Polarized optical absorption of Nd^{3+} in $KTiOPO_4$ crystals

Polarized optical absorption of Nd³⁺ in KTiOPO₄ crystals

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Abstract. The optical absorption of Nd³⁺ ions in KTiOPO₄ crystals grown from W-rich fluxes has been characterized in the 4.2–300 K temperature range. It has been found that the intensity of the optical absorption bands depends on the polarization state of the light (E) with regard to the crystal lattice axes (a, b, c). For $E \parallel c$ all bands appear with maximum intensity. For $E \parallel a$ and $E \parallel b$ the band intensity decreases, but the spectra observed in the two configurations are inequivalent. It is suggested that several Nd centres contribute in KTP:W crystals. The segregation coefficient estimated for Nd in KTP crystals grown using W-rich flux is 5×10^{-3}, being at least one order of magnitude lower in crystals grown from KTP self-flux.

1. Introduction

KTiOPO₄ (KTP) crystals are currently used as nonlinear optical (NLO) media. Most of the present applications involve bulk crystals but NLO phenomena have also been demonstrated in waveguides produced in KTP substrates [1] and increasing attention is being paid to waveguides with a periodically modified refractive index for second-harmonic generation [2].

So far, KTP has been used as a passive medium but successful growth of Nd-doped KTP has not been reported, to the best of our knowledge. This would enable one to combine the laser emission properties of the neodymium and the NLO properties of the matrix.

In this work we have studied the incorporation of Nd in KTP crystals grown by the top-seeded solution growth (TSSG) technique under different experimental conditions. The Nd incorporation has been monitored by optical absorption spectroscopy. It has been found that KTP crystals grown from W-rich solvents have a Nd segregation coefficient of 5×10^{-3}, this being more than one order of magnitude larger than that in crystals grown from solvents without W.

2. Crystal growth

Neodymium-doped KTP crystals were grown by the TSSG slow-cooling technique. The partial substitution of TiO₂ by Nd₂O₃ reduces the KTP region in the phase diagram, because of the nucleation of NdPO₄ as a new phase. Using the K₆P₄O₁₃ self-flux, we found that the solution with highest neodymium concentration in which it is possible to grow KTP crystals was 49.8K₂O:33.2P₂O₅:16.15TiO₂+0.85Nd₂O₃ (hereafter denoted as KTP self-flux). Using

W-rich fluxes (hereafter denoted as KTP:W flux) it was found that the optimum composition was $43.19K_2O:19.85P_2O_5:11.64TiO_2:24.95WO_3 + 0.37Nd_2O_3$ [3].

The Nd concentration in single crystals grown from the two types of fluxes was measured by an induced coupled plasma–mass spectrometry (ICP–MS) technique using a Perkin Elmer spectrometer model 6000. The Nd concentration determined for KTP crystals grown using self-fluxes was close to the resolution limit of the spectrometer. In order to try to improve the neodymium concentration in the crystal we investigated the effects of two different kinds of co-doping. By doping simultaneously with Al and Nd and assuming that both ions substitute for Ti, we tried to compensate the large ionic radius of Nd with the smaller one of Al ($r_{Al} < r_{Ti} < r_{Nd}$). On the other hand, by doping simultaneously with Na and Nd we tried to test the ionic radius compensation in the case of substitution of different cations ($r_{Ti} < r_{Nd}$ and $r_{Na} < r_K$). In both cases the Nd concentration determined by ICP–MS was close to the resolution limit of the spectrometer. In these crystals only a very poorly resolved optical absorption was observed and it was tentatively ascribed to the most intense optical absorption of Nd^{3+} ions.

Nd-doped KTP:W crystals show optical absorption bands which correspond well to those expected from the Nd^{3+} ion. The intensity of these bands is much higher than that observed in crystals grown in KTP self-flux. Therefore it must be concluded that the Nd segregation coefficient is much larger for crystals grown in W-rich flux than it is for those grown using KTP self-flux. The use of W-rich solvent eases the crystal growth because of the reduced melt viscosity and volatility [4]; however, the crystals grown in W-rich solvents have lower optical damage thresholds than those grown in self-flux solvents [5]. The Nd concentration determined by ICP–MS in KTP:W crystals was 42 ppm. Within the experimental uncertainty, this value agrees well with that calculated later by the analysis of the optical absorption. The intensity of the optical absorption observed in KTP crystals grown in self-fluxes is much weaker, thus it must be concluded that the Nd concentration determined from ICP–MS measurements for these crystals was not very reliable due to the low level of impurity considered. It is worthwhile to note that W is incorporated into the crystal lattice, [W] = 4500 ppm. This incorporation agrees with previous results in other KTP crystals grown by us [6].

3. Optical absorption

The optical absorption of Nd-doped KTP crystals was measured using a Varian spectrophotometer, model 5E. The sample temperature was been varied in the temperature range 4.2–300 K by using an Oxford cryostat controlled with a Lake Shore temperature controller, model DRC 91C. The dichroism of the optical absorption was determined at 4.2 K using a Glan–Taylor polarizer.

In our samples, the optical absorption of Nd^{3+} ions overlaps with a residual absorption observed in most KTP samples. The latter is related to the presence of a minor concentration of Ti^{3+} ions and other lattice defects [6].

Figure 1 shows a selected portion of the unpolarized optical absorption of Nd^{3+} in KTP:W crystals. Because of the low concentration of Nd in the crystals the room tempera- ture (RT) optical absorption of Nd^{3+} appears poorly resolved from the background absorp- tion. Below RT, namely at 77 K, the Nd^{3+} bands appear well enough resolved but some of the bands observed at 77 K disappear at 4.2 K. This is related to the thermal population of sub-levels of the $^4I_{9/2}$ ground state of Nd^{3+}. Lowering the temperature to 4.2 K greatly simplifies the understanding of the spectrum because the main bands appear narrower and bands related to the thermal population of sub-levels in the ground state mostly disappear.
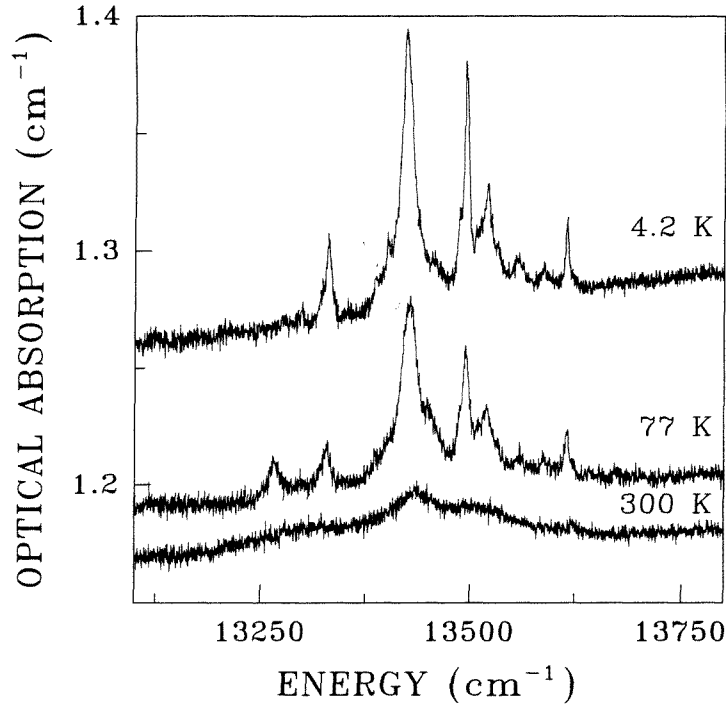
Figure 1. The unpolarized optical absorption of Nd^{3+} in KTP:W crystals measured at several temperatures. The spectra correspond to the electronic transition from the $^4I_{9/2}$ ground state to $^4F_{7/2}$ and $^4S_{3/2}$ levels. Spectra corresponding to different temperatures have been arbitrarily shifted along the y axis for clarity.

Due to the uncertainty of the Nd concentration determined by the ICP–MS technique and in order to obtain an independent estimation of the Nd^{3+} concentration in the crystal, we integrated the unpolarized RT optical absorption corresponding to the $^4F_{7/2}$ and $^4S_{3/2}$ states. The RT integrated absorbance, Γ, is related to the transition cross section, σ by

$$\frac{1}{\rho}\Gamma = \int \sigma(\lambda)\,d\lambda$$

where ρ is the Nd^{3+} density and $\int \sigma(\lambda)\,d\lambda$ is the integrated absorption cross section. Even though the Nd^{3+} cross section depends on the crystal field strength, we can obtain a rough approximation by using the integrated absorption cross section of $YAlO_3$:Nd for the selected transition of Nd^{3+}, namely 550×10^{-28} cm³ [7]. This selection is justified by the fact that the energy position of the $^4I_{9/2} \rightarrow ^2P_{1/2}$ transition (which is very sensitive to the crystal field strength) is similar in the two crystals: $23\,154$ cm^{-1} in $YAlO_3$:Nd [7] and $23\,095$ cm^{-1} in KTP:W:Nd (see table 1). This procedure yields a Nd concentration of 5×10^{17} cm^{-3} (equivalent to 54 ppm) in the KTP:W:Nd crystals. Taking into account the Nd concentration used in the melt, the segregation coefficient is $S = $ [Nd atoms in crystal]/[Nd atoms in the melt] $= 5 \times 10^{-3}$. By comparison of the optical absorption observed in Nd-doped KTP crystals grown from self-flux and with observed in those grown from KTP:W flux, the neodymium segregation coefficient of the former is at least one order of magnitude lower than in that of the latter.

Table 1. Energy positions at 4.2 K of the best resolved bands observed to grow during cooling of Nd-doped KTP:W crystals.

Excited state	Energy (cm^{-1})
$^4F_{3/2}$	11 368
	11 481
$^4F_{5/2} +^2 H_{9/2}$	12 326
	12 347
	12 428
	12 465
	12 514
	12 629
	12 725
	12 782
$^4F_{7/2} +^4 S_{3/2}$	13 330
	13 423
	13 494
	13 521
	13 555
	13 615
$^2G_{7/2} +^4 G_{5/2}$	16 729
	16 941
	16 992
	17 236
	17 393
	17 421
	17 467
$^4G_{7/2}$	18 594
	18 776
	18 812
	18 944
$^2D_{3/2} +^4 G_{9/2} +^4 G_{11/2}$	20 584
	20 616
	20 810
	20 828
	21 004
$^2P_{1/2}$	23 095

These values are as much as half of the segregation coefficients found for other trivalent ions with smaller ionic radii, namely Ga^{3+} ($S = 1.5 \times 10^{-2}$, $r = 0.62$ Å) or Al^{3+} ($S = 2.6 \times 10^{-2}$, $r = 0.5$ Å) [8]. This shows that the incorporation of Nd into the lattice is difficult, probably due to the large size of Nd making it difficult for Nd to replace Ti or to perform the lattice rearrangement possibly required if K is replaced (see later). The failure of the attempt to enhance the incorporation of Nd by co-doping with Al or Na suggests that Nd and the co-dopants used do not form pairs which may relax the local lattice distortion.

Figure 2 shows the Nd^{3+} optical absorptions observed at 4.2 K in different spectral regions using polarized light. In table 1 we have summarized the spectral positions at 4.2 K of the main bands the intensities of which grow during the cooling of the sample. We recorded the optical absorption with the electric field of the light (E) parallel to the three crystallographic axes of the crystal. It is worth noting that polarization selection rules are observed: all bands appear when $E \parallel c$; however, when E is parallel to b or a the intensity of most of the bands decreases but the spectra observed in the two latter configurations
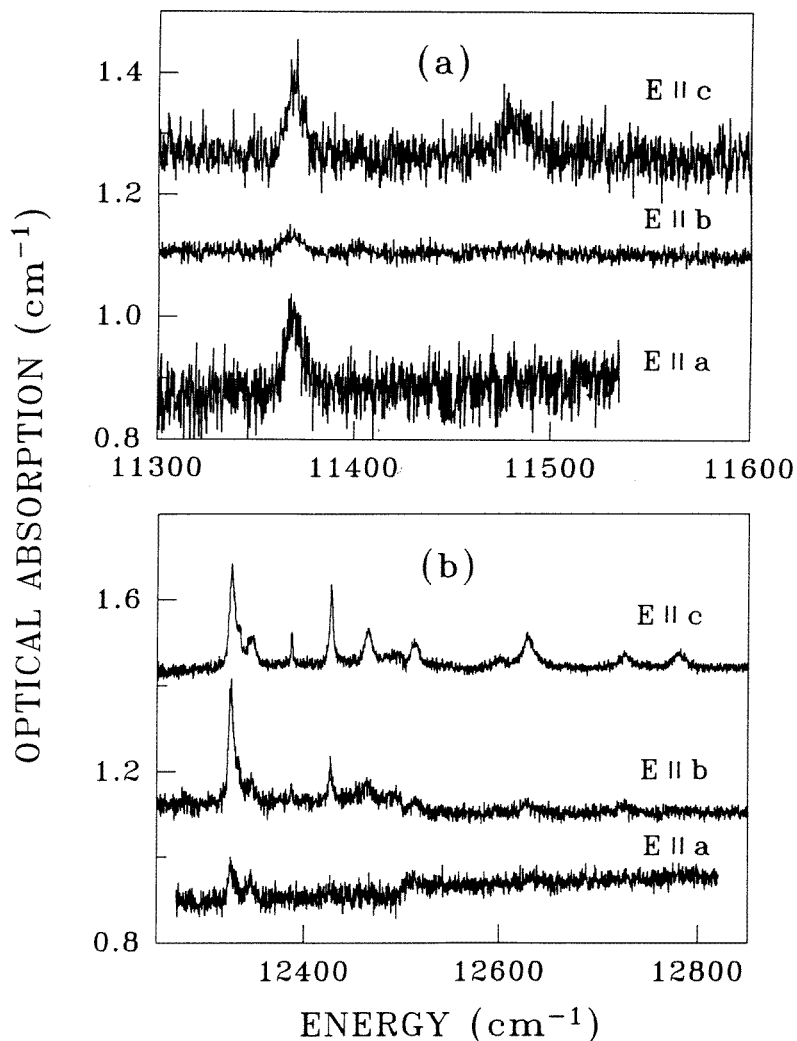
Figure 2. The polarized optical absorption of the Nd^{3+} ion in KTP:W crystals. The spectra were measured at 4.2 K. The three spectra in each part correspond to the light electric field, E, oriented parallel to each one of the three crystallographic axes. The optical absorptions correspond to the transitions from the $^4I_{9/2}$ ground state to (a) $^4F_{3/2}$, (b) $^4F_{5/2}$ and $^2H_{9/2}$, (c) $^4F_{7/2}$ and $^4S_{3/2}$, (d) $^2G_{7/2}$ and $^4G_{5/2}$, (e) $^4G_{7/2}$, (f) $^2D_{3/2}$, $^4G_{9/2}$ and $^4G_{11/2}$ and (g) $^2P_{1/2}$. The spectra corresponding to different polarization orientations have been arbitrarily shifted along the y axis for clarity.

($E \parallel b$ and $E \parallel a$) are not equivalent. The number of bands observed and their polarization behaviour must be considered in relation to the symmetry of the local crystal field.

The crystalline structure of KTP belongs to the orthorhombic $Pn2a_1$ space group, with crystalline lattice parameters $a = 12.819$ Å, $b = 6.399$ Å and $c = 10.584$ Å [9]. Figures of the structure have often been reported [1,9]. For each cation there are two inequivalent lattice sites, usually labelled 1 and 2 respectively. The cations are bonded to oxygens with different coordinations: P is tetrahedrally bonded to four oxygens, Ti is octahedrally bonded
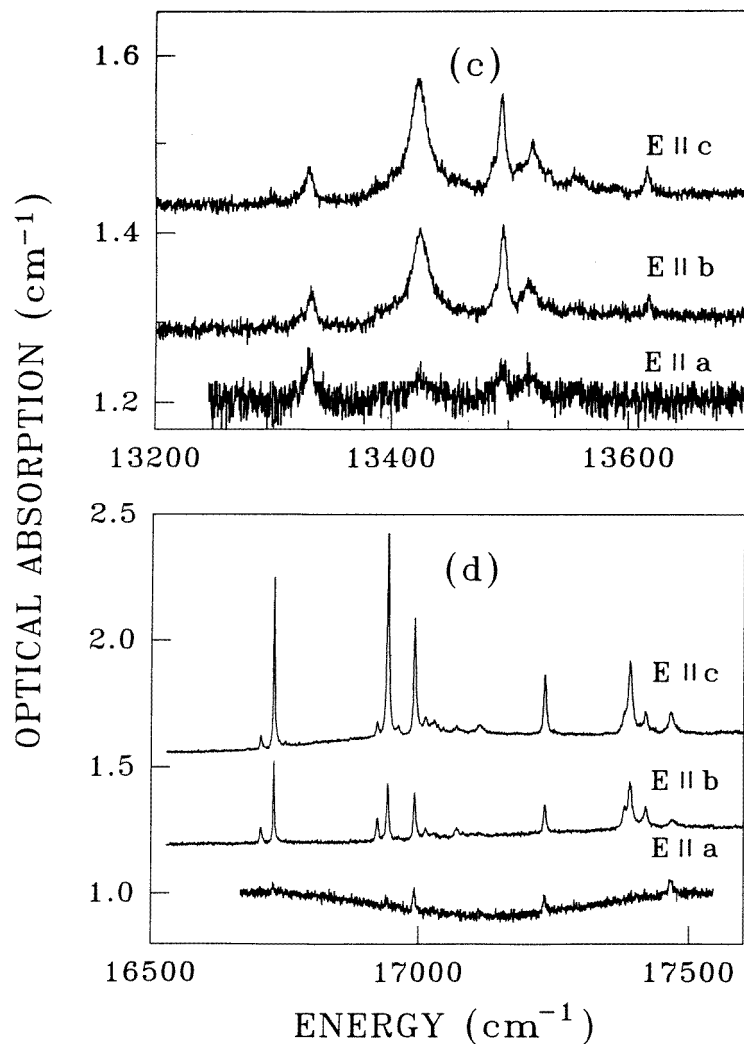
Figure 2. (Continued)

to six oxygens and K is weakly bonded to eight and nine oxygens in the K1 and K2 positions respectively. The local symmetry of the cations with respect to the first oxygen shell is C_1 for all the lattice sites.

At present there is not information on the lattice site incorporation of Nd or of other rare earth ions into KTP crystals. From the crystal growth and spectroscopic studies performed up to now with other impurities some rules can be inferred. (i) Si^{4+}, Ge^{4+} and As^{5+} cations with low ionic radii (0.4–0.5 Å) may substitute for the tetrahedrally coordinated P^{5+} ($r_P = 0.34$ Å) [10, 11]. (ii) Transition metal impurities with ionic radii in the range 0.6–0.7 Å have been found to substitute for Ti^{4+} ($r_{Ti} = 0.68$ Å) in the two inequivalent Ti lattice sites, for instance W^{5+} [12], Fe^{3+} and Cr^{3+} [13], Al^{3+} [14], V^{4+} [15] and Mo^{5+} [16]. (iii) Finally, alkali metals with ionic radii larger than 1 Å substitute for K^+ ($r_K = 1.33$ Å) [17]. The ionic radius of Nd^{3+} is 1.08 Å. Therefore the substitution of P^{5+} can be disregarded
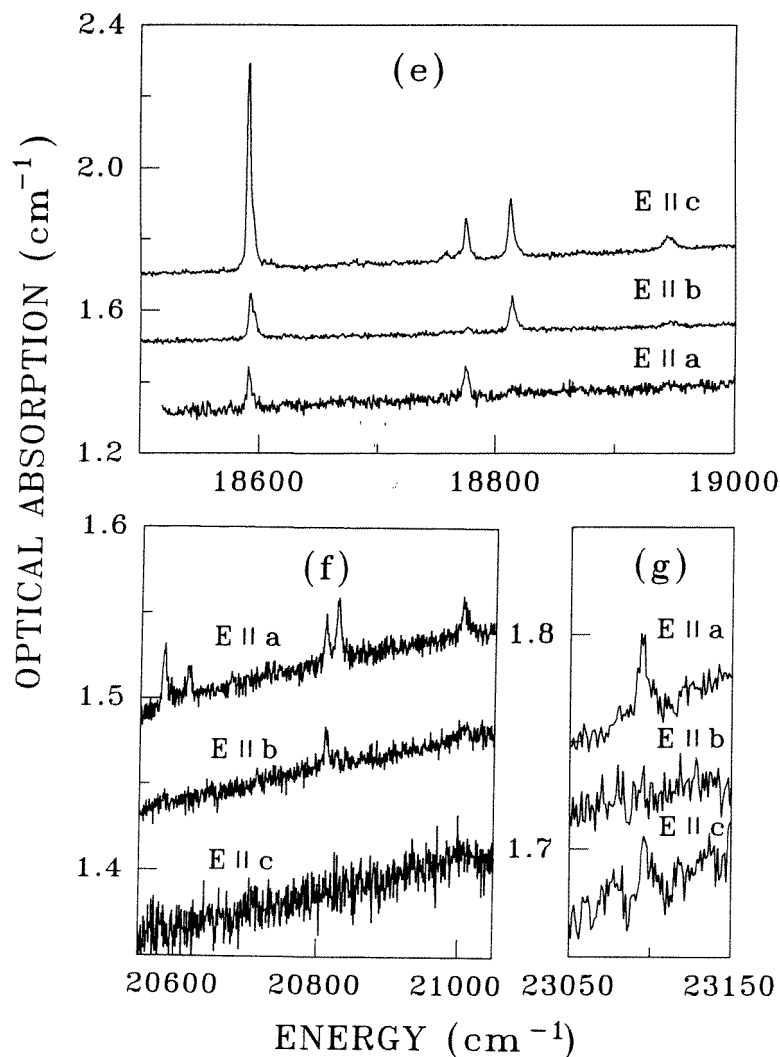
Figure 2. (Continued)

but, *a priori*, the Ti or K lattice positions must be considered.

The optical absorption of Nd^{3+} corresponds to electronic transitions from the ground $^4I_{9/2}$ state to the higher energy states inside the 4f^3 configuration of the ion. The Nd^{3+} states are Stark multiplets which are split by the crystal lattice field. In table 1 we have assigned the different sets of optical absorption bands observed at 4.2 K to the most likely states known for Nd^{3+} [18]. Some weak bands the intensities of which decrease under cooling are most probably related to the thermal population of ground state sub-levels and therefore they have not been included in table 1. Ignoring these small features of the spectrum, it may be observed that the defect symmetry is low enough to remove the $2J+1$ degenerancy of the energy levels but for the Kramers one. This is consistent with the C$_1$ symmetry expected for the K and Ti lattice sites; however, in this symmetry no polarization selection rules are expected. Thus the Nd^{3+} ion increases the local defect symmetry around it.

The energy position of the $^2P_{1/2}$ level of Nd^{3+} is very sensitive to the crystal field strength and to the chemical nature of the ligands [19]. As a rule of thumb, on approaching the ligands the energy position of the $^2P_{1/2}$ level increases. In KTP the $^2P_{1/2}$ level is observed at 23095 cm^{-1}. The comparison of this with other Nd compounds yields a Nd–O average distance of 2.5 Å if the coordination with eight oxygens is considered, the value being 1.9–2.0 Å if compounds with only six oxygen coordination are considered [19, 20]. An eight-coordinated position may be expected if Nd substitutes for K ions in KTP, the average K–O distance being 2.84 and 2.93 Å for the K1 and K2 sites respectively. These distances are too large in comparison to the 2.5 Å expected from the $^2P_{1/2}$ level position, thus the K substitution leaving the oxygen environment unchanged seems unlikely. The Nd–O average distances expected from substitution for Ti are 1.958 and 1.953 Å for Ti1 and Ti2 respectively. These distances are quite similar to those deduced from the $^2P_{1/2}$ position assuming a six-fold oxygen coordination. Therefore, it seems likely that Nd enters into Ti positions and maybe into K ones with strong anion relaxation.

We have previously concluded that Nd is likely to be in a six-fold oxygen coordination and that the local symmetry of the defect is higher than C_1. If Nd were to replace both Ti1 and Ti2 positions, two centres would be expected. The largest distortion of the Ti position arises from the Ti1-O_{Ti2} and Ti2-O_{Ti1} bonds [1, 9]; thus, ignoring other distortions, the local symmetry may be approximated by the C_{4v} point group, the C_4 axis of each octahedron being roughly at 45° to the *a–c* plane for Ti1 and in the *b–c* plane for Ti2. In this situation the optical absorption observed for light polarized parallel to the crystallographic axes would be the proper combination of σ and π bands of the two centers. All bands would be observed for $E \parallel c$, whereas π bands of Ti1 and Ti2 positions would not be observed for E parallel to *b* and *a* respectively.

Some of the properties of the optical absorption shown in figure 2 correspond to this situation, in particular the fact that all bands are observed for $E \parallel c$, but the intensity changes observed are not fully understood. It seems likely to us that a more complex situation should be considered and perhaps Nd may replace simultaneously Ti and K ions, breaking some oxygen bonds in the latter case. In order to analyse the polarization behaviour of the optical absorption further, more information on the local structure of the defects formed and their relative concentrations is required.

4. Conclusions

It has been shown that the incorporation of Nd into to the KTP lattice is enhanced by using a W-rich flux. Optical absorption bands corresponding to Nd^{3+} have been identified and their dichroic behaviour characterized.

Acknowledgments

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