

[o.m1.p3] Evolution of the NLO material analogues of KTiOPO₄ in the temperature range 293 - 973 K (structural and SHG properties). P. Delarue, C. Lecomte, LCM³B UPRESA 7036, Université Henri Poincaré, Nancy I, Faculté des sciences, BP 239, 54506 Vandoeuvre Lès Nancy Cedex, France. M. Jannin, G. Marnier, J.P. Feve, O. Pacaud LPUB UMR 5027, Faculté des sciences Mirande, BP 47 870, 21078 Dijon Cedex, France.

Keywords: KTiOPO₄, second-harmonic-generation, electron density.

At room temperature, potassium titanyl phosphate, KTiOPO₄ (KTP) crystallizes in the acentric Pna2₁ space group. At high temperature, the crystal structure belongs to the centrosymmetric space group: Pnan. Since KTP was introduced as an interesting non-linear optical material in 1976 [1], various definite compounds were studied in different ways[2-5] to find correlation between the structural distortions and the optical non-linearities (measured as second harmonic generation, SHG). In that way, we have studied the evolutions of KTP and isotype structures and theirs divergence from centrosymmetry versus temperature.

The studies on RbTiOPO₄ [6], (K,Rb)TiOPO₄ [7], and KTP [8] by using single-crystal x-ray diffraction techniques in the range 273-973 K, permits to precise the role of the alkaline ions displacements in their properties. On the other hand, the deviation to the centrosymmetric structure study correlates directly the change towards centrosymmetry of the titanyl groups with the observed variation of the KTP SHG efficiency versus temperature. The NLO phase-matching measurements on single crystal permits to obtain the variation of d_{eff}^2 . With a charge bond model, we show that all Ti-O and near all P-O charge bonds contribute to the d_{eff} . Then, to characterize the important Ti-O bonds, an electron density study has been performed on KTP. In spite of high temperature measurements, the results conclude about the quality of the model and of the refinements.

[o.m1.p4] Y₂Be₂SiO₇: Growth, Structure, Solid Solution. G.Kuz'micheva and D. Larin, M.V.Lomonosov State Academy of Fine Chemical Technology, Moscow 117571, Russia; S. Kutovoi and V. Panyutin, Scientific & Production Association "Firn", Krasnodar 350000, Russia; V.Rybakov, M. V. Lomonosov State University, Moscow 119899, Russia.

Keywords: new laser material, structure, composition

Single crystals of Y₂Be₂SiO₇ and solid solution on their base doped with Nd³⁺ or Cr⁴⁺-ions are new active media for lasers. Potential advantages of these crystals are associated with a possibility of introducing Nd³⁺ dopants into Y positions and Cr⁴⁺- ions into Si positions. The Y₂Be₂SiO₇ and solid solution of Y₂(Al,B)₂BeO₇ nominal composition have been grown by the Czochralski technique. The Y₂Be₂SiO₇ and Y₂(Al,B)₂BeO₇ crystals are tetragonal with a space group of P-4₂m and lattice parameters a=7.281(4), c=4.755(1)Å and a=7.267(8), c=4.708(11)Å, respectively.

The crystal structure and atoms distribution on sites of Y₂(Al,B)₂BeO₇ were refined by the Rietveld method (DBWS-9411 program). Partial incorporation of B atoms at the tetrahedral sites occupied by Be in Y₂Be₂SiO₇ structure and full occupation of the tetrahedral sites of Al atoms has been found. The refined composition of solid solution is Y₂(Be_{0.5}B_{0.5})₂AlO₇.

The coordination of Y in Y₂Be₂SiO₇ and Y₂(Be_{0.5}B_{0.5})₂AlO₇ structures is eight-fold, the coordination polyhedron can be considered to be a tetragonal antiprism ($d_{\text{Y-O}}^{\text{m}}=2.408\text{Å}$ and $d_{\text{Y-O}}^{\text{m}}=2.391\text{Å}$, respectively), Atoms Al and Si occupy the centres of regular tetrahedra ($d_{\text{Si-O}}=1.630(2)\text{Å}$ and $d_{\text{Al-O}}=1.740(2)\text{Å}$). Atoms Be and (Be,B) are coordinated by four oxygen atoms and the coordination polyhedron is a distorted tetrahedron ($d_{\text{Be-O}}^{\text{m}}=1.637\text{Å}$ and $d_{\text{(Be,B)-O}}^{\text{m}}=1.554\text{Å}$). Change of interatomic distances in tetrahedra agrees with cationic radii of Si ($r_{\text{Si}}=0.26\text{Å}$) and Al ($r_{\text{Al}}=0.39\text{Å}$), of Be ($r_{\text{Be}}=0.27\text{Å}$) and (Be,B) ($r_{\text{(Be,B)}}=0.19\text{Å}$). Change of Y-O distances in Y polyhedron is associated with the Be (Be,B) distances in tetrahedra.

X-ray diffraction data were collected for a crystal ground into a sphere on an Enraf-Nonius CAD-4 automated diffractometer at room temperature (MoK_α radiation, graphite monochromator). It was found that Y₂Be₂SiO₇ and Y₂(Be_{0.5}B_{0.5})₂AlO₇ crystals are inclined to twinning. Obviously such a behaviour is due to the possible oxygen vacancies like isostructural Ca₂(AlSi)AlO₇ crystals (cell parameters a=7.833, c=5.002Å).

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