

## Electron density distribution of the nonlinear optical crystal $\text{KTiOPO}_4$

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### Introduction

The  $\text{KTiOPO}_4$  (KTP, potassium titanyl phosphate) crystal has a non-centrosymmetric structure. Its highly asymmetric interatomic bonds indicated its potential as a nonlinear optical (NLO) material. The KTP crystal family has now become one of the most well known materials for various NLO applications. KTP is the material of choice in applications that utilize the second harmonic generating effect for laser-frequency doubling. The transparent crystalline material has favorable material properties, for example, a high thermal stability, chemical resistivity, high optical nonlinearity, and high optical damage threshold. The crystals have also a wide optical transmission window that covers both the UV and IR spectra. These properties are as well found in some isostructural  $\text{ATiOBO}_4$  materials, particularly for those with  $A = \text{K, Rb, Cs or Tl}$  and  $B = \text{P or As}$ .

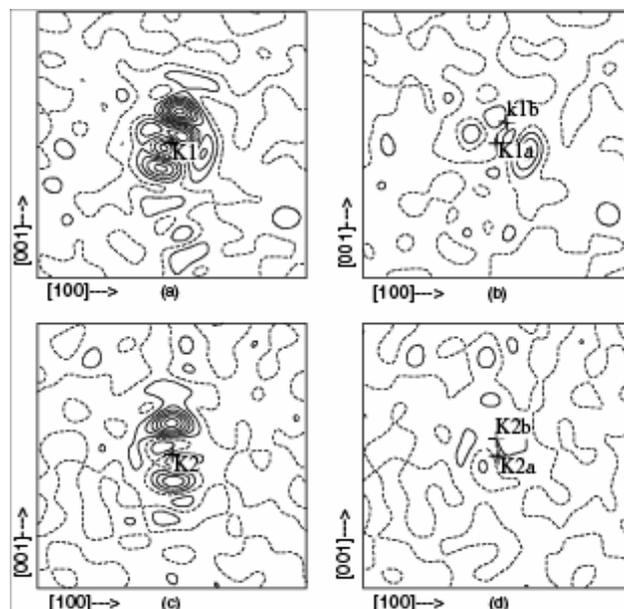
### Experimental

A small transparent crystal was used for the data collection at the Photon Factory, Tsukuba, Japan, using the beamline 14A four-circle diffractometer. Vertically polarized X-ray radiation from a vertical wiggler was monochromated by a double  $\text{Si}(111)$  crystal monochromator, and focused using a curved fused-silica mirror coated with platinum. The beam optics are automatically adjusted every 20 min for maximum flux. A high-speed avalanche photodiode detector with counting linearity up to  $10^8$  cps was employed (Kishimoto et al., 1998). Diffraction intensities were measured at room temperature with  $\lambda = 0.75052(1)$  Å using the  $\omega/2\theta$  continuous scan with a range of  $0.30^\circ$  in  $\omega$ . The collected X-ray intensities were corrected for experimental intensity variations as indicated by measured standard reflections, and for absorption using the analytical model. An isotropic extinction parameter using the Larson's implementation was refined for both models. About 1.3% of the reflections were affected by extinction. The maximum correction of  $y = 0.94$  was applied to the 800 reflection (the observed structure factor,  $F_{\text{obs}}$ , is  $yF_{\text{kin}}$ , where  $F_{\text{kin}}$  is the kinematic value).

The collected data were refined utilizing the Xtal3.7 software package, first as KTP without any alkaline disorder (model I). This model converged to  $R = 0.021$ ,  $wR = 0.027$ ,  $S = 1.078$  and residual electron densities  $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$  of  $1.56/-0.91$   $\text{e}\text{\AA}^{-3}$  [ $\sigma(\Delta\rho) = 0.09$   $\text{e}\text{\AA}^{-3}$ ]. The residual electron density maps obtained from the model I are extremely flat and clean from peaks everywhere but close to each potassium site. A peak of  $1.56$   $\text{e}\text{\AA}^{-3}$  is located  $0.496(1)$  Å from the K1 site and another peak of  $1.31$   $\text{e}\text{\AA}^{-3}$  is located  $0.474(1)$  Å from the K2 site (see

figure (a) and (b) respectively), and they are both shifted from their nearby alkaline site along the  $c$  direction.

The remaining electron density peaks in model I prompted a second refinement model (model II) with disordered alkaline sites. This structural model converged to  $R = 0.019$ ,  $wR = 0.025$ ,  $S = 1.001$  and residual electron densities  $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$  of  $1.05/-0.64$   $\text{e}\text{\AA}^{-3}$  [ $\sigma(\Delta\rho) = 0.08$   $\text{e}\text{\AA}^{-3}$ ]. The refined alkaline disorder sites named K1b and K2b are located  $0.358(14)$  Å and  $0.257(14)$  Å from their individual original sites, having population occupancies of  $0.058(5)$  and  $0.127(17)$ , respectively. Surrounding residual electron density features are seen in the figure (c) and (d).



Reasons of earlier failures to correctly characterise alkaline site disorder in KTP are either due to low resolution or not enough intense diffraction, or a combination of both. KTP isostructures are characterised by having a noteworthy amount of weak reflections, so studies based on X-ray sealed tube data suffer, supposedly, from low statistical significance of weak reflections.

### References

- [1] S.T. Norberg & N. Ishizawa., *Acta Cryst.* **C61**, i99 (2005).
- [2] S. Kishimoto et al., *Rev. Sci. Instrum.* **69**, 384 (1998).

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