-Diplex cryostat driven with an automatic controller. For the measurements between room and high temperature the sample was mounted in a temperature-controlled furnace. Because of the complex domain structure we were not able to realize defined scattering geometries. Therefore variations of the Raman spectra with the polarization directions of incident and scattered light have not been investigated. The data were collected systematically using a fitting procedure including an adjustable Debye function for the quasielastic scattering, and a Lorentzian-like function for the phonon peaks.

**Table 1.** Classification of frequencies and total intensities of different Raman lines in the antiferroelectric (A) and paraelectric (P) phases.

Antiferroelectric phase, $T = 10$ K			Paraelectric phase, $T = 315$ K		
$\omega$ ( $\text{cm}^{-1}$ )	Line	Integrated intensity (%)	$\omega$ ( $\text{cm}^{-1}$ )	Line	Integrated intensity (%)
32	a				
42	b				
50	c				
60	d	24.2			
67	e				
78	f		65	f	58.3
87	g				
107	h				
114	i	11.6	110		0.5
121	j		126		
172	m		152		
241					
250			248		
261					
265		18.5	275		8.2
282					
304					
307					
316					
346					
350					
358					
376		16.8			12.8
383	v		389	v	
394					
404					
411					
443					
446					
449					
471					
488		7.2	509		3.2
494					
500					
520					
610		1.4			
720		0.8			
854	w	19.5	846	w	17.0

### 3.1. Raman spectra for the antiferroelectric and paraelectric phases

The spectra recorded from 0 to  $1000 \text{ cm}^{-1}$  for the PMW crystal in the low-temperature antiferroelectric phase (10 K) and above the I-P phase transition (315 K) are reported in figure 1. At low temperature, very rich well resolved spectra are observed which



**Figure 1.** Raman spectra of PMW at 10 K and 315 K.

show similarities to the spectra of the pure  $\text{PbZrO}_3$  (PZ) antiferroelectric compound [18]. Nevertheless the PMW spectra seem to be more rich than those for the PZ. This fact was expected due to the presence of two different ions in the B sublattice.

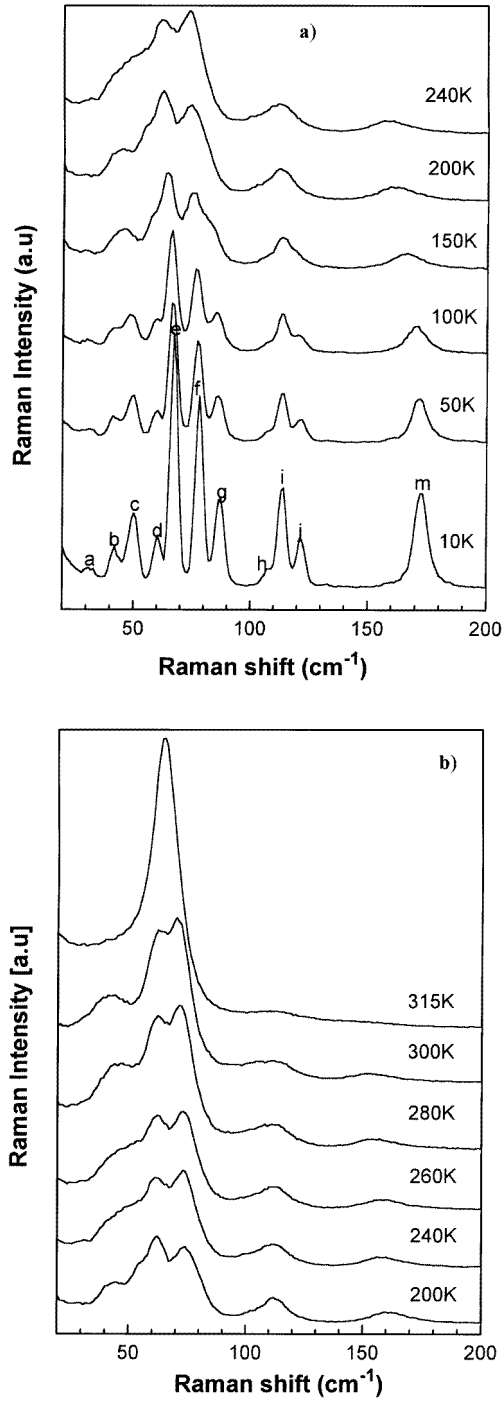
The damping constants are clearly lower in comparison to those observed even for other highly ordered PIN and PST crystals [10, 12] (e.g. 200 K above  $T_c$  the damping constants of line f for PMW, PIN and PST were 11, 15 and 16  $\text{cm}^{-1}$ , respectively). This could be attributed to the existence in the PMW samples of a large coherence length in comparison to that in ordered PIN or PST samples. The spectra in the paraelectric phase  $Fm3m$  each consist of three main structures: f (65  $\text{cm}^{-1}$ ), v (389  $\text{cm}^{-1}$ ), and w (846  $\text{cm}^{-1}$ ), together with low-intensity diffusion bands at 110, 126, 152, 248, 275 and 509  $\text{cm}^{-1}$ . The 846  $\text{cm}^{-1}$  line can be assigned to the stretching of the highly rigid Mg–O–W bonds consisting, in fact, in a breathing vibration of the oxygen octahedra. The f and v lines correspond to antiphase vibration between the A (Pb) and B (Mg and W) ions, and the O octahedra respectively. The frequency of different lines observed in the A and P phases are summarized in table 1 with the frequency range classification in which the total integrated intensity has been calculated.

### 3.2. Temperature-dependent Raman spectra from 10 K to 315 K

The main changes have been observed in the frequency range from 10 to 200  $\text{cm}^{-1}$ , and are shown in figure 2. The differences between the spectra at 300 K and 315 K are clearly attributable to the main I–P phase transition at about 312 K.

A careful observation of the Raman spectra, especially in the low-frequency range, showed visible change between 200 and 240 K. In order to obtain a more detailed insight into these modifications, the Raman spectra have been systematically computed to find the dependencies of the frequency, damping and intensity of the lines as functions of temperature. Frequency and damping were assigned with an accuracy of  $\pm 1 \text{ cm}^{-1}$  (see figures 3, 4, 6, 7, later).

The results for the most significant lines are shown in figures 3 and 4. The functions of the frequencies versus temperature reveal two main behaviour patterns:



**Figure 2.** Temperature evolution of the low-frequency Raman spectra for PMW: (a) 10–240 K, (b) 200–315 K. The intermediate phase (I) lies in the range 220–312 K. The spectrum at 315 K corresponds to the  $Fm3m$  paraelectric phase.

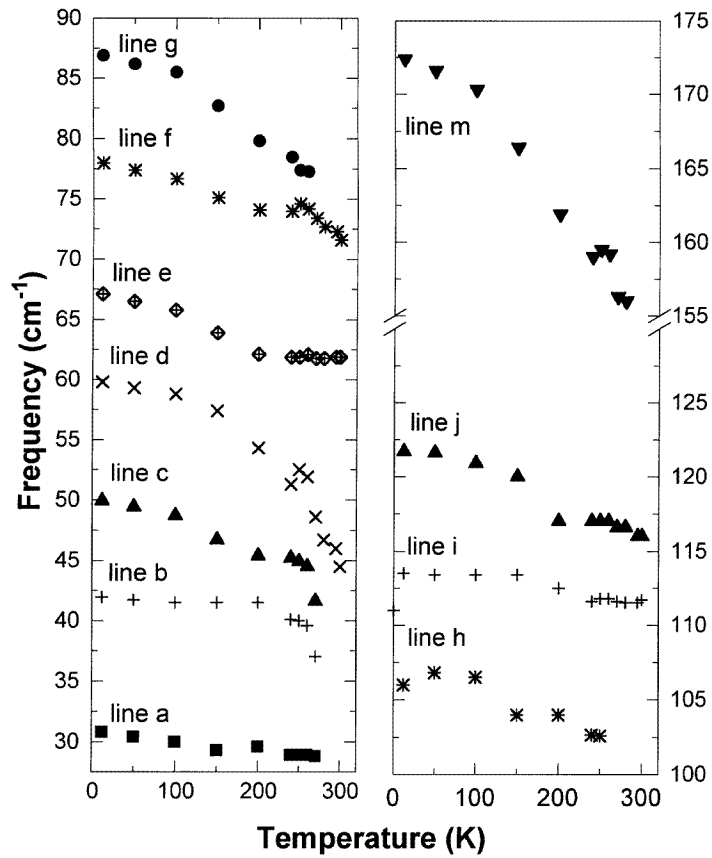


Figure 3. Raman line frequencies versus temperature.

- (i) a clear softening of d and m lines on approaching the I-P phase transition; and
- (ii) a distinct change in the slope of other lines (e, j) at about 220 K.

This latter result might indicate the occurrence of the additional phase transition mentioned in the introduction. Furthermore, the temperature dependence of the damping constant (linewidth)  $b$ , and the positions of lines c, e, f and m, distinguish this temperature even more clearly.

### 3.3. High-temperature Raman spectra

Figure 5 presents the temperature-dependent Raman spectra exhibiting the lowest-frequency structure f between 318 K and 956 K. Above 550 K this line (as well as lines v and w) progressively diminishes in intensity, and eventually its disappearance can be expected from extrapolation to occur at 1000 K.

The values of the frequency, damping and integrated Raman intensities of the lines f, v, and w are represented respectively in figures 6, 7, and 8. The lines exhibit stable intensities of distinctly different values for each of them up to about 550 K, followed by a nearly linear decrease up to 956 K (above this temperature, traces of the f, v, and w lines were still present). The frequency and width of the line f behave differently to

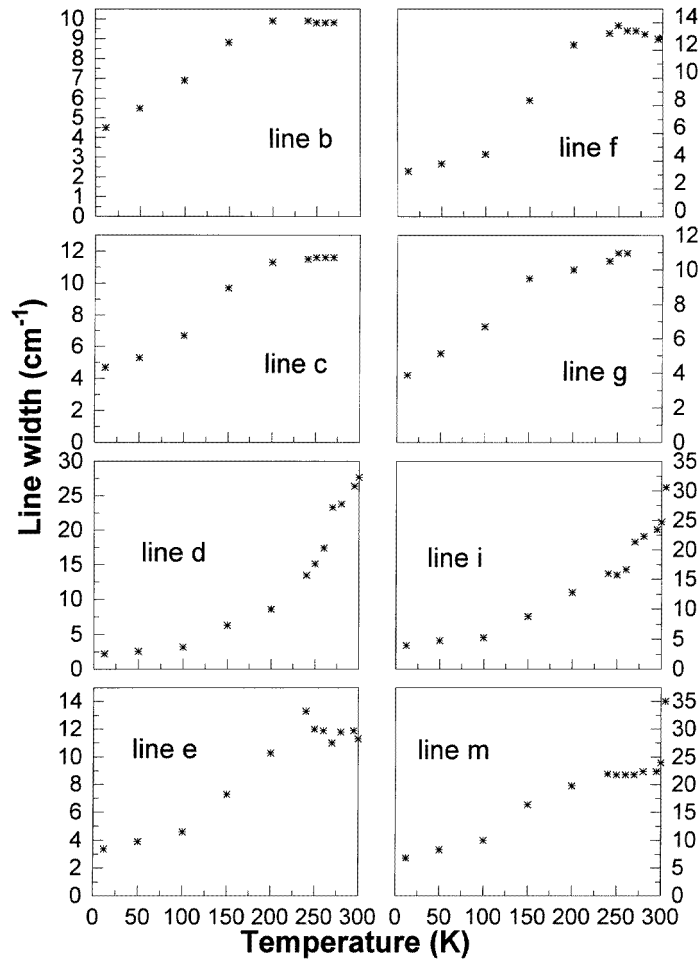


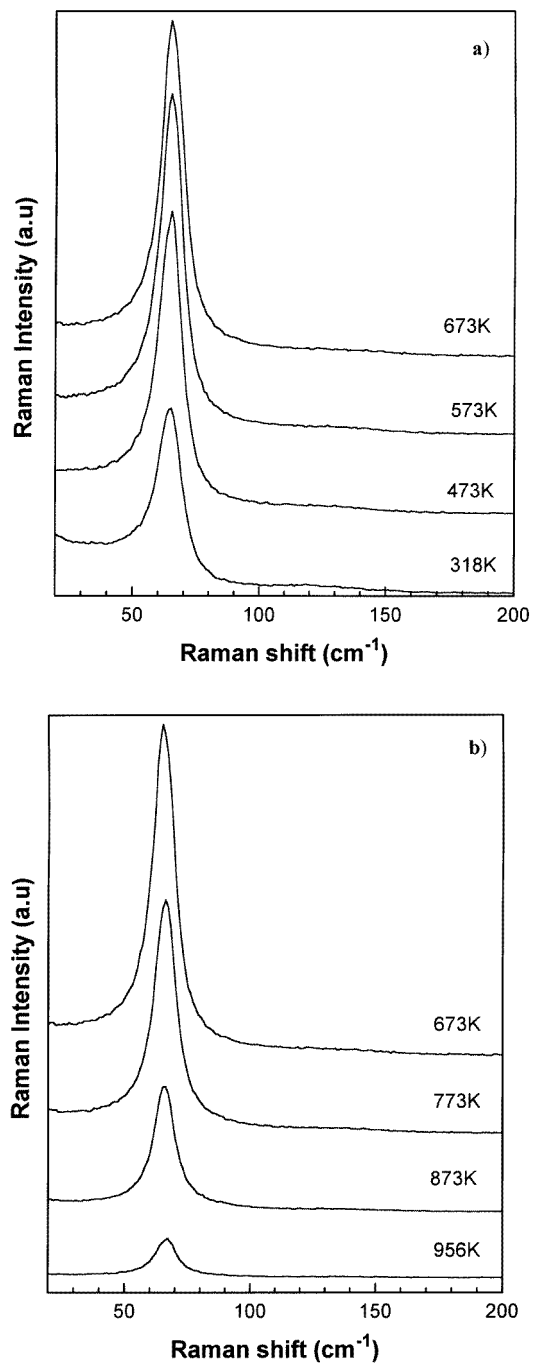
Figure 4. Raman line half-widths versus temperature.

those of  $\nu$  and  $w$ . While  $\nu$  and  $w$ , with increasing temperature, exhibit normal behaviour, i.e. progressive lowering of the frequency and increasing of the linewidth, the  $f$  line stays at nearly constant frequency (otherwise an increase of  $2 \text{ cm}^{-1}$  could be considered), and surprisingly decreases in linewidth. These characteristics will be more thoroughly discussed and interpreted in section 5.

#### 4. Dielectric measurements

Characteristic anomalies in the temperature dependence of the electric permittivity confirm the existence of phase transitions in the PMW single crystals investigated. The measurements were performed for silver-electroded samples using a BM 595 RLC Meter. The temperature dependence of the electric permittivity  $\epsilon$  and losses  $\tan \delta$  for the measuring frequency 2 kHz are shown in figure 9. There is no diffuseness of the phase transition, and in the frequency range 200 Hz–20 kHz no dispersion of  $\epsilon$  has been found. The  $\epsilon(T)$ -





**Figure 5.** Low-frequency Raman spectra of PMW at high temperatures: (a) 318–673 K; (b) 673–956 K.

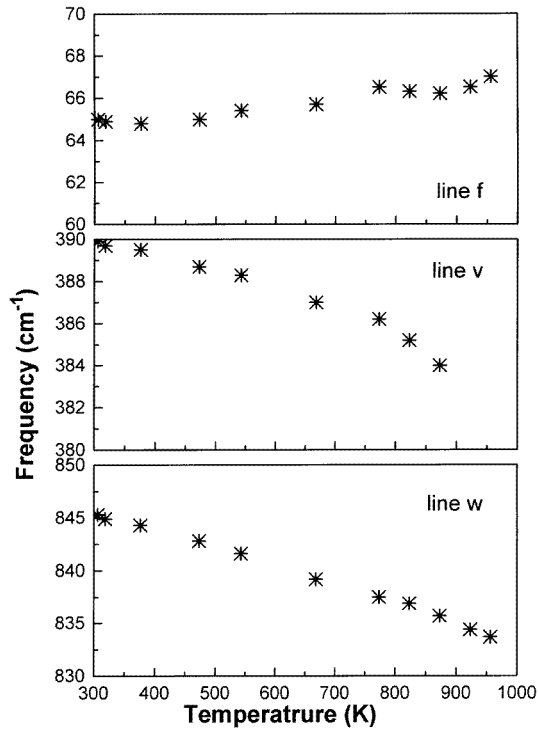


Figure 6. Temperature dependencies of the f, v, and w Raman line frequencies.

dependence near 310 K supports the existence of the highly ordered state in the B-ion sublattice for the PMW.

Additional to the main change at 312 K, a significant anomaly of  $\tan \delta$  appears inside the antiferroelectric phase. However, it should be mentioned that in every cycle of measurement this anomaly was detected at a different temperature, from the range 220–250 K.

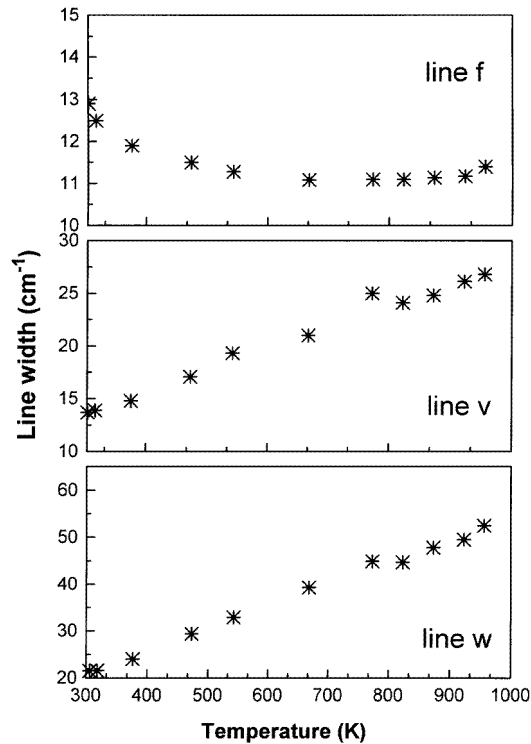
## 5. Discussion

Our Raman scattering measurements in this paper indicated several features:

- (1) the occurrence in the temperature range 220–240 K of spectral modification indicating certainly an additional phase transition;
- (2) clear changes around the main transition at 312 K; and
- (3) the presence of strong first-order Raman spectra in the paraelectric phase with structures disappearing near 1000 K.

As already mentioned in the experimental section, the low-temperature Raman spectra recorded for PMW show some analogies to those measured for pure  $PbZrO_3$  (PZ) [18], but seem to present significant differences as regards in the number and position of lines. This can be explained in view of the following two features:

- (i) the influence of the different cations in the B sublattice with masses of strongly differing values, i.e. Mg: 24, W: 183, and Zr: 91, in atomic mass units;



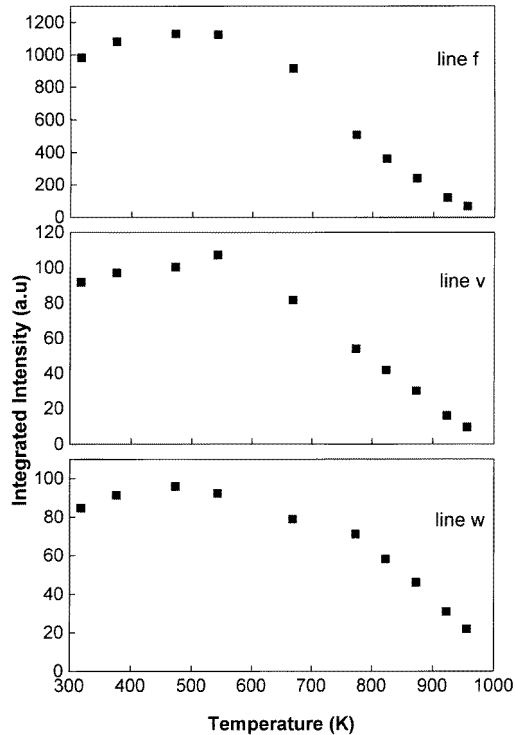
**Figure 7.** Temperature dependencies of the half-widths of the f, v, and w Raman lines.

(ii) the difference between the crystallographic structures of the PMW and the PZ as indicated by Baldinozzi *et al* [16] and connected to the Pb-ion displacement.

On the other hand the excellent resolution and quality of the spectra observed are supplementary proof of the ordered character in the B sublattice. The singularities pointed out at 240 K in the frequency and damping of some Raman lines confirm the presence of the additional phase transition, whose nature is at the moment not definitely identified [13, 16, 17]. It should be pointed out that for other highly ordered  $\text{PbB}'\text{B}''\text{O}_3$  materials, such as  $\text{PbCo}_{0.5}\text{W}_{0.5}\text{O}_3$  and  $\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$  [15, 19], the existence of an intermediate incommensurate phase has already been confirmed. Considering the nature of the transition to the paraelectric phase, it obviously develops a mixed character:

- (i) order–disorder, due to the shifts of the Pb and O ions in both A and P phases [16]; and
- (ii) displacive, as seen in the soft character of some specific structures (b, c, d, and m) in the A phase (a similar behaviour of line softening has been observed for ordered  $\text{BaYb}_{0.5}\text{Ta}_{0.5}\text{O}_3$  [20]).

Our main result in this report comes from the investigation of the Raman scattering in the paraelectric phase. The high-temperature measurements undoubtedly proved that in our purely ordered compound the disappearance of the Raman spectra at 1000 K is definitely not related to the order–disorder transformation in the B sublattice, as it would have been expected to be in less ordered systems. The ordered state in the PMW forms at



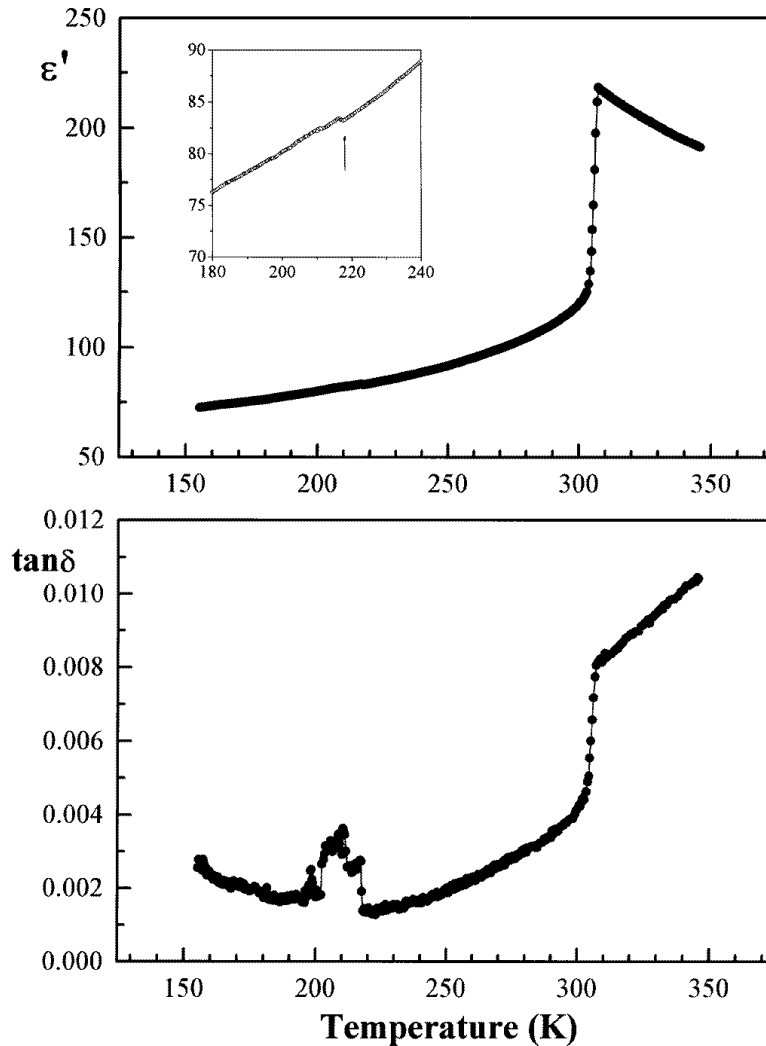
**Figure 8.** Temperature dependencies of the integrated Raman intensities of the f, v, and w lines. The calculated intensity was assigned with an accuracy of  $\pm 100$  in the case of line f and  $\pm 10$  for lines v and w.

considerably higher temperature, i.e. at the temperature of the crystal growth. Moreover, as was discussed earlier [12], the disappearance is not a manifestation of opacity appearing at such high temperatures.

The existence of Raman spectra for the cubic phase of  $Fm\bar{3}m$  symmetry is allowed by symmetry considerations, but since the symmetry modification originates—in contrast with that for pure perovskite structure—in the substitutional order in the B sublattice, no drastic activity of the allowed Raman lines is expected. This is in contradiction with the experiment, which shows intense lines—especially the low-frequency f line. This clearly means that the activity is enhanced by strong amplification of the electric susceptibility modulation in which Raman scattering finds its physical origin. The same arguments can be used in the explanation of the disappearance of the lines. It was shown that the cubic phase is characterized by:

- (i) static distortion, i.e. different sizes of oxygen octahedra surrounding the Mg and W ions [15]; and
- (ii) dynamic disorder of the displacement of both Pb and O ions supposed to be located in multim minima potentials around their special positions [19].

Both of these effects depend strongly on the lattice parameters—in other words on the compactness of the structure—and lead to a dynamic (or static) enhancement of the Raman susceptibility. Compared to PIN ( $a_0 \simeq 4.07 \text{ \AA}$ ) and PYN ( $a_0 \simeq 4.15 \text{ \AA}$ ), the PMW ( $a_0 \simeq 4 \text{ \AA}$ ) may be considered as a rather strongly compact system. The disappearance of



**Figure 9.** Temperature dependencies of the electric permittivity and dielectric losses of PMW upon heating. The inset indicates the small anomaly of  $\epsilon$  near 220 K.

the Raman lines at high temperature can, within the framework of this consideration, be described as the vanishing of this specific amplification. This would mean then that the lattice looks, from the point of view of Raman susceptibility, like pure perovskite. This could be so, since the lattice progressively thermally expands (as is clearly observed from the significant increasing of the unit-cell volume from about  $512 \times 10^{-30} \text{ m}^3$  at room temperature to about  $526 \times 10^{-30} \text{ m}^3$  at 1000 K), and thus impedes the static distortion. The fact that preliminary investigations for  $\text{Pb}(\text{Yb}_{0.5}\text{Ta}_{0.5})\text{O}_3$  (PYT), the compound of less compact structure ( $a_0 \simeq 4.15 \text{ \AA}$ ), show the disappearance of the Raman lines in the paraelectric phase at lower temperature (700 K) clearly favours the proposed explanation. Furthermore, the shape of the multipotential well can be thermally modified towards the simpler potential well form, which implies that the dynamic displacement of the Pb and O ions randomly

disappears, leading to surroundings of the Pb, B, and O ions identical to those in pure perovskite. As a consequence of this, the Raman tensor susceptibility vanishes. This effect must be important for the f line in particular, as its origin lies in the Pb–O vibrations, as indicated by lattice dynamics considerations [20]. Unusual behaviour of the f linewidth connected with a diminishing in value with increasing temperature, as also reported for PST [10] and PIN [12], must be related to the disappearance of the disorder in the Pb and O sublattices.

Finally, we note that recently Baldinozzi *et al* [21] have reported a Raman study of the structural phase transition in a powdered sample of  $PbMg_{0.5}W_{0.5}O_3$ .

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