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Cation Split Positions in KTP-type Ferroelectrics

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Introduction

Recently, attention has been drawn to cation split positions in $KTiOPO_4$ (KTP) although there are few examples of structural refinement of these small shifts in position. Different cation positions are in most cases just a result of the mixture of different cations in the crystal structure. However, cation split positions have also been found in pure non-doped KTP isomorphic structures and in mixed cation materials of the KTP-family. Cation split positions for potassium in the KTP-like material $KFeFPO_4$ were observed in [1] and there was mentioned the existence of a similar phenomena in KTP. Using high resolution X-ray diffraction experiments in KTP, it was found [2] that the potassium cations do split in two or more positions at higher temperatures (673 K and above). Similar split position phenomena were also found in $(CsRb)TiOPO_4$ [3].

In the present work the structures of pure $RbTiOAsO_4$ [4] and KTP containing strontium and chromium ($Sr_{0.06}K_{0.87}Cr_{0.05}Ti_{0.95}OPO_4$) [5], and KTP containing barium ($Ba_{0.06}K_{0.88}TiOPO_4$) [5] are reported.

Experimental

Diffraction data was collected with synchrotron X-ray radiation at BL14A, Photon Factory (Tsukuba, Japan). Full spheres of reciprocal space data sets up to $2\theta=110^o$ at wavelength $\lambda=0.75$Å, and room and 120K temperatures were collected. A high-speed eight-channel avalanche photodiode counter (APD8) was used for data collection.

Results and discussion

The accurate synchrotron single-crystal data for $RbTiOAsO_4$ [4] is of sufficient quality and resolution to detect the splitting positions of the Rb cations at room temperature. Strong accumulation of the $\Delta\rho$ difference charge density (Fig. 1*a*,*b*) near the Rb atoms at the distance of ~0.5 Å in -*c* direction can be attributed to the partial occupancy of additional sites related by pseudo-symmetry. This type of static or/and dynamic disorder is temperature dependent and seems to be universal for the $KTiOPO_4$ family of compounds. The best modelling of the experimental data was obtained with the Rb in split positions described within the harmonic approximation and the multipole functions for the other atoms. The $\Delta\rho$–density features in the Ti-O and As-O covalent bonds can be related to the linear and non-linear susceptibility using bond-polarization theory. The charge density maps reflect the anisotropy of non-liner susceptibility, which is larger for directions where locally anti-symmetric components of $\Delta\rho$ are strong.

The refinement of the dopant positions in $Sr_{0.06}K_{0.87}Cr_{0.05}Ti_{0.}95OPO4$ and $Ba_{0.06}K_{0.88}TiOPO_4$ showed that the barium dopant is positioned in the larger K2 cavity of KTP while the smaller strontium ion is located in both cavities [5]. Split cation positions are found for the strontium dopant in both cavities positioned in the positive *c* direction from the potassium cation (Fig. 1*c*,*d*). The chromium dopant is composed of two different oxidisation states, namely +III and +VI, and both are located inside the TiO_6-octahedra. Both structures shows slightly less distorted TiO_6-octahedra.

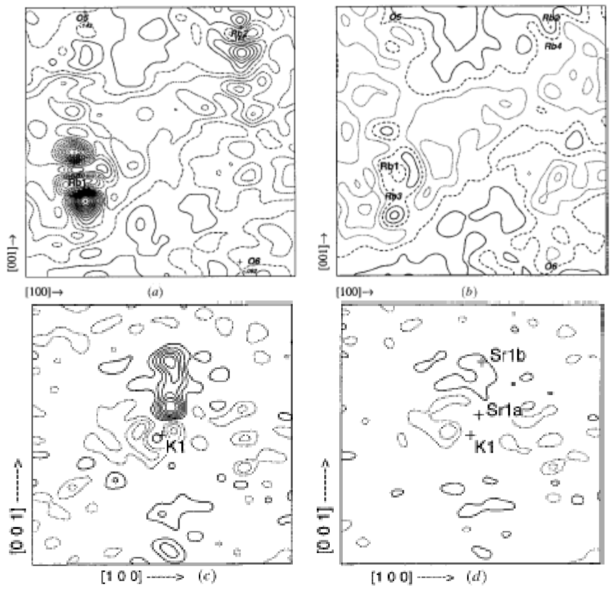

Fig.1 Difference electron density ($\Delta\rho$) in the (010) plane for RTA (*a*,*b*) and SrCrTA (*c*,*d*) before (*a* and *c*) and after (*b* and *d*) the addition of cation split positions. Contour interval 0.3 eA^{-3}; positive contours are solid and negative are short dashed.

References

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