Pressure Study on Mn Doped KDP System under Hydrostatic Pressure

W. Paraguassu, S. Guerini, C. M. R. Remédios, P. T. C. Freire

Abstract—High Pressure Raman scattering measurements of KDP:Mn were performed at room temperatures. The X-ray powder diffraction patterns taken at room temperature by Rietveld refinement showed that doped samples of KDP-Mn have the same tetragonal structure of a pure KDP crystal, but with a contraction of the crystalline cell. The behavior of the Raman spectra, in particular the emergence of a new modes at 330 cm$^{-1}$, indicates that KDP:Mn undergoes a structural phase transition with onset at around 4 GPa. First principle density-functional theory (DFT) calculations indicate that tetrahedral rotation with pressure is predominantly around the c crystalline direction. Theoretical results indicates that pressure induced tetrahedral rotations leads to change tetrahedral neighborhood, activating librations/bending modes observed for high pressure phase of KDP:Mn with stronger Raman activity.

Keywords—Dipotassium molydbate; High pressure; Raman scattering; Phase transition; ab initio

I. INTRODUCTION

The potassium dihydrogen phosphate crystal (KDP) exhibits interesting physical properties such as ferroelectricity and ferroelasticity and is well known to present a series of phase transitions [1]. At atmospheric pressure and temperature below 60 K, KH$_2$PO$_4$ system is monoclinic C$\text{I}$ with $\text{I}=1,2,3$ or 4; in the temperature range 60 – 122 K, this system is ferroelectric with an orthorhombic structure belonging to Fdd$\text{2}$ (C$\text{2n}_1$) space group; and in the temperature range 122 – 453 K, KDP is paraelectric with a tetragonal structure belonging to I-42d ($D_{2d}$)$^{12}$space group. Studies by X-ray diffraction and dielectric measurements have showed that KDP undergoes structural phase transitions at high pressure [2-4]. X-ray diffraction pattern show that the crystal system of phase $5 > P > 7$ GPa is orthorhombic, and the volume reduction for the IV-V phase transition (that occurs at 4 GPa) was estimated to be 2.9% at 5.4 GPa.[3]

On the other hand the influence of the introduction of a dopant into KDP crystal lattice has often been studied. Firstly, because it can modify the physical properties of this material for technological applications. Secondly because certain transition metals incorporated into a crystal lattice often modify its growth habit and KDP, in particular is a model material in industrial crystalization systems. The optimization of size and shape of a sample is of fundamental importance in industrial crystallization [5-7]. Previous works have suggested that KDP doped with manganese ions (KDP:Mn) can be obtained from solutions containing manganese salts, permanganates or mixtures of both (in proportions of 1:1, 1:2 or 1:4).

The effect of impurities on the growth kinetics of crystals is provided by numerous physical and chemical factors such as concentration and oxidation states of the incorporated manganese ions as well as the pH of the solutions [8]. In a previous paper [9], for Mn concentration of 4 wt.%, we have shown that each Mn ion occupy the position of the K ion substitutionally, causing two vacancies of neighboring protons. Several other works can be found in the literature reporting the impurity influence on growth kinetics, surface morphology and physical properties of KDP crystal by using techniques like: X-ray standing waves, X-ray absorption spectroscopy, Raman scattering, Electron Spin Resonance (ESR), Mossbauer, Electron Paramagnetic Resonance (EPR), Glancing angle EXAFS and others. However there is a controversial debate in the literature about the nature of the incorporation mechanism of the Mn ion in the KDP structure. Some authors have suggested that the impurity is incorporated interstitially [10-12] while other authors suggested that impurity is incorporated substitutionally in the K ion site or in the P ion site causing vacancies in order to satisfy the charge compensation [7].

In this work we report the results of High Pressure Raman scattering measurements of KDP:Mn. We will discuss the observation of a pressure induced phase transition at 4 GPa, i.e. 1 GPa lower than the one observed for pure KDP. In addition, in order to shed light on the observed modifications in the Raman spectra and in the structural changes of KDP:Mn under hydrostatic pressure, first principle density-functional theory (DFT) calculations, were performed on I-42d ($D_{2d}$)$^{12}$ structure of KDP [9].

II. EXPERIMENTAL

Single crystals of KDP doped with Mn ions were grown by slow evaporation of a supersaturated aqueous solution containing stoichiometric KH$_2$PO$_4$ and KMnO$_4$ powders, at a controlled temperature of 300 K and pH = 3.8. Elemental composition analysis of resultant crystals was made by using Rutherford backscattering spectroscopy (RBS) The results of RBS analysis show that the samples prepared had Mn concentration of 0.9 % (weight).

X-ray powder diffraction was carried out on a Philips XPert MRD diffractometer operating at 40 kV/40 mA and using Cu Ka radiation with pyrolytic graphite diffracted beam monochromator. The diffraction patterns were obtained in the angular range of 16° – 100° (2θ) a counting time of 15 s/step and step of 0.02°. The sample oscillated to prevent preferred orientation effects. The diffraction patterns were analyzed by Rietveld refinement using the General structure analysis system (GSAS) [13,14].

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 excitation source was 514.5 nm radiations from an argon ion laser with a 2 cm$^{-1}$ spectral resolution set by the slits.
A long working distance planoachromatic objective with \( f = 20.5 \) mm was used to avoid the propagation of oblique phonons.

III. RESULTS AND DISCUSSIONS

A. Experimental results

The x-ray powder diffraction and analysis by Rietveld refinement were performed for the KDP:Mn crystal. The starting point for the Rietveld refinement was the well known structure of pure KDP at room temperature. The results show that doped KDP:Mn crystal has the same tetragonal structure as undoped KDP. Doped KDP has an anisotropic contraction of the lattice parameters. Figure 1 shows the result of the Rietveld refinement of the diffraction pattern of KDP:Mn at room temperature. The final values of the R factors were \( R_p = 6.1\% \), and \( R_{wp} = 8.4\% \).

![Fig. 1 Results of the Rietveld profile refinement of the X-ray powder diffraction patterns of KDP:Mn](image)

Raman spectra of KDP:Mn were studied as a function of hydrostatic pressure up to 6.8 GPa in the spectral region from 50 to 1250 cm\(^{-1}\). Raman spectra of KDP:Mn at atmospheric pressure are very similar to characteristic spectra of pure KDP crystal. At room temperature, and atmospheric pressure, KDP crystal has tetragonal structure and its primitive cell contains two formula units, which gives the total of 48 normal modes that are distributed among the irreducible representations of \( D_{2d} \) factor group as \( 4 A_1 + 5 A_2 + 6 B_1 + 7 B_2 + 13 E \).

Figure 2a and Figure 3a show Raman spectra of KDP:Mn as a function of hydrostatic pressure. A careful observation of the spectra sequence in Figures 2a and 3a indicates the onset of abrupt structural changes at around 4 GPa. The Raman spectra show quantitative and qualitative changes in the wave number and intensities of the bands (for example, at 200 and 460 cm\(^{-1}\)) above such pressure. In particular, it is impressive the emergence of a strong new band at 330 cm\(^{-1}\). These changes in the KDP:Mn Raman spectra are evidence that it undergoes a pressure induced structural phase transition probably related to symmetry lowering.

This hypothesis is reinforced by observation of pressure induced phase transition at 5 GPa in pure KDP as investigated through dielectric and X-ray diffraction measurements [2-4]. The phase stable above 4 GPa in KDP:Mn is probably the same phase stable above 5 GPa in pure KDP system (named phase V). Actually, modes in the spectral range 200 – 600 cm\(^{-1}\) can be observed in polarized experiments for pure and Mn doped KDP [15]. However for unpolarized spectra these modes are not visible at all, probably for intensity sake. After the phase transition IV-V (at 4 GPa) in KDP:Mn, the activated modes of the new phase are much stronger, and can be visible in the unpolarized spectra. Preliminary results of lattice dynamics calculation indicate that the modes in the 200 – 350 cm\(^{-1}\) range present high contribution of PO\(_4\) librations (coupled to bending modes) at around the c axis (see Figure 4). On the other hand, our \textit{ab initio} calculations, that will be further discussed, indicate that one among pressure effects in KDP is octahedral rotations around the c axis. We infer from these results that pressure induced tetrahedral rotations leads to changes on H – O neighborhood of PO\(_4\) units (see Figure 4), activating librations/bending modes of high pressure phase of KDP:Mn (KDP) with stronger Raman activity.

![Fig. 2 (a) Raman spectra of KDP:Mn as a function of high pressure, for wavenumber less than 600 cm\(^{-1}\). (b) wavenumbers (w) vs. pressure (P) plot](image)

![Fig. 3 (a) Raman spectra of KDP:Mn as a function of high pressure, for wavenumber higher than 600 cm\(^{-1}\). (b) wavenumbers (w) vs. pressure (P) plot](image)
some general behavior of pressure dependent Raman spectra could be better accessed in the wavenumbers \( (w) \) vs. pressure \( (P) \) plot. After the spectra are collected, the Raman modes are determined by curve fitting using a fitting software. In this process we fit several bands using a Lorentzian band shape. This relation can be fitted to the equation

\[
\frac{V}{V_0} = \left(\frac{B_0}{B_0 + 1}\right)^{\frac{1}{3}}
\]

(1)

In this equation \( V_0, B_0 \) and \( B_1 \) are the volume at zero pressure, the bulk modulus and its first pressure derivative, respectively. In doing so, we obtained \( V_0 = 386 \) Angs\(^3\), \( B_0 = 22.7 \) GPa and \( B_1 = 13.3 \). This is consistent with values obtained from experimental results [2] of \( V_0 = 389 \) Angs\(^3\), \( B_0 = 26.1 \) GPa and \( B_1 = 6.7 \).

The pressure was increased from 0 to 6 GPa in steps of 1 GPa.

For the calculations, we have used a start parameter of reduced cell, with \( a = 7.444 \) Å; \( b = 7.444 \) Å and \( c = 6.967 \) Å; \( \alpha = \beta = \gamma = 90^\circ \); after optimization, we have used the Platon software developed by professor Anthony L. Spek, in order to determine the symmetry of the structure in each pressure step [24]. We observed that the optimized KDP structure at 0.0 GPa presented the I-42d (D\(_{2d}^+\)) space group symmetry and it remains with this symmetry in the entire studied pressure range.

The Bulk modulus was determined by fitting the Murnaghan equation, see (1), to the calculated volumetric dependence with a pressure data (see Figure 5).

![Fig. 5 (left axis) Fitting the Murnaghan equation, see (1), to the calculated volumetric dependence with a pressure data. (right axis) Dependence of tetrahedral rotation angle with the pressure [\( \theta P \)]](image)

The analysis of the dependence in the lattice unit cell parameters with pressure, indicates that the volumetric changes with pressure are nearly isotropic, which is consistent with a low dispersion for the pressure slope coefficients in the wavenumber vs. pressure curves (Figs 2a and 3a).

Generally, symmetry changes in molybdate and tungstate systems are governed by tetrahedral tilting. Therefore, analyses of polyhedral rotations were carried out by defining, for each polyhedron, a quantity that represents the rate of the angular rotation with pressure. This is defined here as a vector \( \vec{R}_p \), oriented along the axis of rotation, and can be written as

\[
\vec{R}_p = \sum \frac{\Delta \theta_i}{\Delta P}.
\]

(2)

where \( \Delta P \) are the steps of pressure, and \( \Delta \theta_i \) represent the...
oxygen rotation vector, parallel to the rotation axis, for the ith oxygen atom belonging to the polyhedral units (the summation ranges from 1 to 4). Figure 6 shows the dependence of the components of vector $\vec{R}_p$ with pressure. We could firstly observe that, at moderated pressure, the $R_c$ component is stronger, indicating that the rotation with pressure is predominantly around the $c$ crystalline direction. The ab initio approach used in this case, is not sensitive enough to predict nonisomorphic structural phase transitions, however, this result is useful to give us an idea of the lesser energetic, i.e., more likely tendencies of changes in this system. So this result support our hypothesis discusse above that tetrahedral rotations rotation gives rise to activation of Raman modes of phase stable above 4 (5) GPa in KDP:Mn (KDP) system.

![Diagram](image)

**Fig. 6 (a) Dependence of the components of vector $\vec{R}_p$ with pressure. (b) evolution of O – P – O bond angles of PO4 tetrahedral unities with pressure (calculation results)**

The inset of Figure 5 (right axis) shows the dependence of the tetrahedral rotation angle itself with the pressure [$\theta (P)$].

We have detected the presence of the Mn ions, and measured their concentration, by using the RBS technique. From the X-ray diffraction measurements and analyzed by the Rietveld method, we have identified that the symmetry of the KDP:Mn crystal is the same as that of the pure KDP but with a contraction of the unit cell. Raman spectra show that KDP:Mn under pressure undergoes a structural phase transition beginning at around 4 GPa. The phase stable above 4 GPa in KDP:Mn is probably the same phase stable above 5 GPa in pure KDP system (named phase V). Ab initio calculation indicate that, at moderated pressure, the tetrahedral $R_c$ component is stronger, indicating that the rotation with pressure is predominantly around the $c$ crystalline direction. Theoretical results indicates that pressure induced tetrahedral rotations leads to changes of H – O neighborhood of PO4 unities, activating librations/bending modes observed for high pressure phase of KDP:Mn with stronger Raman activity.

**ACKNOWLEDGMENT**

The authors acknowledge the financial support from the Brazilian agencies CNPq and CAPES.

**REFERENCES**