Temperature studies of KH$_2$PO$_4$:Mn crystals using x-ray diffraction and polarized Raman scattering

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KH$_2$PO$_4$ (KDP) crystals doped with Mn ions were studied by an x-ray multiple diffraction technique using synchrotron radiation at room temperature. Asymmetric peaks were observed for both undoped and doped crystals, a characteristic of perfect crystals. X-ray powder diffraction at room temperature and analysis by Rietveld refinement were also performed, showing that doped KDP has the same tetragonal structure as undoped KDP, but with contraction of the lattice parameter for [100], [010], and [001] directions. The polarized Raman spectra of KDP and KDP:Mn were obtained for temperatures in the range 10–300 K. Some of the features observed in the spectra were interpreted as consequences of phase transitions. Although group theory analysis shows that both doped and undoped crystals have the same symmetry at room temperature, at low temperature they have different symmetries: a previously reported phase transition for KDP at 60 K was not observed for KDP:Mn.

I. INTRODUCTION

KH$_2$PO$_4$ (KDP) is a typical order-disorder ferroelectric exhibiting interesting physical properties.[1–3] Several works show that KDP undergoes a ferroelectric phase transition at 122 K changing the crystal symmetry from tetragonal (D_{2d}^{12} space group) to orthorhombic (C_{2v}^{19} space group). Also, under both uniaxial pressure or static eletric fields it is observed that KDP can undergo other phase transitions.[4–8] In addition, the influence of doping introduced into the crystal lattice has been studied extensively in various ferroelectrics, in particular because they can improve physical properties of materials for technological applications. In general, studies performed on various ferroelectrics of the perovskite type, Triglicine sulphate, and in Rochelle salt show that the spontaneous polarization reversibility and the Curie point anomalies are strongly influenced by doping introduced into the crystal lattice.[1,9] Additionally, it is well known that certain transition metal ions incorporated into a crystal lattice often modify its growth. The growth-modifying additives are often used to control the relative growth rates of the various crystal surfaces of the material in order to achieve a desired particular shape. The optimization of size and shape is of fundamental importance in industrial crystallization, and this is other motivation for research on doped KDP crystals.[10–14]

The purpose of our investigation was threefold: (i) to investigate the modification in the structure of the KDP single crystal due to doping; (ii) to present a Raman scattering study of the KDP:Mn doped crystal; (iii) to compare the temperature dependence of Raman scattering between the doped KDP:Mn crystals and the pure KDP crystal, and identify their phase transitions at temperatures ranging from 300 to 10 K.

II. EXPERIMENTAL

Single crystals of KDP and KDP:Mn used in the experiments were grown from supersaturated aqueous solutions containing stoichiometric concentrations of KH$_2$PO$_4$ and KMnO$_4$ powders, in distilled water by the slow evaporation method at a controlled temperature (313 K). Powder x-ray diffraction patterns were recorded with a Rigaku DMAXB diffractometer using Cu K$_\alpha$ radiation monochromated with a graphite crystal. Composition analysis was performed using an x-ray fluorescence technique. The high-resolution Renninger scan of KDP crystals was carried out using the Brazilian synchrotron radiation facility at LNLS, Campinas, with the wavelength of $\lambda = 1.65382$ Å. This value was determined through the use of a silicon [111] crystal. In the LNLS there is a Huber three-axes goniometer (ω, φ, and 2θ), fixed on top of a χ table that was able to rotate the incidence plane of the goniometer from $\chi = -90°$ to $+90°$ in steps of 4°. $\chi = 0$ corresponds to the incidence plane in the horizontal position, and at $\chi = \pm 90°$ it is vertical; the signs stand for the detector above ($+$) and below ($-$) the storange-ring horizontal plane. The minimum step sizes of the ω and φ axes are 0.0004°.

Two samples for x-ray diffraction and Raman measurements were prepared: (i) samples of KDP:Mn doped with a 4% weight of Mn ions with brown coloration; (ii) samples of pure KDP, grown transparent and with good optical quality.

The backscattering light was analyzed using a Jobin Yvon Triplemate 64000 micro-Raman system equipped with a nitrogen-cooled charge-coupled device (CCD) system. The slits were set for a 2-cm^{-1} spectral resolution. The excitation source for the Raman experiments was 514.5 nm radiation from an argon ion laser. In order to avoid the propagation of oblique phonos, all measurements were performed using a long working distance planoachromatic objective with $f = 20.5$ mm. The crystallographic x' and y' axes of the orthorhombic structure are rotated 45° relative to the crystallographic x and y axes of the tetragonal structure. Raman measurements at low temperature were obtained with samples placed in a closed-cycle helium refrigerator. The temperature was controlled with a precision of ±0.1 K.
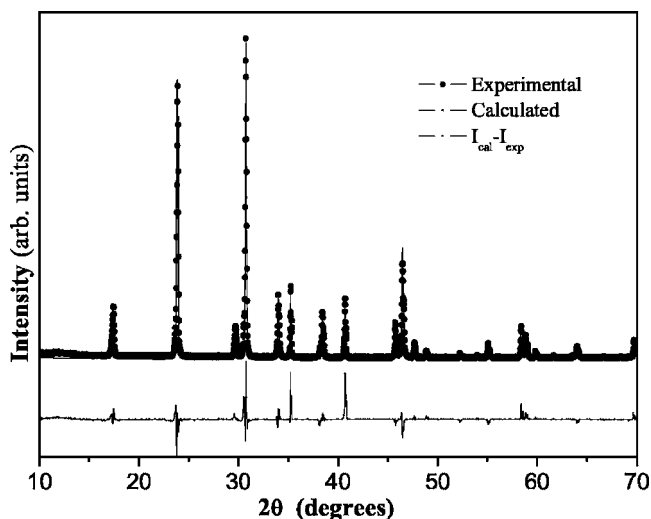
FIG. 1. Results of the Rietveld profile refinement of the x-ray powder diffraction of KDP:Mn. The scale of I_{cal}-I_{exp} line is the same as that of the diffractogram spectrum with a downward shift.

III. RESULTS AND DISCUSSION

The characterization of KDP and KDP:Mn crystals was made using the x-ray powder diffraction technique and analysis by the Rietveld refinement[15] of the structural model of tetragonal phase of the KDP. Figure 1 shows the results of the Rietveld refinement of the diffraction pattern of KDP:Mn at room temperature, which were obtained by the DBWS-9411 program.[16] The final values of the R factors were R_p =15.22%, R_{wp}=13.87%, and R_{exp}=4.88%. Both KDP and KDP:Mn crystals at room temperature have tetragonal symmetry (space group D_{2d}^{12}). The variations of the unit cell parameters between KDP and KDP:Mn crystals after the refinement procedure were found to be $\Delta a/a$=−0.26% and $\Delta c/c$=−1.1%, thus, for KDP:Mn there is a nonisotropic contraction of the unit cell along the [100] and [001] directions. This contraction can be ascribed to the difference between the interaction of PO_4 with K and Mn.

In order to investigate small lattice distortions in KDP due to the incorporation of Mn ions, the Renninger scan measurements were carried out in the interval of 90° around a ϕ=0° mirror for both crystals at room temperature. The (400) primary reflection was chosen for this experiment. Both crystals, KDP and KDP:Mn, exhibit asymmetric peak profiles for most peaks and no extra peak appears in the whole KDP:Mn Renninger scan. There is also a shift in the secondary-peak positions that is associated with the change in the doped unit cell. Figure 2 shows two Renninger scan peak profiles' asymmetry due to the constructive and destructive interference in multiple diffraction phenomena, which is a characteristic of a perfect crystal lattice.[17] These results are consistent with Mn-ion incorporation via a substitutional mechanism within the KDP unit cell, showing that the material studied in this paper is quite different from that investigated by Lay *et al.*[11]

The Raman spectra of KDP and KDP:Mn were studied as a function of temperature in the range 10 to 300 K. Representative spectra, taken for three scattering geometries at
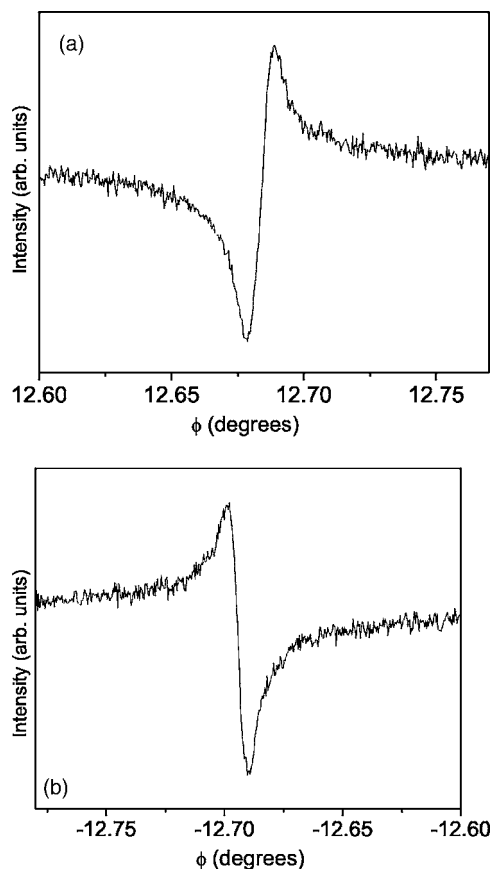

FIG. 2. (0 4 0) KDP:Mn Renninger scan peaks profile. The peaks (a) (0 0 0), (0 4 0), ($\bar{2}$ 0 0) ($\bar{3}$ 1 0), (1 1 0), ($\bar{3}$ 3 0), (1 3 0), ($\bar{2}$ 4 0), and (b) (0 0 0), (0 4 0), (2 0 0), ($\bar{1}$ 1 0), (3 1 0), ($\bar{1}$ 3 0), (3 3 0), (2 4 0).

300 K are show in Fig. 3. These spectra are characteristic of KDP in its tetragonal (paraelectric) phase in agreement with results reported in the literature.[18] The spectra for KDP:Mn at 300 K have the same characteristics as those of KDP, confirming that both crystals have the same room-temperature structure. In fact, if we observe carefully the region between 350 and 400 cm^{-1} at the $Y(ZX)\bar{Y}$ scattering geometry, we note the presence of peaks with low intensities in the KDP spectrum. The same peaks are present in the KDP:Mn spectrum but with lower intensities; however, they are present in both spectra.

Just below the transition temperature of 122 K, KDP is in its orthorhombic (ferroelectric) phase. The Raman spectra of KDP and KDP:Mn taken for the $Y(XX)\bar{Y}$, $Y(ZX)\bar{Y}$, and $Y(ZZ)\bar{Y}$ scattering geometries for temperatures below 122 K are characteristic of the phase belonging to the $Fdd2$ (C_{2v}^{19}) space group. Figure 4 shows the spectra for several temperatures near 122 K in the low wave-number region for the $Y(XZ)\bar{Y}$ scattering geometry. No significant differences in the Curie temperature were observed between KDP:Mn and KDP.

Figure 5 shows the Raman spectra of KDP and KDP:Mn for the $Y(XX)\bar{Y}$, $Y(ZX)\bar{Y}$, and $Y(ZZ)\bar{Y}$ scattering geometries, at 10 K. The spectra of KDP are characteristic of its mono-
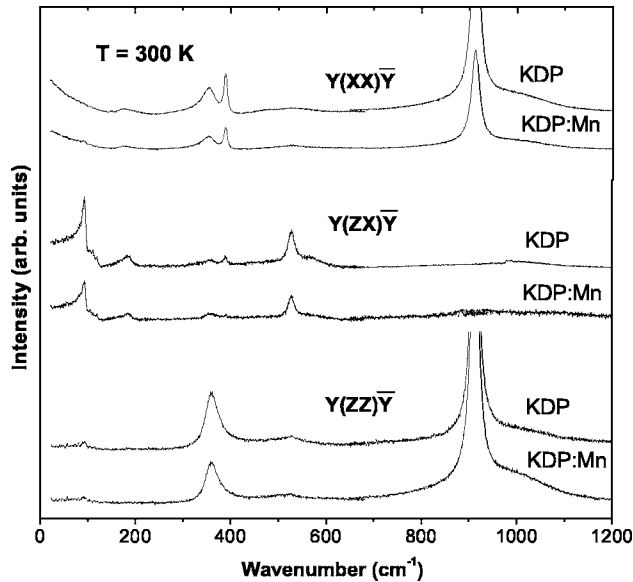
FIG. 3. Raman spectra of KDP and KDP:Mn at 300 K for $Y(XX)\bar{Y}$, $Y(ZX)\bar{Y}$, and $Y(ZZ)\bar{Y}$ scattering geometries.

FIG. 5. Raman spectra of KDP and KDP:Mn at 10 K for $Y(XX)\bar{Y}$, $Y(ZX)\bar{Y}$, and $Y(ZZ)\bar{Y}$ scattering geometries.

clinic structure belonging to the C_s^i space group.[8] Undoped KDP changes, at around 60 K, from the orthorhombic structure with the C_{2v}^{19} space group to a monoclinic structure with the C_s point group, when a disorder created by the rapid rotation of the PO$_4$ inside the unit cell disappears with the freezing of this motion. After the phase transition the ions occupy sites with C_1 symmetry as is discussed by Melo *et al.*[8] However, KDP:Mn exhibits the same Raman spectra below 60 K as those of the orthorhombic structure belonging to C_{2v}^{19}. When KDP:Mn undergoes a phase transition to the orthorhombic (C_{2v}^{19}) phase at 122 K, the PO$_4$ ions freeze in $C_2(z)$ sites and stay in this configuration down to $\sim$10 K because the hard interaction among the PO$_4$ and Mn ions. This phase transition is clearly inhibited by introduction of Mn ions into the KDP structure. KDP:Mn crystal maintains for temperatures lower than 60 K the orthorhombic structure with PO_4^{3-} ions located in sites with $C_2(Z)$ symmetry.

In the KDP:Mn crystal it appears that the Mn ions replace the K ions and a proton vacancy is formed near the Mn ions. Since the Mn ion has more excess charges than the K ion, it
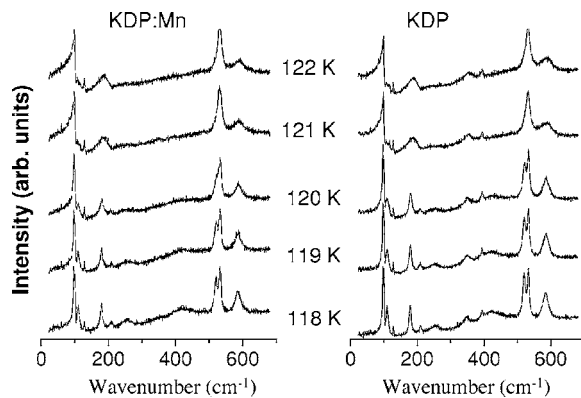

FIG. 4. Raman spectra of KDP and KDP:Mn crystals for several temperatures near of 122 K in the low wave-number region.
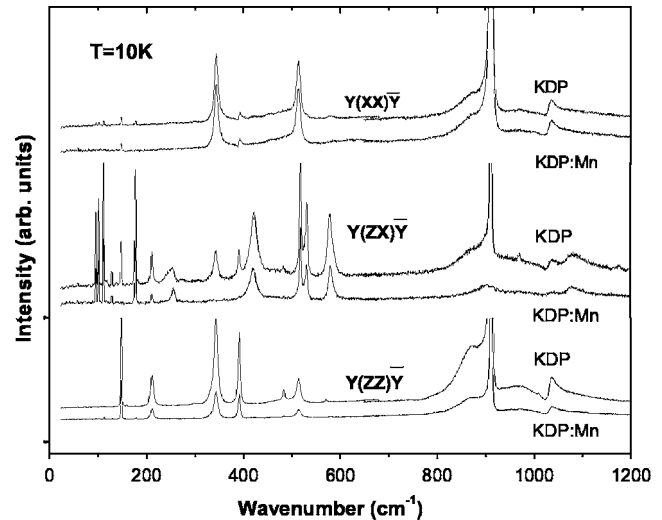
is natural that H ions (or K ions) are vacant in order to complete charge compensation. This model can explain the results obtained by the three techniques: (i) X-ray powder diffraction and Rietveld refinement show that doped KDP at room temperature has a tetragonal symmetry with contraction of the unit cell. Since the doped crystal does not exhibit additional phases, the doped crystal has the same tetragonal structure as pure KDP. (ii) Some of the Renninger scan peaks for both pure KDP and doped KDP show a large multiple diffraction asymmetry due to constructive and destructive interference, which is a characteristic of perfect crystal lattices.[17] No extra peak was observed in the Ranninger scan of the doped sample. These x-ray multiple wave results show that Mn ions take the position of K ions or of P in the PO$_4$ molecule group by a substitutional incorporation mechanism. (iii) No extra mode was observed in the Raman spectrum of doped KDP at room temperature. If a group of Mn and O atoms were present in the KDP structure, their internal modes should appear in the Raman spectrum. These results suggest that each of the Mn ions takes the position of K sites substitutionally causing vacancies. This process is accompanied by a deformation of the crystal structure similar to that induced in pure KDP by uniaxial stress or a dc electric field.

IV. CONCLUSION

We have investigated KDP and KDP:Mn crystals using three techniques: x-ray powder diffraction, x-ray multiple diffraction at room temperature, and Raman spectroscopy in the temperature range 10–300 K. At room temperature, the KDP:Mn shows a nonisotropic contraction of the unit cell with the same structure as KDP. At low temperature, the Raman spectra of KDP:Mn show qualitative differences from undoped KDP.

The Raman spectra of KDP indicate the occurrence of a phase transition in KDP taking place at a temperature near

60 K, in agreement with Melo *et al.*[8] This phase transition was not observed in doped KDP. These results suggest that each Mn ion takes the positions of a K site substitutionally causing two vacancies of neighboring protons. Mn ions have more excess charges than K ions. The interaction of Mn with PO_4 is stronger than the interaction of K with PO_4. This explains the suppression of the phase transition at 60 K for doped KDP.

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