

Effect of rhodium incorporation in KTiOPO_4 single crystals grown from self-flux

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The presence of an impurity like rhodium in the platinum crucible used for the growth of KTiOPO_4 (KTP) single crystals can have severe consequences in the performance of devices made from these crystals. In the present study the effect of rhodium incorporation has been investigated. Rhodium-incorporated KTP crystals have a lower ionic conductivity (1.3×10^{-7} S/cm at 100 kHz) than pure KTP crystals (3.5×10^{-6} S/cm at 100 kHz) along the c-axis. And the optical absorption in the green-wavelength regime leads to a detrimental effect on their SHG performance.

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1 Introduction

Excellent characteristics like high thermal stability, good mechanical properties, transparency over a large wavelength range, large nonlinear-optical coefficients, high damage threshold, and broad angular acceptance have made potassium titanyl phosphate (KTiOPO_4 ; KTP) an excellent crystal for second-harmonic conversion of Nd:YAG laser radiation [1]. As KTP decomposes upon melting at 1172°C , its growth in the single-crystal form is mainly done by the high-temperature solution (flux) growth route [2–8].

Among the choices from phosphates, tungstates, molybdates etc. as solvent, poly-phosphate $\text{K}_6\text{P}_4\text{O}_{13}$ has been identified as the most suitable for the crystal growth of KTP crystals because it does not contain any ion different from those in KTP [7]. But even after avoiding the possibility of impurity incorporation in the crystal by choosing this self-flux, one is left with at least two more possibilities of contamination. One, of course, is from the starting chemicals, and the other one is through impurities from the crucible. In this article we report rhodium (Rh) incorporation in the crystal from the crucible, and the consequences of this on properties like optical transmission, dielectric response, and ionic conductivity. Finally, the effect of the impurity on the performance of Type II phase-matched SHG device for Nd:YAG laser output is reported.

2 Experiment

For the growth of KTP crystals a five-zone resistance-heated furnace made of Kanthal A1 heating element was used. To prevent degradation of the ceramic muffle, a quartz tube was placed inside the furnace. This also helped in achieving better temperature stability. Details of the crystal-growth set up can be seen in [6,8].

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Radial and vertical temperature gradients were about $\pm 0.3\text{K}$ for a distance of 10 cm around the middle part of the furnace. All the crystal-growth runs were performed with a gKTP/gK_6 ratio of 0.6. The saturation temperature for this composition is around 972°C . The saturation temperature was established with an accuracy of 0.5K by a novel seeding technique developed by us [8]. Crystal growth experiments were carried out using the optimised growth parameters reported in [8].

Powder X-ray diffraction studies were performed on the grown crystals. X-ray fluorescence analysis was carried out on powdered samples with Fe^{55} and Am^{241} source over the energy range 5–60 keV. AC conductivity and dielectric permittivity studies were performed at room temperature on the crystal along different orientations, using HP 4194A impedance analyser in the frequency range 300 Hz - 1 MHz. Polished crystal plates were subjected to optical transmission studies (Shimadzu UV-PC-3101) over the wavelength range 300–900 nm. SHG elements were fabricated for Type-II phase matching; the polishing of the elements was better than $\lambda/10$.

3 Results and discussion

The as-grown crystals exhibit typical KTP morphology. By the method described above, we were able to grow inclusion-free crystals repeatedly. Some crystals, grown in commercially available platinum crucible containing Rh as impurity, were reddish-orange in colour.

Rh is a very common impurity in platinum crucibles because of their identical ionic states. Practically no ore exists in Nature which has any one element of the platinum group as a major constituent (example: irarsite [(Ir, Ru, Rh, Pt)AsS]). Unlike gold and silver, which can be isolated in a pure state by simple fire refining, the platinum group metals require rather complex aqueous chemical processing for their isolation [9]. This increases the probability of occurrence of Rh in Pt crucible. Moreover, platinum being soft, sometimes manufacturers add rhodium deliberately to increase the strength of the crucible. One such Rh-incorporated platinum crucible was used in the present study to grow KTP single crystals. As the growth period of KTP crystal is high (typically 30 days), Rh ions get into the molten charge through diffusion. Repeat growth runs performed from the old charge from the same crucible result in more reddish coloured crystals.

X-ray fluorescence The powder XRD pattern of Rh-incorporated crystal of KTP was not different from that of pure KTP crystal. X-ray fluorescence (XRF) studies were carried out to check the presence of impurities in the grown crystals. Fe^{55} , Cd^{109} and Am^{241} sources were tried. Fe^{55} and Cd^{109} , being lower-energy excitation sources, clearly showed the presence of K, Ti and P, but the presence of Rh could be detected only by using the Am^{241} source (Fig. 1).

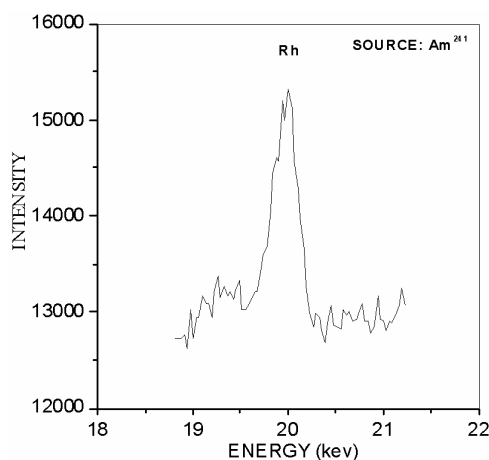


Fig. 1 X-ray fluorescence analysis of Rh:KTP.

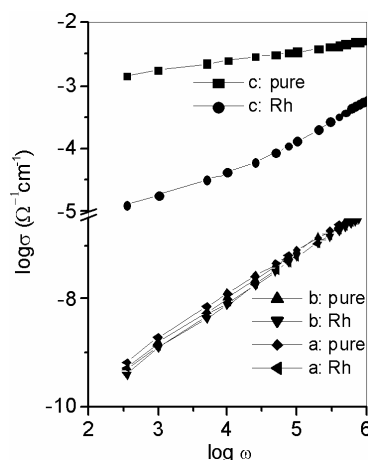


Fig. 2 Ionic conductivity along a, b and c axes of pure and Rh-incorporated KTP crystals.

XRF analysis carried out on the Pt crucible used for the growth of coloured crystals of KTP confirmed the presence of Rh impurity in the crucible. Thus the crucible used for growing this particular crystal was identified as the source of the Rh impurity in the crystal.

Conductivity measurement Room-temperature a.c. conductivity and dielectric-permittivity measurements were carried out. Samples were prepared in the form of plates, of dimensions 5 mm x 5 mm x 0.8 mm, for directions perpendicular to a-, b- and c-axis for both pure and Rh:KTP. Silver paste coating was used as electrodes.

The ionic conductivities along a- and the b-direction are found to be one order of magnitude lower than that along the c-direction (Fig. 2) for both pure and Rh-incorporated samples. The Rh-incorporated crystal shows a lower ionic conductivity, especially in the c-direction (Fig. 2). The Rh ions presumably alter the channel structure and dimensions, and thus influence the ionic conductivity. It has been experimentally proved that, the intrinsic defects present in KTP are vacant potassium and vacant oxygen sites [10]. As K^+ ions are loosely bound to both TiO_6 (octahedra) and PO_4 (tetrahedra) along the c-screw axis, on thermal activation they hop to the intrinsically present vacant sites, thus leading to ionic conduction. But with Rh incorporation, modifying the model proposed by Morris et al. [11], the electrical neutrality equation for KTP can be written as:

$$[\text{V}'_{\text{K}}] + [\text{Rh}'_{\text{Ti}}] = [\text{V}^{\circ\circ}_{\text{O}}]$$

where $[\text{V}'_{\text{K}}]$ and $[\text{V}^{\circ\circ}_{\text{O}}]$ are intrinsic defects due to vacant potassium and vacant oxygen sites respectively, and $[\text{Rh}'_{\text{Ti}}]$ denotes the trivalent rhodium ion at the Ti^{+4} site. If we assume that $[\text{V}^{\circ\circ}_{\text{O}}]$ is fixed by the intrinsic nonstoichiometry at the growth temperature, the equation implies that if the trivalent ion sits at the tetravalent Ti ion sites, the concentration of potassium $[\text{V}'_{\text{K}}]$ must decrease, and hence the ionic conductivity goes down.

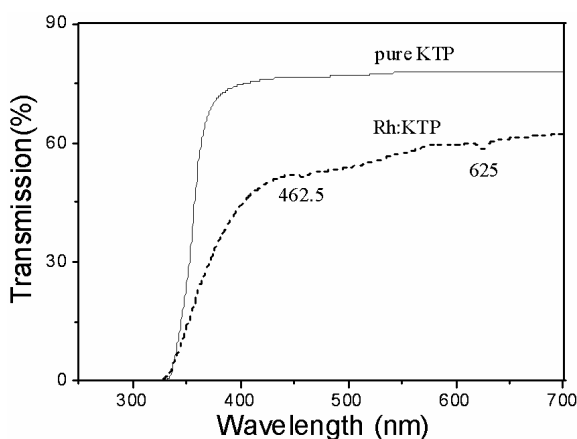


Fig. 3 Transmission spectra for KTP and Rh:KTP.

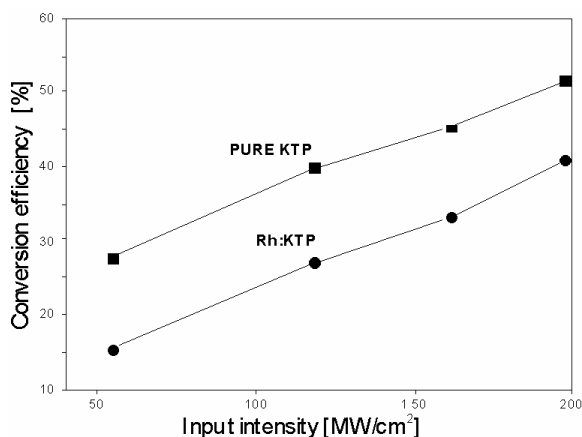


Fig. 4 SHG efficiency of 4mm x 4mm x 4mm elements of KTP and Rh:KTP for various input powers of Nd:YAG laser radiation.

UV-visible transmission More than 80 % transmission was observed even for a specimen of thickness exceeding 5 mm (Fig. 3). The cut-off wavelength of the UV band edge, defined here as the “1/e point”, is near 360 nm for the pure crystal, and 409 nm for Rh:KTP. The pure crystal shows a very sharp fall in transmission at the UV cut off, unlike the coloured crystal. In the latter, the transmission curve shows two absorption peaks at 462 and 625 nm.

Second-harmonic generation performance SHG elements were cut from both coloured and Rh-incorporated KTP crystals for the following configuration: $\theta=90^\circ$; $\phi=23.5^\circ$ (Fig. 4); Type II phase matching for Nd:YAG laser operating at 1.064 μm . Measurements for second-harmonic conversion efficiency were made with electro-optically Q-switched pulsed Nd:YAG laser in an extra-cavity configuration. The beam had a nearly flat-top intensity profile in the near field, with pulse duration of 8-9 ns. The second harmonic conversion efficiency at different input intensities of the fundamental laser was measured by varying the input fundamental energy (ω) to the crystal. Energy was varied using a halfwave-plate and polariser combination. The maximum intensity incident on the pure KTP crystal of 6 mm interaction length was $\sim 207 \text{ MW/cm}^2$. The intensity obtained at 2ω was 127 MW/cm^2 . Thus conversion efficiency exceeding 60%, without accounting for Fresnel losses, was achieved [8].

A comparison of SHG efficiency between the pure and the Rh-incorporated KTP crystal of identical interaction length (4 mm) show that Rh incorporation has a detrimental effect on SHG (Fig. 4). This is due to the strong absorption band found in the UV spectrum of Rh:KTP.

4 Conclusion

Rhodium incorporation during crystal growth poses a serious problem for KTP crystals. To obtain a size suitable for device fabrication, the growth run for KTP generally lasts around 30 days, so the problem is even more serious as Rh present in the crucible gets more time to diffuse into the solution, and finally to the crystal. The presence of Rh results in absorption of light, especially in the green region. This decreases its SHG performance for 1.064 μm laser source. Also, being a trivalent ion, Rh decreases the ionic conductivity along the 'free' c-direction.

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