

**LIGHT-INDUCED POLARONIC ABSORPTION AT LOW TEMPERATURE IN
PURE AND (Fe, Ce, Cr) DOPED $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ OR $\text{Ba}_{1-y}\text{Ca}_y\text{TiO}_3$ CRYSTALS
AND PHOTODISSOCIATION OF VIS CENTERS INTO SMALL POLARONS.**

S. E. KAPPHAN*, I. KISLOVA*, M. WIERSCHEM*, T. LINDEMANN*, M. GAO*,
R. PANKRATH*, V. S. VIKHNIN**, A. B. KUTSENKO*

*FB Physik, University of Osnabrueck, Barbara Str.7, 49069 Osnabrueck, Germany;

**A. F. Ioffe, Phys.-Technical. Inst., RAS, 194021, St.- Petersburg, Russia

Abstract.

Congruent SBN and BCT crystals doped with Fe,Cr,Ce to enhance photorefractive properties, are investigated at low temperature ($T > 1$ K) under illumination with Ar^+ - and Kr^+ - laser light. Light-induced absorption changes in a wide spectral range from UV to IR indicate photoinduced charge transfer processes from impurities to polaronic centers. Broad NIR absorptions (at about 0,7 eV) associated with Ti^{3+} polarons in BCT or with Nb^{4+} polarons in SBN are observed and their non-linear behaviour with illumination intensity, polarization and temperature is described on the basis of the simple model for the photo charge transport (in SBN: $\text{Ce}^{3+} + \text{Nb}^{5+} \leftrightarrow \text{Ce}^{4+} + \text{Nb}^{4+}$). A broad visible absorption VIS (at about 2 eV) appearing together with the NIR polarons, is shown by photodissociation (with a Kr^+ -laser) to consist at least partly of small polarons (in BCT and SBN).

Keywords: Light-induced absorption, small polarons, light-induced dissociation, charge transfer model, (BCT) Barium-Calcium-Titanate, (SBN) Strontium-Barium-Niobate.

INTRODUCTION.

Both promising photorefractive crystal systems $\text{Ba}_{1-y}\text{Ca}_y\text{TiO}_3$ and $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ possess a congruently melting mixture (for SBN $x=0,61$ and for BCT $y=0,23$), where melt and crystal have the same composition^{1,2}. This allows to grow large, homogeneous crystals of excellent optical quality, which is the basis for a wide range of optical applications³. Further favourable features of these crystals are the lack of a destructive phase transition (in contrast for instance to BaTiO_3) and the ease of poling of the crystals into a monodomain state¹. Due to the statistical distribution of the constituents and a partially unfilled (tungsten bronze) structure for SBN, the ferroelectric phase transition ($T_c \sim 100^\circ\text{C}$ for congruent BCT pure and $T_c \sim 80^\circ\text{C}$ for congruent SBN pure) shows a relaxor type character with polar contributions well above T_c .

The addition of doping ions (like Fe,Ce,Cr) in most cases shifts T_c toward low temperatures with increasing doping content (for instance from 80°C in SBN pure to about room temperature for dopings of 20 000 ppm, p.f.u., Ce or Cr⁴). The electro-optical coefficients of the pure crystals are already large and can be enhanced considerably by suitable doping with polyvalent ions like those mentioned above^{5,6}. For some of the dopants (like Ce and Cr in SBN) a majority charge state 3+ has been determined^{7,8}, however with a individual site occupancy, Ce^{3+} replacing Sr^{2+} ions and Cr^{3+} sitting on Nb^{5+} sites^{9,10}. These dopants can be identified by their broad impurity induced absorption bands in the visible range, a shift of the UV- absorption edge to longer wavelength in the case of Cr doping and additional Far-IR bands (near 2000cm^{-1}) in the case of Ce-doping⁷. A light-induced charge transport from these doping ions and trapping in shallow polaronic states (Ti^{3+} in BCT respectively Nb^{4+} in SBN) has been identified by photo-EPR¹¹ and optical experiments¹² to constitute the underlying

processes for the enhanced photorefractive properties in doped crystals. The majority of photo-excited charge carriers have been determined by laser beam coupling experiments¹³ and Hall-effect¹⁴ measurements to be electrons. The trapping of these photo-induced charge carriers in certain centers can be considered as the first step in the build-up of space charge fields which modify the refractive index and are the basis of the photorefractive effect under non-uniform spatial illumination. The properties and physical nature of the centers created under illumination has been identify so far only in part and is investigated further in this study with several techniques. In particular we report on experiments on light-induced dissociation of VIS centers in SBN:Ce and in BCT:Fe.

EXPERIMENTAL TECHNIQUES.

SBN and BCT crystals of the congruent composition were grown (Czochralsky method, University of Osnabrueck)^{1,4,5} with various amounts of Fe, Cr, Ce doping added to the melt. Poling of the crystal samples was performed at about 10⁰C below T_c under electric fields of about 10kV/m. A Fourier spectrometer (Bruker HR 120) was used to measure the polarized absorption spectra of the crystals from UV to the FIR. The samples under illumination with Ar⁺- and Kr⁺ - laser light (spectra physics 171) were kept immersed in superfluid LHe or LN₂, where possible, to warrant temperature stability. Some of the samples have been reduced prior to the measurements (at 800⁰C for several hours in H₂) to initiate a change in the charge distribution of the centers.

EXPERIMENTAL RESULTS.

A)Optical absorption.

The concentration dependent absorption in the uv-visible range in BCT:Fe, SBN:Ce and SBN:Cr reveals characteristic features reported in earlier publications ^{15,16}. In SBN:Ce FIR bands of Ce³⁺ near 2000 cm⁻¹ give additional direct evidence of these centers ⁷. Fe^{2+/3+} centers in BCT have been detected in photo-EPR experiments with absorptions at 2eV respectively 3,5eV ¹¹.

B)Light-induced absorption changes and their discussion.

Under illumination with Ar⁺ - laser light (488 nm) at low temperature (2K, crystal immersed in superfluid LHe) two broad dichroitic light-induced absorption bands can be observed in BCT:Fe (see Fig.1a) ¹⁷ and very similarly in SBN:Cr,Ce (see Fig.1b)^{15,16}. The first absorption band (VIS centers) is observed around 2eV and the second in the NIR around 0,7eV (6000 cm-1). The NIR absorption has been identified previously by photo-EPR as belonging to Ti³⁺ small polarons in BCT or to Nb⁴⁺ small polarons¹¹ in SBN. Theoretical calculations predict both, the stability ¹⁸ and the large width of the optical transitions characteristic for such polarons ¹⁹. The centers responsible for the VIS absorption have not been identified yet , but obviously are produced simultaneously with the NIR polarons. Both, the VIS and the NIR light-induced absorption bands depend on polarization and nonlinearly on illumination intensity, as mentioned earlier^{16,17}. The temperature dependence in the production of these centers shows a steep change at about 100K for the NIR polarons in SBN (at about 40 K for BCT) and at about 200K for the VIS centers (at about 80 K for BCT) ^{16,17}. It is interesting to note that these characteristic temperatures are also revealed in thermoluminescence studies of SBN:Ce, Cr as intensity peaks ^{20,21}, where charge carriers (electron-polarons) are thermally liberated for radiative recombination with deep trapping centers. The steady state of the light-induced absorption under illumination and the kinetics of its decay

after a switch-off of the illumination, can be described by a simple model of a charge transport from doping centers ($\text{Fe}^{2+} + \text{Ti}^{4+} \leftrightarrow \text{Fe}^{3+} + \text{Ti}^{3+}$ in BCT, $\text{Ce}^{3+} + \text{Nb}^{5+} \leftrightarrow \text{Ce}^{4+} + \text{Nb}^{4+}$ in SBN) with subsequent recombination as reported previously for SBN^{12,17}.

C) Light-induced dissociation of VIS centers

The Ar^+ light-induced VIS centers are rather stable at 2 K, whereas the NIR centers decay rather fast and disappear completely within less than 50 sec in BCT:Fe (100 sec in SBN:Ce)^{17,22}. This allows to perform experiments in the following way. After first creating a sizeable population of NIR polarons and of VIS centers at 2 K, we then switch-off the Ar^+ -laser and wait about 7 min. to let the NIR-polarons decay completely. If we then switch-on the Kr^+ - laser (647 nm) light, first a build-up of NIR polaron absorption (see Fig.2a) and then a transient decay of this NIR absorption (depending strongly on the Kr^+ - laser intensity) (see Fig.2b) with a simultaneous decay in the VIS-absorption is observed.

If the Kr^+ -laser is switched-off, the NIR polaron absorption decays with its own, temperature dependent characteristic recombination decay time (Fig.2a). This clearly demonstrates the dissociation of the VIS centers into small polarons and has been observed both, in BCT:Fe and in SBN:Ce.

CONCLUSIONS.

The nature of the NIR centers as small polaron centers is well established. Their temperature and intensity dependent behaviour is not fully understood yet and warrants further studies.

The VIS-centers are discussed as possibly being either bipolarons (in analogy to such centers in LiNbO_3), or polarons trapped at charged centers, or charge transfer vibronic

excitons (CTVE) being trapped at charged centers²². The present experiments do not allow to draw unambiguous conclusions – but one of the dissociation products must be a electron polaron – and further experiments are needed to clarify this situation.

ACKNOWLEDGEMENTS:

Support by DFG (Grad.College 695), by DAAD (HSPIII, V.V.) and by NATO (PST.CLG 977348) is gratefully acknowledged.

REFERENCES

- 1.C.Kuper, R.Pankrath, H.Hesse, *Appl.Phys.*, **A65**,301 (1997)
- 2.R.Neurgaonkar, W.Cory,J.Oliver,H.Ewbank,W.Hall *Opt.Eng.* **26**,392 (1987)
- 3.P.Guenter,J.P.Huignard, *Top.inAppl.Phys.:Photorefr.Mat.* **61/62**(Springer-Berlin) (1988)
- 4.J.Seglins,S.Mendricks,R.Pankrath,V.Vikhnin,S.Kapphan, *Verhandl.DPG(VI)* **33**,601 (1998)
- 5.C.Kuper,K.Buse,U.v.Stevendaal,M.Weber,T.Leidlo,H.Hesse,E.Kraetzig, *Ferroelectrics*, **208/209**,213 (1998)
- 6.Y.Tomita,A.Suzuki, *Appl.Phys.*, **A 59**,579 (1994)
- 7.G.Greten,S.Hunsche,U.Knuepfer,R.Pankrath,U.Siefker,N.Wittler,S.Kapphan, *Ferroelectrics* **185**,289 (1996)
- 8.R.Niemann,K.Buse,R.Pankrath,M.Neuman, *Sol.St.Comm.*, **98**,209,(1996)
- 9.T.Woike,G.Wekwerth,H.Palme,R.Pankrath, *Solid St.Comm.* **102**, 743 (1997)
- 10.T.Woike,U.Doerfler,L.Tsankov,G.Weckwerth,D.Wolf,M.Woelecke,T.Granzow, R.Pankrath,M.Jmlau,W.Kleemann, *Appl.Phys.*, **B72**,661(2001)
- 11.A.Mazur,C.Veber,O.Schirmer,C.Kuper,H.Hesse, *J.Appl.Phys.*, **85**,6751 (1999)
- 12.M.Gao,R.Pankrath,S.Kapphan,V.Vikhnin, *Appl.Phys.*, **B68**,849 (1999)
- 13.M.Ewbank,R.Neurgaonkar,W.Cory,J.Feinberg, *J.Appl.Phys.*, **62**,374 (1987)
- 14.A.Gerwens,K.Buse,E.Kraetzig, *J.Opt.Soc.Am.*, **B15**,2143 (1998)
- 15.M.Gao,S.Porcher,R.Pankrath,S.Kapphan, *J.Korean.Phys.Soc.*, **32**,542 (1998)
- 16.M.Gao,S.Kapphan,S.Porcher,R.Pankrath, *J.Phys.:Cond.Matter.*, **11**,4913 (1999)
- 17.M.Wierschem,T.Lindemann,R.Pankrath,S.Kapphan, *Ferroelectrics*, **264**,315 (2001)
- 18.R.Baetzold, *Phys.Rev.*, **B48**,5789 (1993)
- 19.H.Reik,D.Heese, *J.Phys.Chem.Sol.*, **28**,581(1967)
- 20.M.Gao,S.Kapphan,R.Pankrath, *J.Phys.Chem.Sol.*, **61**,1959 (2000)

21. I. Kislova, M. Gao, S. Kapphan, R. Pankrath, A. Kutsenko, V. Vikhnin, Ferroel., **273**, 187 (2002)
22. M. Gao, S. Kapphan, R. Pankrath, X. Fenq, Y. Tang, V. V. Vikhnin, J. Phys. Chem. Sol., **61**, 1775 (2002)

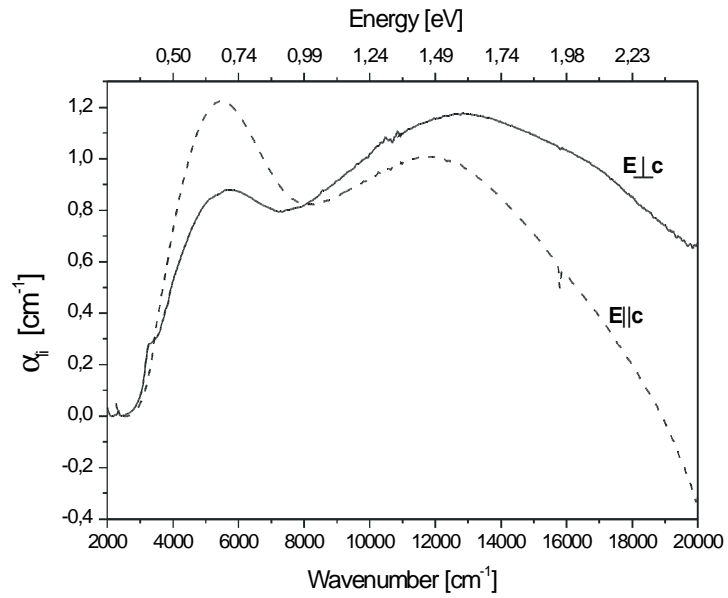


FIGURE 1a:

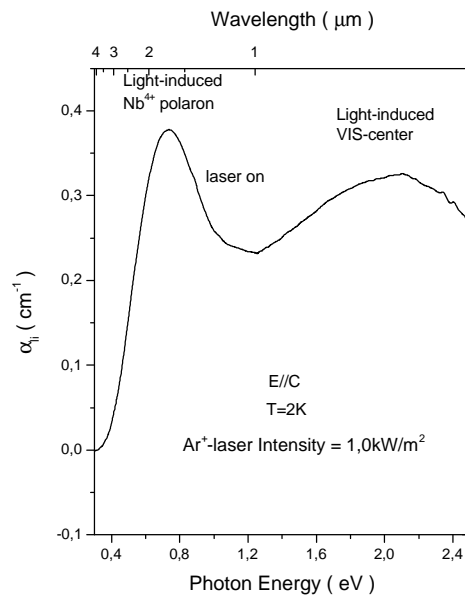


FIGURE 1b:

FIGURE 1: VIS and NIR light-induced (Ar^+ -laser, 488 nm; at 2 K) absorption for (a) BCT:Fe (77 ppm in the melt) ($I=33\text{kW/m}^2$); (b) SBN:Cr (500 ppm) at 2 K with measurement light polarization $E_{\perp c}$ and $E_{//c}$.

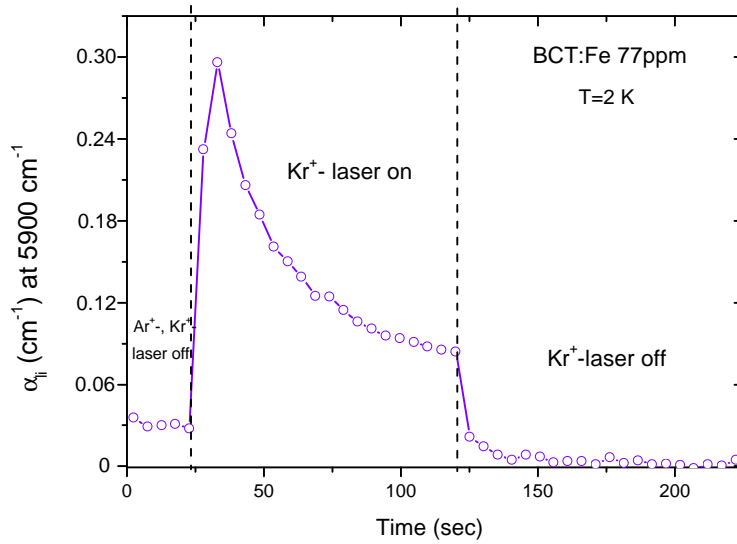


FIGURE 2a:

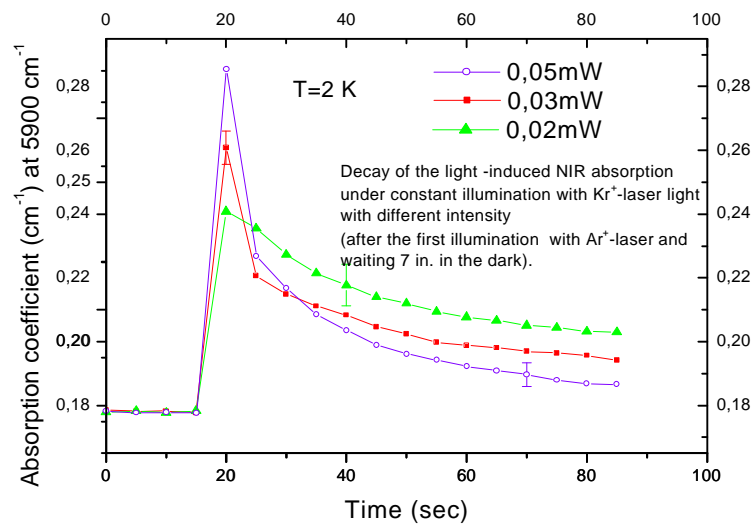


FIGURE 2b:

FIGURE 2: (a) NIR Polaron absorption $E_{\perp c}$ build-up and decay at 2 K upon illuminating in the VIS region with a Kr^+ - laser (647 nm, $I=0,0025\text{kW/m}^2$); (b)

comparison of polaron decay upon illumination with a Kr⁺-laser (with different intensity I). The Kr⁺-illumination was switched on about 7 min after switching-off the Ar⁺ (488 nm, I=65kW/m²) illumination.