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"Inclusion Tuning of Nonlinear Optical Materials: KTP Isomorphs"

by

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Abstract:

$KTiOPO_4$ or KTP has shown itself to be a premier material for optical second harmonic generation, or SHG. Cations ranging in size from Ag^+ to Cs^+ can be partially or completely exchanged for K^+, altering the structure and changing the reactivity and SHG coefficient of the material. In particular, partial deammoniation of NH_4TiOPO_4 results in changes in the Ti-O bond lengths and a dramatic reduction in SHG. Many isomorphic derivatives of KTP have been made in which 3- and 4- valent transition and main group metals are substituted for Ti, balancing charge by substituting F^- or OH^- for oxide in the Ti-O chain. Guest and host modification can be used to define nonlinear optic properties over a wide range.

Key [illegible]

Inclusion Tuning of Nonlinear Optical Materials:

KTP Isomorphs

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1. INTRODUCTION: Potassium titanyl phosphate (KTP) has in recent years proven to be the material of choice for use in optical applications requiring a large second-order nonlinear coefficient, such as laser frequency doubling (SHG), and the fabrication of electrooptic waveguides. One of the reasons for its versatility is the openness of the $-TiOPO_4$ framework, which allows the possibility of tuning by means of ion exchange. This has been exploited in waveguide manufacture to yield zones or channels in which the refractive index of the bulk material has been altered. This paper will describe some of the results of our exploratory synthesis studies of the KTP structural family. The recently synthesized KTP isomorphs contain main group metals or other transition metals besides Ti, with a view toward enhanced second order optical nonlinearity and controlled phase matching as well as transparency in the near UV for higher order and higher frequency harmonic generation. Our goal is to correlate the changes in electrooptic properties with the concommittant structural deviations from the original KTP.

KTP is an acentric metal oxide framework, and crystallizes in the orthorhombic space group $Pna2_1$ (point group mm2). a=12.814Å, b=6.404Å, c=10.616Å, and the unit cell volume = 871.16Å^3. There are four asymmetric units per unit cell, and two formula units per asymmetric unit. There are therefore two different Ti sites, as well as two different cation sites. The framework is characterized by TiO_6 chains along the c direction; these chains are linked to each other by phosphate bridges.[1] The open nature of this framework allows cations to diffuse easily along the c direction or polar axis.[2] It is this ease of diffusion which allows ion exchange to take place, and it is also responsible for KTP's relatively large, and highly anisotropic, ionic conductivity. The nonlinear optic properties of KTP are well characterized; in addition to its large second order nonlinear susceptibility,[3] KTP is noncritically phase matchable in Type II frequency mixing of 1064nm (YAG) and 809nm light, a condition that exhibits little temperature dependence.[4,5] The structural feature believed responsible for KTP's high second harmonic coefficient is the asymmetry of the Ti-O bonds linking the TiO_6 octahedra, which alternate long-short along the chain; this Ti-O bond distance varying by as much as 0.38A. According to B.F. Levine's bond charge theory,[6] it is this bond length difference in other ferroelectrics (e.g. $LiNbO_3$, $Ba_2NaNb_5O_{15}$, $LiTaO_3$) that results in unequal bond nonlinear susceptibilities and thereby a net contribution to one or more components of second order polarizability, and it is not unreasonable to suspect that KTP can be treated in similar fashion.

The tunability of KTP's refractive index through cation exchange has been exploited by Bierlein and coworkers in the fabrication of electrooptic waveguides.[2] In this procedure, a portion of a KTP single crystal is exposed to the molten nitrate salt of the desired cation for several hours at approx. 400° C. The cations diffuse preferentially along the c direction (polar axis) to a depth of several microns, creating a bed or channel in which the refractive index exceeds that of the bulk KTP by an amount depending on, among other factors, the cation (max. $\Delta n=0.02$ for Rb^+, 0.03 for Cs^+, and 0.23 for Tl^+). The depth to which the cations diffuse is self-limiting, since the larger cations diffuse much less readily than K^+ (ratio Rb^+/K^+ diffusivity = .001, as measured by ionic conductivity). Since the ion diffusion in KTP occurs almost entirely along the c axis at the temperatures studied, lateral diffusion of the exchanged cations out of the waveguide is minimal.

We have found that an excellent example of inclusion tuning in the KTP system occurs in NH_4TiOPO_4 (NTP),[7] whose nonlinear optic coefficient can be switched off, then on, by gas-phase desorption and reabsorption of NH_3 or H_2O. Structural data indicates that on desorption, one of the Ti atoms is displaced toward the center of its O-Ti-O link, causing the Ti-O bond distances to become nearly identical.

Investigation of additional inclusion tuning possibilities has led us to widen our scope to the synthesis of over forty-five compositions which are structurally isomorphous to KTP. Our structural and optical studies are directed toward obtaining a broader insight into the range of inclusion tuning possibilities in the KTP family, and subsequently using inclusion modifications to synthesize materials with optimized eloctrooptic properties. In our studies we have identified a similar number of compositions isomorphic to KTP in which 3- and 4-valent transition and main-group metals replace Ti, balancing charge by substituting F^- and OH^- for oxide in the Ti-O chain. We are now studying their structural and optical properties in detail.

Table 1 contains a partial list of $M_xM'_{1-x}TiOPO_4$ compounds, with lattice constants and SHG measurements. Experimental and structural details of some of these species are discussed in detail subsequently.

2. EXPERIMENTAL: All of our host frameworks were synthesized from one or more of the following techniques:

Solid State: The reagents are wetted, ground together, sintered in a Pt or Al_2O_3 crucible, reground and refired. The crystallite sizes of products obtained by this method are usually very small.

Example: $KH_2PO_4 + TiO_2 \xrightarrow{750°C} KTiOPO_4 + H_2O$

Flux Growth: The starting materials are combined with flux reagents in a Pt or Al_2O_3 crucible, heated to solution, slowly cooled through the saturation temperature, and quenched. The flux material is then usually dissolved away in water. This method allows growth of large single crystals, however, flux inclusions often result if the flux is too viscous or the cooling rate is to rapid.

Example: $4K_2HPO_4 + 2TiO_2 + 3WO_3 \xrightarrow[-1°/hr]{1000°C} 2KTiOPO_4 + 3K_2WO_4 \cdot P_2O_5 + 2H_2O$ [9]

Hydrothermal (subcritical): The reagents are combined with water and shaken to form a gel, which is then autoclaved at autogenous pressure. The products, occasionally in the form of large single crystals, are recovered by filtration.

Example: $KOH + KH_2PO_4 + TiCl_4 \xrightarrow[15 bar]{200°C} KTiOPO_4 + KCl + H_2O$

Hydrothermal (supercritical): The reagents are added to a collapsible gold tube, which is sealed and autoclaved in a thick-walled steel bomb. Because of favorable kinetics and low viscosity at the high temperatures used, large, high quality single crystals are often obtained by this method.

Example: $KOH + KH_2PO4 + TiO_2 \xrightarrow[4000 bar]{600°C} KTiOPO_4 + H_2O$

$AgTiOPO_4$ is not synthetically accessible from any of the routes previously described; it is instead made by exchanging KTP crystals in molten salts containing Ag^+. Pure AgTP is readily made by melting $AgNO_3$ over KTP crystals or powder at 250°C, however, crystal quality is lost under these conditions. Up to 89% silver exchanged (as determined by weight gain and the use of Vegard's Law) single crystals are obtainable at lower temperatures using eutectic melts of silver salts, the most useful one being the $AgNO_3$-$AgClO_3$ eutectic (mp=140°C). AgTP undergoes ion exchange with K^+ and NH_4^+ in aqueous solution at room temperature, as well as in molten salts. Silver can be removed by complexation with KCN or $NH_3(aq)$, the Ag^+ being replaced by K^+ and NH_4^+, respectively. The extent of exchange can be readily determined by powder X-ray, using Vegard's Law, or in the case of ammonium exchange, through TGA.

All SHG measurements were made on powder samples using the method of Dougherty and Kurtz[8]. The values quoted are in reference to quartz samples.

3. RESULTS: Inclusion tuning of NTP: In this series of experiments, single crystals of NH_4TiOPO_4 were synthesized using supercritical hydrothermal techniques. These crystals were then partially deammoniated under vacuum at 225°C to yield $(NH_4)_{.50}H_{.50}TiOPO_4$ (NHTP). This stoichoimetry was confirmed by TGA measurements. Some of these crystals were reammoniated to regenerate the original NTP, others were hydrated to give the composition $(NH_4)_{.50}(H_3O)_{.50}TiOPO_4$ (NOTP). The structures of NTP and NHTP were determined through refinement of single crystal X-ray data, and NOTP was characterized by Rietveld analysis of high resolution synchrotron X-ray powder data. The important structural changes with regard to inclusion tuning and SHG are the bridging Ti-O bond distances, shown in Table 2, with KTP added for comparison [Appendix 1.1, 1.2]. From these data, it is evident that the lengthening of

the Ti(1)-O(10) bond, which caused the two Ti-O bond lengths to become nearly equal, is associated with a dramatic loss in the second harmonic coefficient. Another significant structural change is the Ti(1)-O(9)-Ti(2) bond angle, which changes from 136.8° to 127.4°. Protonation of O(9) is thought responsible; neutron studies are currently underway to confirm this. Upon reammoniation or hydration, the Ti(1)-O(9) bond is shortened, the Ti(1)-O(9)-Ti(2) bond is expanded, and the SHG is restored. This suggests that the bonds responsible for the nonlinear susceptibility of NTP are the O(9)-Ti-O(10) bonds. It is relevant to note that Ti(1) corresponds to the Ti atom whose bridging Ti(1)-O-Ti(2) are cis to one another (angle O(9)-Ti(1)-O(10)=95.5° in NTP), while the bridging atoms are trans to one another in Ti(2), the atom unaffected by deammoniation [Figures 1,2]. Also, there is complete site selectivity in NHTP, with the NH_4^+ in a *nine-fold coordinate* site.

<u>Tuning effects of other ions:</u> Structure studies were undertaken on several compounds, including $K_{.5}(NH_4)_{.5}TiOPO_4$ (KNTP), $K_{.5}Rb_{.5}TiOPO_4$ (KRbTP), and $K_xH_{1-x}TiOPO_4$ (KHTP) in the search for other examples of site selectivity and SHG modification through inclusion. A particularly interesting compound illustrating both of these features is $Ag_{.85}K_{.15}TiOPO_4$. Both unexchanged $AgTiOPO_4$ and $Ag_{.85}K_{.15}TiOPO_4$ have very low SHGs (approx. 5 and 7 times quartz, respectively). To account for this result in terms of structure, X-ray data were taken on a single crystal of composition $Ag_{.85}K_{.15}TiOPO_4$ using a Huber 4-circle automatic diffractometer [Appendix 1.3]. The unit cell is orthorhombic, space group $Pna2_1$. a=12.535Å, b=6.294Å, c=10.524Å, and the volume =830.29Å^3. The Ti-O bond distances in $Ag_{.85}K_{.15}TiOPO_4$, with KTP's added for comparison, are given in Table 3, along with the occupancy factors for the silver and potassium atoms. Note the marked difference between Ag^+

and K^+ in their preference for the two cation sites. The most likely explanation for the difference in site preference is that silver, which generally prefers lower coordination numbers, exhibits a strong preference for the four-coordinate Ag(1) site, rather than the Ag(2) site, in which it is six-coordinate (using the criterion Ag-O < 3.0Å). The Ag(1) is most strongly coordinated to O(1) and O(9), with Ag-O distances of 2.388Å and 2.338Å, respectively. The O(9) and O(1) are located in adjacent chains, with the Ag-O bonds in a trans configuration. This has the effect of elongating the Ti(1)-O(1) bond, which is trans to the short Ti(1)-O(10) bond, to the unusually high value of 2.23Å [Figure 3]. The coordination of Ag(1) to O(9) decreases the Ti(1)-O(9)-Ti(2) bond angle from 136.8° to 129.9°. This decrease in bond angle is analogous to the result of protonation of O(9) in NHTP, where the Ti(1)-O(9)-Ti(2) bond angle decreased to 127.4°. These results illustrate another approach to switching SHG through guest inclusion in KTP structures.

Other transition and main group metal KTP isomorphs: In addition to the $M_xM'_{1-x}TiOPO_4$ series of compounds already presented we have synthesized several dozen KTP analogues in our laboratories which contain transition metals other than Ti, main group metals, or both. A partial list is presented in Table 4.

Synthesis and Characterization of $KGaPO_4F_{.7}(OH)_{.3}$: $KGaPO_4F_{.7}(OH)_{.3}$ was prepared in single crystal form from a gel containing KF, KOH, KH_2PO_4, and Ga_2O_3 using supercritical hydrothermal techniques; it has also been obtained in powder form from the same reagents using subcritical hydrothermal methods. Analysis (by Galbraith) and TGA data were used to arrive at the formula given above. NMR data were obtained on a powdered sample with a 7-tesla GN-300 spectrometer using a Chemagnetics probe. The hydroxyl proton gives a single peak at 5.27 ppm downfield from hydroxy-apatite in the ^{1}H MAS NMR spectrum on the powder obtained subcritically; a single resonance appears in the ^{31}P CPMAS spectrum of the same sample, located at 10.03 ppm upfield from H_3PO_4. Single crystal data show that the cell is orthorhombic, a=12.7167(15)Å, b=6.3021(8)Å, c=10.4310(13)Å; the structure was refined in the space group $Pna2_1$ [Appendix 1.4]. Refinement showed that the bridging Ga(O,F) distances were all nearly identical: Ga(1)-(O,F)(9)=1.996Å, Ga(1)-(O,F)(10)=1.941Å, Ga(2)-(O,F)(9)=1.925Å, and Ga(2)-(O,F)(10)=1.981Å [Figure 4]. The hydrogen atom was not located, although we suspect it to be protonating the bridging oxygens.

The SHG of this material is rather low - 0.31 times quartz, which is not surprising in light of the similar bridging Ga(O,F) distances, but it is not clear whether the different bond nonlinear susceptibilities that Ga and F would introduce also play a role in altering the nonlinear optic coefficients in either direction. Inclusion tuning studies in these isomorphs are being devised to address this problem by determining the effect of altered M-O bond distances on the SHG.

4. SUMMARY: KTP, a compound whose utility in electrooptic applications has been well demonstrated, belongs to a structural family of great diversity and versatility. The inclusion host-guest relationship, and the fact that there are two formula units in the asymmetric unit with all atoms in general positions makes possible a large number of synthetic permutations of the KTP structure. Additionally, inclusion tuning of KTP through ion exchange permits structural modification and definition of both linear and nonlinear optical properties over a wide range. Finally, the large shifts in nonlinear susceptibility upon structural modification make the KTP family particularly useful for modeling structure-electrooptic relationships.

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Table 1

FORMULA	a,Å	b,Å	c,Å	VOLUME, $Å^3$	SHG
$AgTiOPO_4$	12.524	6.263	10.53	825.95	5
$Ag_{.87}K_{.13}TiOPO_4$	12.534	6.294	10.524	830.23	7
$(NH_4)_{.5}H_{.5}TiOPO_4$	12.822	6.284	10.598	853.83	60
$KTiOPO_4$	12.816	6.403	10.587	868.68	6000
$(NH_4)_{.5}K_{.5}TiOPO_4$	12.894	6.442	10.58	878.81	1100
$TlTiOPO_4$	12.944	6.484	10.553	885.70	6000
$(NH_4)_{.5}(H_3O)_{.5}TiOPO_4$	12.915	6.495	10.589	888.18	700
NH_4TiOPO_4	12.916	6.492	10.598	888.62	2400
$RbTiOPO_4$	12.960	6.500	10.557	889.32	6000

Table 2

	KTP	NTP	NHTP	NOTP
Ti(1)-O(9)	1.993Å	1.958Å	2.012Å	2.155Å
Ti(1)-O(10)	1.718	1.719	1.901	1.788
ΔTi(1)	0.275	0.239	0.111	0.367
Ti(2)-O(9)	1.738	1.748	2.116	1.704
Ti(2)-O(10)	2.101	2.090	1.763	2.041
ΔTi(2)	0.363	0.342	0.353	0.337
SHG(x quartz)	6000	2400	60	650

Table 3

	Ti(1)-O(9)	Ti(1)-O(10)	ΔTi(1)	Ti(2)-O(9)	Ti(2)-O(10)	ΔTi(2)	SHG
KTP	1.993	1.718	0.275	1.738	2.101	0.363	6000
"AgTP"	1.980	1.720	0.260	1.791	2.068	0.277	7

cation site:	Ag(1)	Ag(2)	K(1)	K(2)
occupancy factor(%):	97	72	3	28

Table 4

Formula	Cell volume	SHG	Synthetic Route
$NaGeOPO_4$	759.9Å^3	4.0	solid state
KGeOPO4	794.6	3.33	flux
$K_2GaGeP_2O_9(F,OH)$	834.4	10	hydrothermal (supercritical)
$KGaPO_4F_{.7}(OH)_{.3}$	838.0	0.72	hydrothermal (supercritical)
$KVOPO_4$	853.2	opaque	flux
$KFePO_4F$	873.9	2.66	hydrothermal (subcritical)
$K_2FeNb(PO_5)_2$	896.3	1.0	hydrothermal (supercritical)
$KSnOPO_4$	920.6	0	solid state
$RbSnOPO_4$	945.8	0	solid state

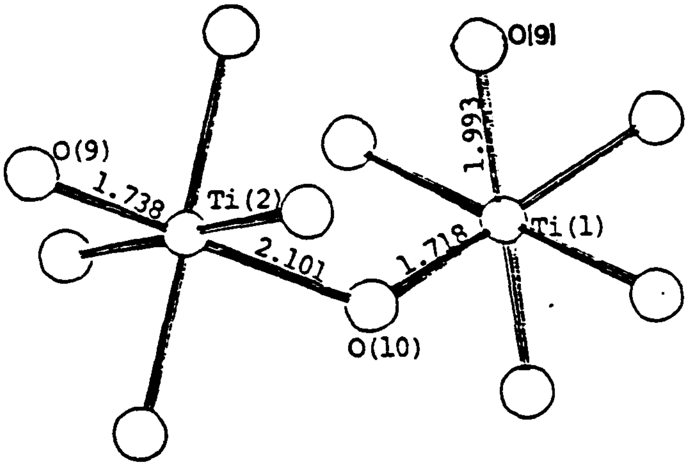

Figure 1: Ti-O bond distances in KTP

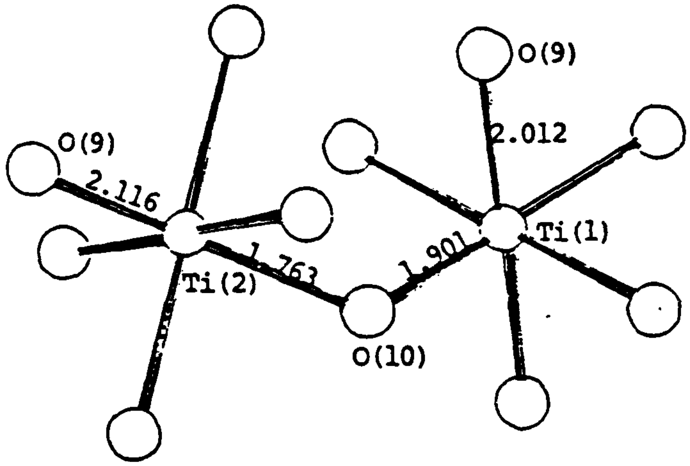

Figure 2: Ti-O bond distances in NHTP

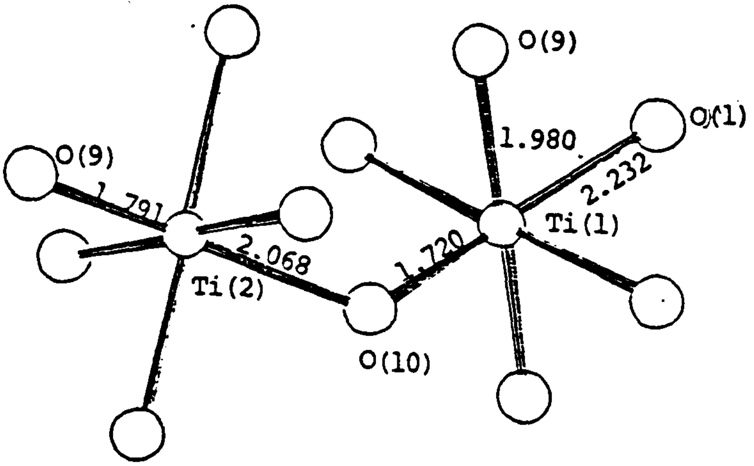

Figure 3: Ti-O bond distances in AgTP

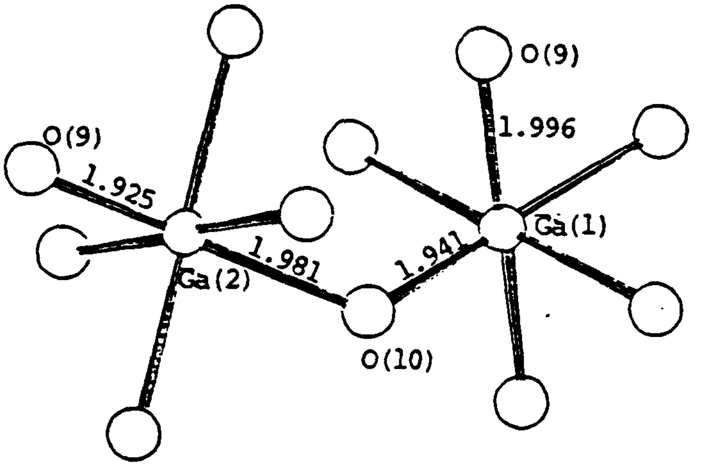

Figure 4: Ga-(O,F) bond distances in $KGaPO_4F_{.7}(OH)_{.3}$

Appendix 1

1.1 For $(NH_4)_2(TiOPO_4)_2$, a crystal of dimensions 0.4x0.35x0.2 mm was mounted on a glass fibre. Thirty-four reflections were computer centered on the diffractometer and the cell parameters refined by least squares to the values a=12.915(2)Å, b=6.492(1)Å, c=10.597(2)Å. Intensity data were collected by the $\theta/2\theta$ scan method using MoKα radiation on a Huber 4-circle diffractometer with a graphite crystal monochromator. Several omega scans showed typical peak widths of 0.2°. Data were collected using a scan rate of 6°/min from 1.3° below $K\alpha_1$ to 1.6° above $K\alpha_2$. Measurements were made up to $2\theta = 65°$, giving a total of 1938 reflections, of which 1878 were independent. With the use of the criterion $F_o^2 > 3\sigma(F_o^2)$, 1600 reflections were considered observed. Three standard reflections were measured every 100 reflections and showed no systematic variations. Intensities were corrected for Lorentz and polarization effects, absorption using the method of Busing and Levy [10] (μ=21.8 cm^{-1}) and extinction. The structure was refined using the model taken from reference 1 in the space group $Pna2_1$. No hydrogen atoms could be located. The function minimized during the least squares refinement was $w(|F_o| - |F_c|)^2$, where w was taken as $1/\sigma(F)$ and $\sigma(F)=[\sigma(I^2)+0.003(I^2)]^{\frac{1}{2}}$. Refinement of the positional parameters using anisotropic thermal parameters for all atoms gave $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|=4.0\%$ and $R_2=\Sigma(w(||F_o|-|F_c||))/\Sigma|F_o|=5.5\%$.

1.2 For $(NH_4,H)(TiOPO_4)_2$, a crystal of dimensions 0.26x0.29x0.32 mm was mounted on a glass fibre. Twenty-seven reflections were computer centered on the diffractometer and the cell parameters refined by least squares to the values a=12.822(1)Å, b=6.2835(5)Å, c=10.5978(8)Å. Intensity data were collected by the θ/2θ scan method using MoKα radiation on a Huber 4-circle diffractometer with a graphite crystal monochromator. Several omega scans showed typical peak widths of 0.2°. Data were collected using a scan rate of 6°/min from 1.3° below $K\alpha_1$ to 1.6° above $K\alpha_2$. Measurements were made up to 2θ= 65°, giving a total of 1869 reflections, of which 1812 were independent. With the use of the criterion $F_o^2>3\sigma(F_o^2)$, 1454 reflections were considered observed. Three standard reflections were measured every 100 reflections and showed no systematic variations. Intensities were corrected for Lorentz and polarization effects, absorption using the method of Busing and Levy [10] (μ=22.6cm^{-1}) and extinction. The structure was refined using the model taken from reference 1 in the space group $Pna2_1$. No hydrogen atoms could be located. The function minimized during the least squares refinement was $w(|F_o|-|F_c|)^2$, where w was taken as $1/\sigma(F)$ and $\sigma(F)=[\sigma(I^2)+0.003(I^2)]^{\frac{1}{2}}$. Refinement of the positional parameters using anisotropic thermal parameters for all atoms gave $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$=4.9% and $R_2=\Sigma(w(||F_o|-|F_c||))/\Sigma|F_o|$=6.8%.

1.3 For $Ag_{.85}K_{.15}TiOPO_4$, a crystal of dimensions 0.5 x 0.5 x 0.15 mm was mounted on a glass fibre. Twelve reflections were computer centered on the diffractometer and the cell parameters refined by least squares to the values a=12.534(2)Å, b=6.294(1)Å, c=10.524(2)Å. Intensity data were collected by the θ/2θ scan method using MoKα radiation on a Huber 4-circle diffractometer with a graphite crystal monochromator. Several omega scans showed typical peak widths of 0.3°. Data were collected using a scan rate of 6°/min from 1.3° below $K\alpha_1$ to 1.6° above $K\alpha_2$. Measurements were made up to 2θ= 65°. With the use of the criterion $F_o^2>3\sigma(F_o^2)$, 1796 independent reflections were considered observed. Three standard reflections were measured every 100 reflections and showed no systematic variations. Intensities were corrected for Lorentz and polarization effects, absorption using the method of Busing and Levy [10] (μ=64.3 cm^{-1}) and extinction. The structure was refined using the model taken from reference 1 in the space group $Pna2_1$. The function minimized during the least squares refinement was $w(|F_o|-|F_c|)^2$, where w was taken as $1/\sigma(F)$ and $\sigma(F)=[\sigma(I^2)+0.003(I^2)]^{\frac{1}{2}}$. Refinement of the positional parameters using anisotropic thermal parameters for all atoms (except for potassium atoms, on which isotropic parameters were refined) gave $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$=7.9% and $R_2=\Sigma(w(||F_o|-|F_c||))/\Sigma|F_o|$=8.7%.

1.4 For $KGaPO_4F_{.7}(OH)_{.3}$, a crystal of dimensions 0.55 x 0.35 x 0.15 mm was mounted on a glass fiber. Twenty-two reflections were computer centered on the diffractometer and the cellparameters refined by the method of least squares to the values a=12.716(2) Å, b=6.302(1) Å, c=10.431(1) Å. Intensity data were collected by the $\theta/2\theta$ scan method using MoKα radiation on a Huber 4-circle diffractometer with a graphite crystal monochromator. Several omega scans showed typical peak widths of 0.15°. Data were collected using a scan rate of 6°/min from 1.3° below Kα1 to 1.6° above Kα2. Measurements were made up to 65° 2θ, With the use of the criterion $F_o^2>3\sigma(F_o^2)$, 1443 independent reflections were considered observed. Three standard reflections were measured every 100 reflections and showed no systematic variations. Intensities were corrected for Lorentz and polarization effects, absorption using the method of Busing and Levy [10] (μ=78.6cm^{-1}) and extinction. The structure was refined using the model taken from reference 1 in the space group $Pna2_1$. No hydrogen atoms could be located. The function minimized during the least squares refinement was $w(|F_o|-|F_c|)^2$, where w was taken as $1/\sigma(F)$ and $\sigma(F)=[\sigma(I^2)+0.003(I^2)]^{\frac{1}{2}}$. Refinement of the positional parameters using anisotropic thermal parameters for all atoms gave $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|=4.46\%$ and $R_2=\Sigma(w(||F_o|-|F_c||))/\Sigma|F_o|=3.48\%$.