Direct evidence of an order-disorder nature of ferroelectric phase transitions in $K_2MgWO_2(PO_4)_2$

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$K_2MgWO_2(PO_4)_2$ single crystal, related to famous optical nonlinear material $KTiOPO_4$, was investigated by micro-Brillouin scattering with a focus on the central components of the relaxation modes. A critical slowing down has been clearly observed in the vicinity of $T_1 = 436$ K while suppressed by the coupling with the order parameter. The temperature dependence of the relaxation time indicates that the former transition is the second order, while the latter is strongly first order. The obtained results show that disorder processes in the sublattice of potassium ions play a major role in the mechanism of these phase transitions. © *2007 American Institute of Physics*.
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$KTiOPO_4$ (KTP) is a well-known nonlinear-optical material.[1-3] Many measurements demonstrated that it undergoes a second-order displacive phase transition at 1206 K.[4-7] However, Raman studies suggested that the phase transition is induced by the diffusive mode.[8] Later studies showed that replacement of Ti^{IV} (PO_4^{3-}) ions by Ge^{IV}, Sn^{IV}, Fe^{III}, or Nb^V (AsO_4^{3-} or GeO_4^{4-}) ions has a significant impact on the phase transition mechanism and properties of KTP isomorphs.[9-11] For instance, it was shown that the phase transition in germanate analogs of KTP is both displacive and order-disorder types,[10] whereas the phase transition in $KFeFPO_4$ is closer to order-disorder type than to displacive.[11]

Recently, a new family of compounds was obtained by replacing two Ti^{IV} ions in KTP with divalent M^{II} ions ($M^{II} = Mg, Ni, Co, Fe, Mn, Cd$).[12-14] It was shown that this type of replacement has a significant impact on structural properties. For instance, the high-temperature phase of $K_2MgWO_2(PO_4)_2$ (KMWP) is piezoelectric (tetragonal, space group $P4_12_12$), in contrast to the orthorhombic symmetry of KTP.[14] Moreover, KMWP was shown to undergo five phase transitions at $T_5 = 782$ K, $T_4 = 637$ K, $T_3 = 537$ K, $T_2 = 535$ K, and $T_1 = 436$ K,[12-14] in contrast to only one transition observed in KTP. Previous studies suggested that the symmetries of the phases are as follows: triclinic (space group $P1$, below 436 K), monoclinic ($P2_1$, in the temperature range of 436–535 K), orthorhombic ($P2_12_12_1$, between 535 and 537 K), and tetragonal ($P4_12_12$, above 537 K).[12-14] However, mechanisms of the phase transitions have not been understood and structures of the phases were established only at room and 773 K temperatures.[13,14]

In the present letter, we report the Brillouin scattering studies of KMWP in 300–800 K range in order to understand the mechanisms of the phase transitions, and to find out whether these transitions are related to relaxation phenomena. Such relaxation modes can be often observed in light scattering spectra as central peaks (CPs).[15,16]

Single crystals were grown from $K_2WO_4-WO_3$ flux (K_2WO_4/WO_3 molar ratio is 0.53/0.47) according to the work of Peuchert *et al.*[13] The starting melt contained the stoichiometric mixture of KH_2PO_4, MgO, and WO_3 corresponding to KMWP compound and the potassium tungstate flux in the molar ratio equal to 2.5/1 (compound/flux). After soaking the melt at 795 °C for 24 h, it was cooled down at the rate of 0.2 °C/h for 14 days and then it was cooled down to room temperature at the rate of 20 °C/h. KMWP crystals were extracted from the solidified melt by its dissolution in water. The Brillouin scattering spectra were measured using a (3+3) tandem Sandercock-type Fabry-Pérot interferometer combined with an optical microscope. The scattered light from the sample was collected in the backscattering geometry. A cryostat cell (THMS 600) with a stability of 0.1 °C was used for temperature variation.

Upon heating, CP appears around 390 K and is observed only in the $y(xx+xz)y$ configuration (see Fig. 1). Intensity of CP increases significantly as the temperature approaches T_1 from below, decreases continuously above T_1, and increases suddenly at around 538 K. This behavior correlates with a sudden increase of the dielectric permittivity ε_{11},[12] and indicates that 538 K temperature corresponds to T_2. The intensity of CP decreases again above 538 K and CP disappears above 750 K. CP is observed above 538 K only in the $y(xz)y$ polarization (see Fig. 2), which implies that it relates to E-symmetry excitation. Below 538 K CP is still observed only in crossed polarizations in the monoclinic phase, which implies that it relates to B symmetry. CP becomes weakly visible below 438 K also in the $y(xx)y$ polarization due to the triclinic distortion of the unit cell.

When the relaxation occurs, the spectral response $S(\omega)$ is usually well described by the Debye relaxation,

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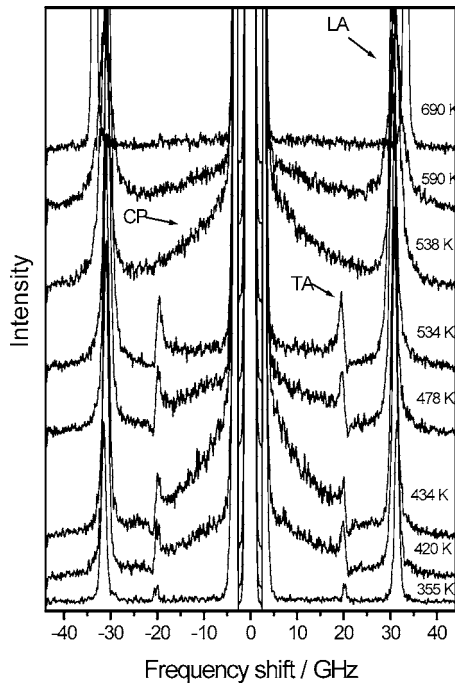
FIG. 1. Typical $y(xx+xz)y$ Brillouin spectra obtained with a free spectral range (FSR) of 44 GHz at a few temperatures. LA and TA denote longitudinal and transverse acoustic modes, respectively. CP denotes central peak.

$$S(\omega) = \chi''(\omega)[n(\omega)+1] \propto \frac{1}{1+\omega^2\tau^2}, \qquad (1)$$

where $S(\omega)$ is approximated by a Lorentzian centered at zero frequency shift with a full width at half maximum (FWHM) equal to $1/\pi\tau$.[15,16] The obtained inverse of the relaxation time τ is shown in Fig. 3. In the vicinity of T_1, KMWP shows the decrease of the relaxation time when temperature approaches T_1 from below and increase with increasing tem-
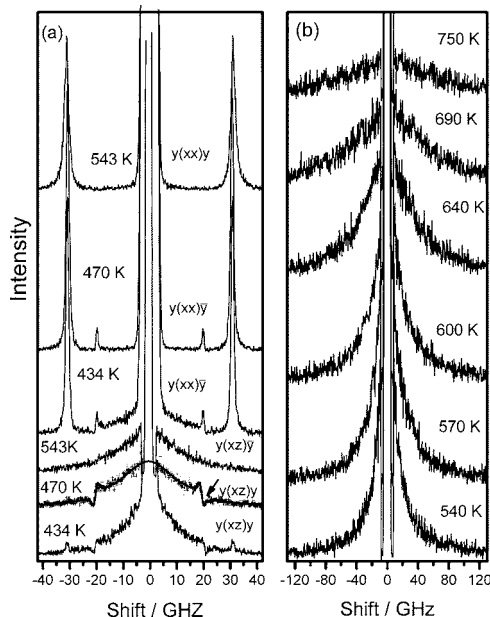

FIG. 2. (a) Polarized Brillouin spectra in the $y(xx)y$ and $y(xz)y$ scattering configurations. The arrow indicates the interference dip resulting from the coupling of the central peak with the c_{66} acoustic mode. The theoretical spectrum for the 470 K $y(xz)y$ geometry is plotted as a solid line. (b) Typical $y(xz)y$ Brillouin spectra obtained with a FSR of 130 GHz. For clarity sake only the temperature region of the tetragonal phase is presented.
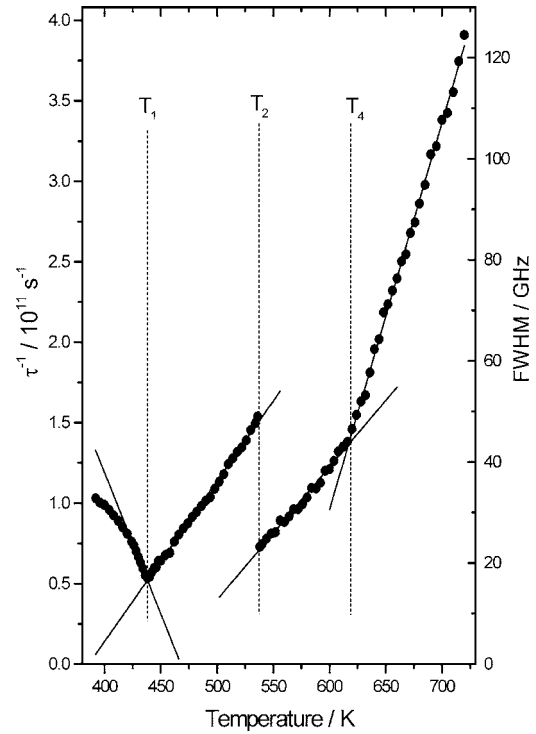

FIG. 3. Temperature dependence of the inverse of the relaxation time. Solid lines are the fits to Eq. (2). The vertical dotted lines show the temperatures corresponding to dielectric anomalies reported in Ref. 12.

perature above T_1 and T_2. This phenomenon is known as a critical slowing down where τ is given by the formula[17]

$$\tau = \frac{\tau_0 T_0}{|T-T_0|}. \qquad (2)$$

Figure 3 shows that the temperature dependence of $1/\tau$ near T_1 and T_2 is well expressed by the straight lines. This observation is direct evidence that the phase transitions at T_1 and T_2 have a significant contribution of an order-disorder mechanism. We conclude that CP originates from the polarization fluctuation. It is also clear that CP cannot be attributed to a diffusive dynamic process since in this case no singular narrowing is expected near T_1 and T_2.[18] Our results give no evidence of the orthorhombic-tetragonal phase transition at T_3. However, $1/\tau$ shows a clear change of the slope around 620 K, in very good agreement with the dielectric anomaly, which was observed at 621 K.[12]

The results of fitting with Eq. (2) in the tetragonal (temperature range of 540–620 K), monoclinic, and triclinic phases give $T_0=451.7$ K ($\tau_0=2.7$ ps), $T_0=385.8$ K ($\tau_0=2.6$ ps), and $T_0=467.8$ K ($\tau_0=1.22$ ps), respectively. Fitting above 620 K yields $\tau_0=0.74$ ps. In the case of continuous order-disorder nonpiezoelectric to ferroelectric phase transition, T_0 should be equal to T_C (in our case T_1 or T_2).[19] When, however, the transition occurs between two piezoelectric phases, the transition is of the first order or coupling between a relaxation and other mode exists, incomplete softening of the relaxation mode should be observed.[19–21] Since our spectra give indication of a coupling between the relaxation and acoustic modes (see discussion below), and all phases of KMWP are piezoelectric, it is not surprising that the observed relaxation modes exhibit incomplete softening. The temperature dependence of the relaxation time shows that the transition at T_2 is strongly first order. On the other

hand, the ratio of τ_0 in the monoclinic to τ_0 in the triclinic phase is 2.13, which shows that the phase transition at T_1 should be a second-order one. It is worth noting that the relaxation times τ_0 are significantly longer than those typically observed for order-disorder phase transitions. For instance, in the ferroelectric phases of PbHPO$_4$, triglycine sulfate, and nearly stoichiometric LiTaO$_3$, τ_0 were found to be 0.04, 0.096, and 0.014 ps, respectively.[22–24] Similar time as for KMWP was found, however, for KD$_2$PO$_4$ (1.3 ps in the piezoelectric tetragonal phase[21]), which is known to exhibit a phase transition of both order-disorder and displacive types.[25]

Our results show that the relaxation mode relates to E-symmetry excitation in the tetragonal phase and it involves ionic motions within the plane perpendicular to the tetragonal z axis. In the monoclinic phase, the observed relaxation mode relates to the B symmetry and involves ionic motions in the xz plane. This behavior is different from that observed for KTP analogs where the relaxation modes were related to ionic motions along the z axis and observed mainly in the zz polarization. According to the literature data, three types of relaxation modes were observed in KTP isomorphs. One very narrow CP in KTP (FWHM 1.2–2.1 GHz) was attributed to diffusive dynamics leading to ionic conductivity.[8] The second, much broader CP in KTP (more than 150 GHz) was attributed to relaxation dynamics of an on site moving nature.[8] The third CP, observed only in a few Kelvin range in the Brillouin study of RbTiOPO$_4$, was attributed to coupling of the soft mode to a relaxator.[26] In our case, the observed CPs are related to the phase transitions but the origin of CP in the tetragonal phase cannot be explained by bilinear coupling of the soft optic mode to the diffusive mode since CP relates to a different symmetry (E) than the diffusive mode (A_2). It seems, however, very likely that there is a coupling between the relaxation mode and a soft optic mode of E symmetry, because the observed elementary relaxation time τ_0 is relatively long.

Our results do not give any information about the microscopic nature of the relaxation modes. Since, however, the x-ray structure determination showed that the $[MgWO_2(PO_4)_2]^{2-}$ network is barely modified by the phase transitions and the main differences between the high- and low-temperature structures can be observed for the positions and thermal displacement factors of potassium,[14] it is plausible to assume that the main contribution to the observed relaxation mode comes from motions of the potassium ions. The potassium ions in the KMWP structure have more freedom to vibrate than the potassium ions in the KTP structure because the average potassium-oxygen bond length is much larger in KMWP [3.356 Å at 773 K (Ref. [14])] than in KTP (2.925 Å at 300 K[27]). Due to this feature, the potassium ions are capable to disorder not only along the z axis, as in KTP, but also within the plane perpendicular to the z axis, leading to richer polymorphism observed in this material.

It is also worth noting that the spectra recorded in the $y(xy)y$ configuration exhibit below 538 K a dip near 20 GHz (see Fig. 2). The presence of such interference dip is a direct indication that a coupling exists between CP and the acoustic mode.[21,28] In the monoclinic phase, the signal can be observed for light propagating along the polar axis (in one type of domains) or perpendicularly to the polar axis (second type of domains). In the first case, the two transverse modes are

forbidden.[29] In the second case, for the $y(xz)y$ configuration the transverse c_{66} mode of B symmetry is allowed.[29] Because the central peak is related to B-symmetry excitation in the monoclinic phase, it is clear that the acoustic mode involved in the coupling with the central peak must be the c_{66} mode. In order to confirm the origin of the observed dip, we have attempted to fit the $y(xz)y$ spectrum recorded at 470 K using the model developed by Reese *et al.* (for details see Ref. [21]). As presented in Fig. 2, the spectrum is fitted very well in the framework of the coupled-mode model with the acoustic phonon frequency of 20.04 GHz.

In conclusion, our results show that the relaxation modes play a significant role in the ferroelectric phase transitions in KMWP. The disorder in this material can be mainly attributed to the potassium ions, similarly as in KTP analogs. In contrast to KTP isomorphs, however, we observe a very clear critical slowing down of the relaxation time.

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