

# *Some new compounds for medicine and industrial applications*

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- Macrocyclic compounds  $C_{27}H_{24}N_4O_3Cl_3Gd$ ,
- $C_{27}H_{24}N_4O_3Cl_3Gd$  (33TGd, 33THo)
- Macrobicyclic  $C_{39}H_{51}N_8O_3$  (1T) - cryptand
- $M_2CrV_3O_{11-x}$  (M=Mg, Ni, Zn) compounds
- $Li_2B_4O_7:Co$  single crystals
- $Sr_xBa_{1-x}Nb_2O_6$  pure and doped with Cr  
single crystals



# 1. Microcyclic compounds. MSc G. Leniec

Taking into account their structure one can recognize a lot of groups, e.g.:

Ligand	Complex
Podant	Podate
Coronant	Coronate
Cryptant	Cryptate
Carcerant	Carcerate

Among them **macrocyclic** and **macrobicyclic** compounds arises showing tendency to form complexes with cation of alkali-metals and rare-earths. The complexes are able to dissolve ionic compounds and inorganic salts in non-polar solvent. Synthesis of the compounds is very important in applied chemistry: separation of selected metals and supramolecular devices, fluorescent probes in biological systems, luminescence labels (detection of small amounts of biomolecules that can tell about the physical state of a patient) and medical diagnostics, treatment of arteriosclerosis, radioimmunology, as the contrast medium, as the synthetic enzyme to split chain of the nucleic acid [1, 2].

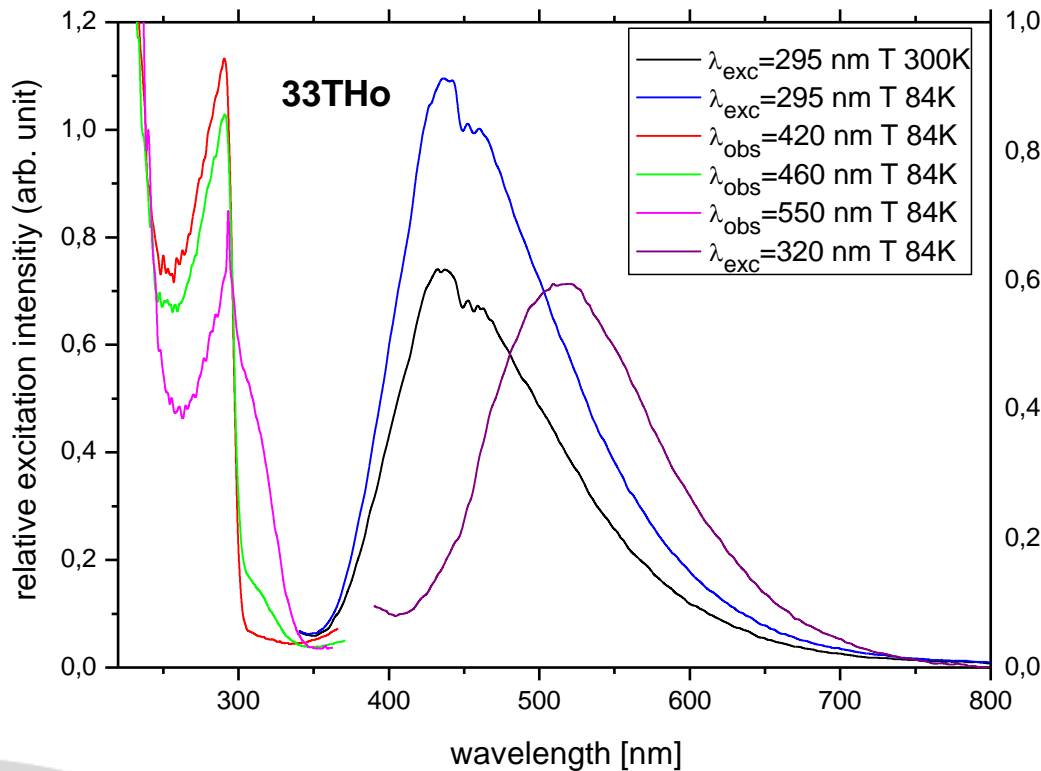
**Gadolinium** and other rare-earth elements are used as gasoline-cracking catalysts, polishing compounds, carbon arcs, and in the iron and steel industries to remove sulfur, carbon, and other electronegative elements from iron and steel. In nuclear research, the rare-earths are usually used in the form of oxides. An important application of gadolinium, because of its extremely large nuclear cross-section, is as an absorber of neutrons for regulating the control level and criticality of nuclear reactors. The nuclear poisons disintegrate as the reactivity of the reactor decrease, in the electronic and magnetic areas. One of the most important rare earths compound is gadolinium gallium garnet (GGG). GGG is used in bubble devices for memory storage [3]

1. B. Dietrich, P.Viout, J.M. Lehn, *Macrocyclic chemistry, Aspects of Organic and Inorganic Supramolecular Chemistry*, VCH, Weinheim, 1993

2. D. Parker, *Macrocyclic synthesis*, Oxford University Press, Oxford, 1996

3. M. Reza Ganjali et al, *Analytica Chimica Acta* 495 (2003),51-59, „Novel gadolinium poly(vinyl chloride) membrane sensor based on a new S-N Schiff's base.”



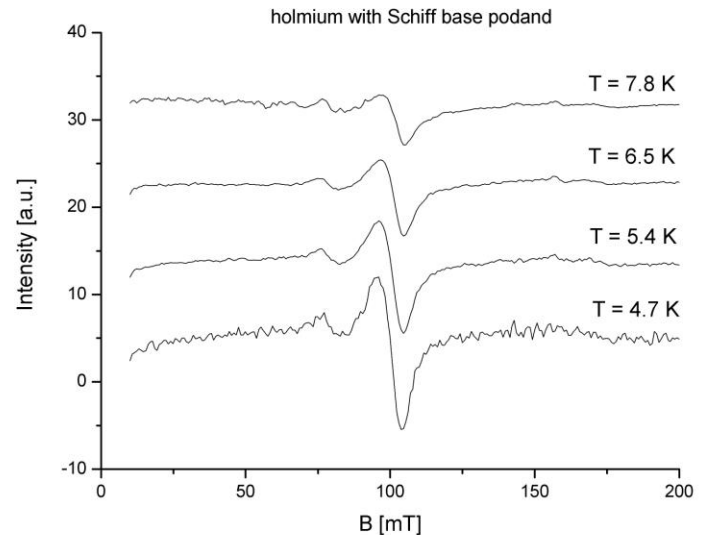


**33THo**  
**Holmium(III) Tripodal Tris(((5-chlorochlorosalicylidene)ethyl)amine**

Hot holmium (III) trifluoromethanesulfonate  $\text{Ho}(\text{CF}_3\text{SO}_3)_3$  was dissolved in the methanol  $\text{CH}_3\text{OH}$  under the reflux condenser, after 10 minutes Tri-(2-aminoethyl)amine was added and kept hot for 5 minutes at ca. 500 °C. The mixture was cooled. The bright green-yellow product was filtered out, washed with the methanol  $\text{CH}_3\text{OH}$ . The precipitate was dried over the silicagel.

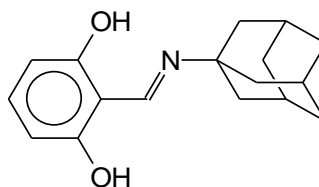
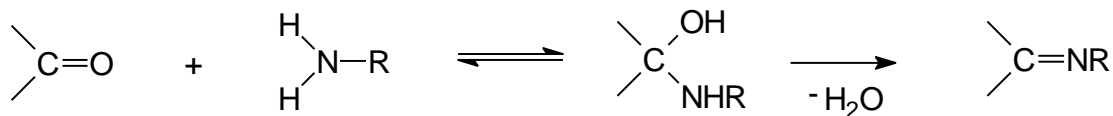
An example of the fluorescent probe

$S=1$  and  $g=6.71$ .



Schiff bases are macrocyclic compounds with imina group. They are applied to cure leukemia, have antiviral activity (Oxphaman), show bactericidal, mycosidals and nailicidal properties. On the other hand they are used as nonlinear optical materials (e.g. N-(R-salicylideno)-R'-anilin), as reversible optical storage, sunny filters, fotostabilizators, dyes for sunny collectors, molecular switches (due to photochromic properties). They are used also in chemical analysis and synthesis (to fix of aminoacid composition, to detect of finger traces).

H. Schiff, 1864 r.



Oxphaman



Formation of macrocyclic complexes depends on the:

- internal cavity,
- rigidity of macrocycle,
- nature of its donor atoms,
- complexing properties of the counter ion

Synthesis of the macrocyclic compound is generally carried out in the presence of a suitable salt, the cation of which is assumed to act as a template for the ring formation [4, 5].

We synthesized and studied the magnetic research of the gadolinium cryptate (1TGd) (macrobicyclic Schiff base) and the gadolinium podate (33TGd) (macrocyclic Schiff base) using  $\text{Gd}(\text{CF}_3\text{SO}_3)_3$  - trifluoromethanesulfonate.

The central metal ions are coordinated by nitrogen atoms N, N1, N2, N3 and the three oxygen atoms O1, O2 and O3. The coordination geometry around the Gd atom is a monocapped distorted octahedron.



1TGd - Tris-(2-aminoethyl)amine (tren) (8 mmol) was added to a solution of  $\text{Gd}(\text{CF}_3\text{SO}_3)_3$  (4 mmol) in hot methanol (70 cm<sup>3</sup>) and refluxed for 10 min. Then 2-hydroxy-5-methylisophthalaldehyde (12 mmol) in methanol (30 cm<sup>3</sup>) was added to this solution and refluxed for 2 min. A yellow solid was precipitated upon cooling for 6 h. The crystalline powder was clarified by filtration. Yield: 88%. **Rigid.**

### Gadolinium Tris Tripodal Tris(((5-chlorochlorosalicylidene)ethyl)amine $\text{C}_{27}\text{H}_{24}\text{N}_4\text{O}_3\text{Cl}_3\text{Gd}$

33TGd - Tris-(2-aminoethyl)amine (tren) (8 mmol) was added to a solution of  $\text{Gd}(\text{CF}_3\text{SO}_3)_3$  (4 mmol) in hot methanol (70 cm<sup>3</sup>) and refluxed for 10 min. Then 5-chlorosalicylaldehyde (12 mmol) in methanol (30 cm<sup>3</sup>) was added to this solution and refluxed for 2 min. A yellow solid was precipitated upon cooling for 6 h. The crystalline powder was clarified by filtration. Yield: 76%. **Soft.**

4. D.E. Fenton, P.A. Vigato, Chem. Soc. Rev. 17 (1988) 69

5. V. Alexander, Chem. Rev. 95 (1995) 273

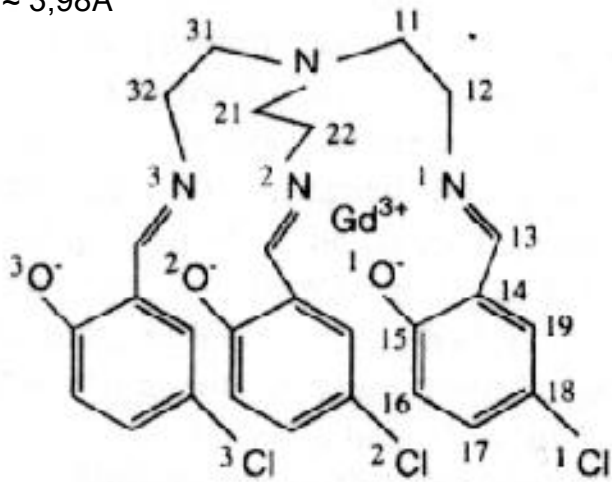


# Gadolinium Tripodal Tris(((5-chlorosalicylidene)ethyl)amine)



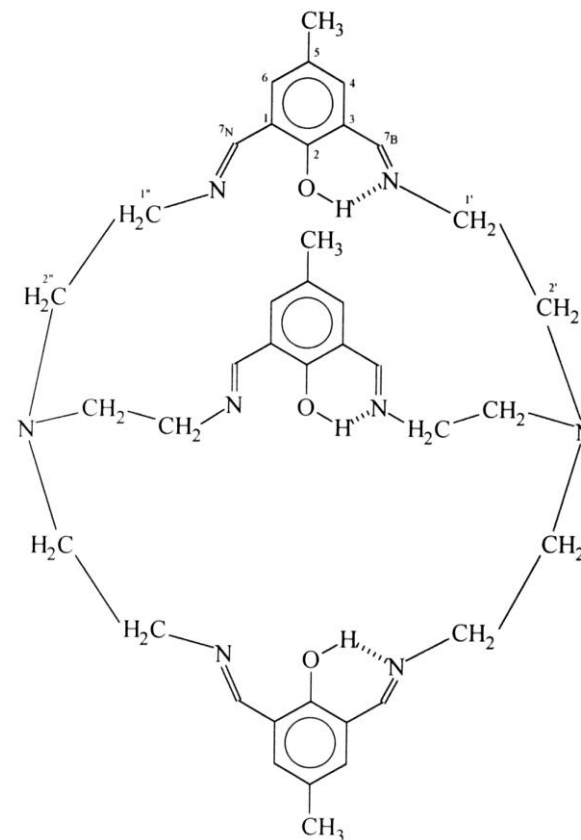
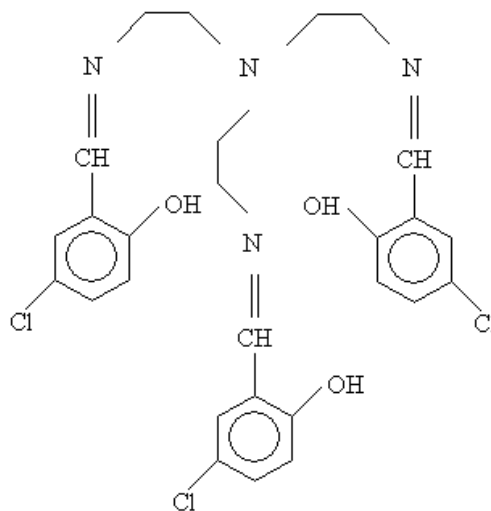
[6] Analytical Sciences, M. Kanesato, F.N. Ngassapa, T.Yokoyoma, „Crystal structure of ...”, 17 (2001) 1359

Gd–Gd  $\approx$  3,98Å



Gd-O1 2.223 Å  
 Gd-N 2.737 Å  
 Gd-N1 2.542 Å  
 Gd-N2 2.539 Å  
 Gd-N3 2.529 Å  
 Space group  $P2_1/c$ ,  
 Crystal system-  
**monoclinic**  
 $a = 10,042 \text{ \AA}$   
 $b = 13,261 \text{ \AA}$   
 $c = 21,635 \text{ \AA}$   
 $\beta = 101.990^\circ$   
 $D = 1.688 \text{ g/cm}^3$

Macrocyclic  
 compound  
 (podant)  
 33TGd



Macrobicyclic compound  
 (cryptant)

1TGd



The **Electron Paramagnetic Resonance** (EPR) and magnetic research are a very useful technique for investigation of complexation of gadolinium complexes, although so far, there are not enough reports on EPR spectra of these complexes. Current interest in new gadolinium compounds derives from their potential applications as magnetic and/or optical probes. The ground state of the  $Gd^{3+}$  is  $^8S_{7/2}$ , with a half-filled shell of seven unpaired electrons, the effect of the crystalline field is small, the zero field splittings are generally very small, and the long spin-lattice relaxation times usually allow the EPR spectra can be observed at room temperature. The EPR spectra of the studied complexes of gadolinium are similar to the EPR spectra of gadolinium in glasses. The characteristic feature is the presence of three lines at  $g=6$ ,  $g=2.8$  and  $g=2$ , assigned to the weak, intermediate and strong crystal field, respectively. The EPR spectra with three and more absorption signals were assigned to isolated  $Gd^{3+}$  ions. While the single broad absorption was assigned to the clusters of  $Gd^{3+}$  ions [7]. The  $Gd^{3+}$  has a  $4f^7$  configuration and ground state  $^8S$ , that leads to a magnetic moment (independent of ligand fields effects) close to the spin only value ( $\mu_{eff}=7.94\mu_B$  per  $Gd^{3+}$ ).

**Infrared spectra** of the 1T ligand show the absorption band at  $1638.21\text{ cm}^{-1}$ , which is characteristic of imine  $C = N$  bonds of the Schiff bases, and the absorption band at  $3449.25\text{ cm}^{-1}$ , which is characteristic of  $O-H$  bonds. Upon coordination to the metal ion the frequencies undergo a shift with a values of  $12.28\text{ cm}^{-1}$  and  $29.46\text{ cm}^{-1}$ , respectively, what confirms complexation of the gadolinium cryptate 1TGd.

The spin Hamiltonian for  $Gd^{3+}$  ion can be written as:

$$H=H_{\text{Zeeman}}+H_{\text{CF}}; \quad H = g_0\beta B \cdot S + D[S_z^2 - (1/3)S(S+1)] + E(S_x^2 - S_y^2) \quad (1)$$

where  $g$ -value of the (S-state) ion is isotropic and equal to  $g_0$  as in the free ion.  $D$  and  $E$  are the zero field-splitting (ZFS) constants and  $H_{\text{CF}}$  is the effective crystal field interaction term.

**In case of 1TGd** we observed wide line appearing at  $g=2.03$  in the superposition with two lines at  $g=1.63$  and  $g=2.76$ , we observed also three additional lines at  $g$  equal to 3.80, 5.61 and 17.46, respectively.

**In case of 33TGd** we observed three strong, superimposed lines with  $g$  value 1.86, 2.11 and 2.77 and two additional lines at 3.84 and 7.11. This indicate strong crystal field for two complexes of  $Gd^{3+}$  with  $S=7/2$ . It means that the Zeeman term is less than the crystal field term.

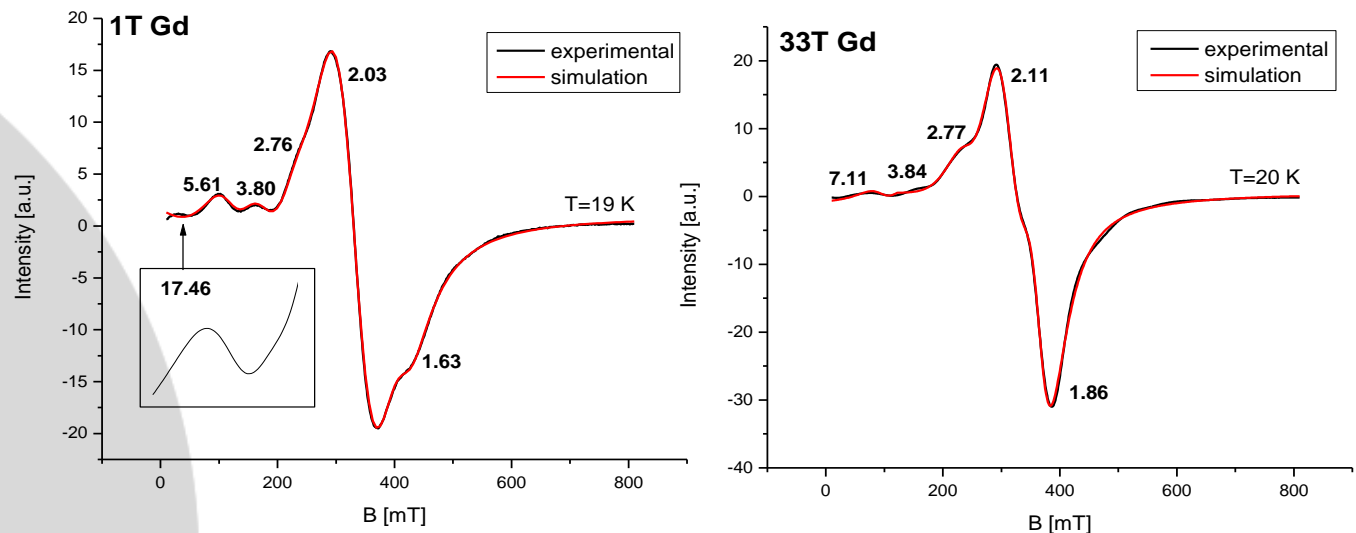
[7] T. Ristoiu, E. Culea, I. Bratu, *Materials Letters* **41**, 135-138, 1999



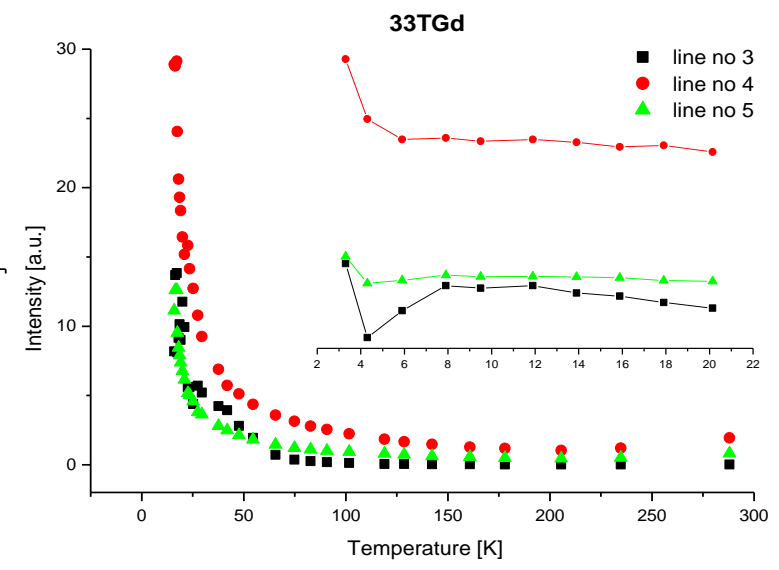
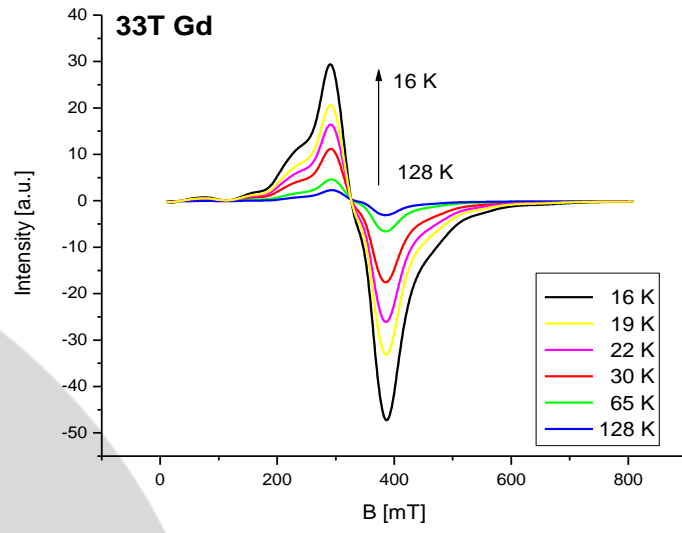
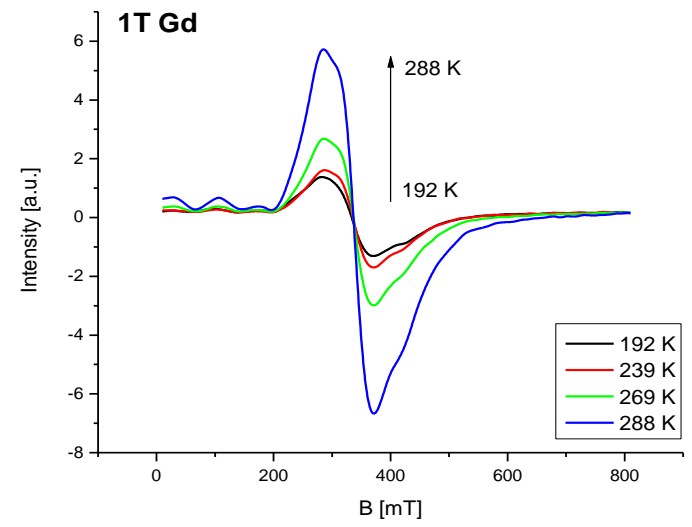
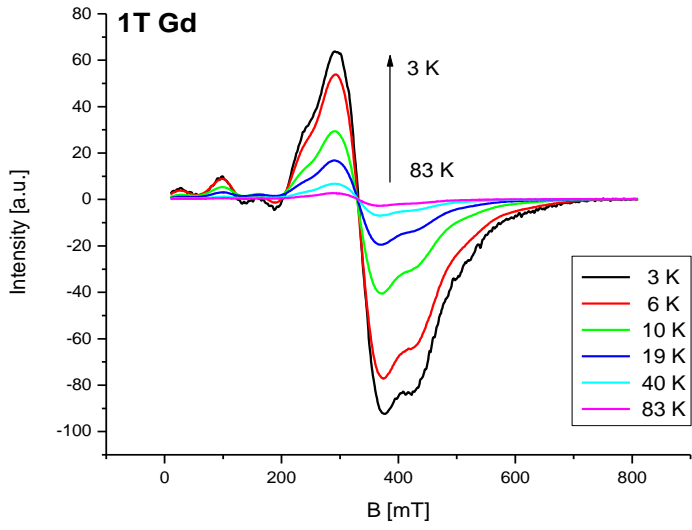
There is eight-fold spin degeneracy in Gd free ion. The strong crystal field split up the free ion level into four doubly degenerate energy levels. The Zeeman field removes such degeneracy. When transition of unpaired electrons occurs between these eight splitted levels, spectral peaks with different  $g$  value can be observed. Moreover, the  $g$ -value of each line does not depend on the temperature. The  $g$ -value was calculated from the following equation  $g=h\nu/\mu_B B_o$ , where  $h$  is the Planck constant,  $\nu$  is the microwave frequency,  $\mu_B$  is the Bohr magneton and  $B_o$  is the value of the external applied magnetic field at the resonance line position.

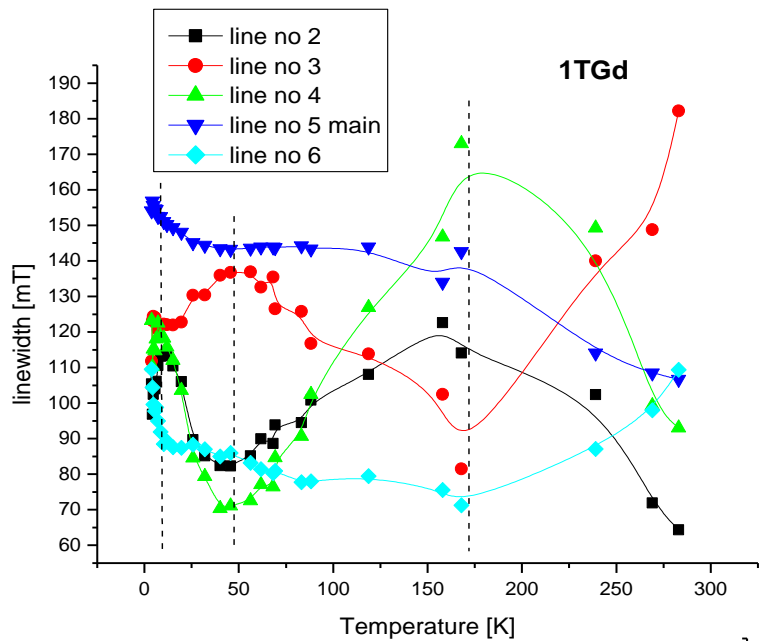
The Electron Paramagnetic Resonance measurements were performed with a conventional X-band Bruker ELEXSYS E500 CW-spectrometer operating at 9.5 GHz with 100 kHz magnetic field modulation. The samples contained ~30 mg of substance in the powder were placed into ~4 mm in the diameter quartz tubes. The first derivate of the power absorption has been recorded as a function of the applied magnetic field. Temperature dependence of the EPR spectra we received using an Oxford Instruments ESP helium-flow cryostat in 3 – 300 K temperature range. The susceptibility was measured on a SQUID magnetometer (MPMS-5 Quantum Design) in the magnetic field up to 5 T in 2 – 300 K temperature range.

**Results** The values of  $g$ -term were calculated from the fitting of EPR data to Lorentzian and Gaussian derivatives functions performed for all the EPR lines of 1TGd and 33TGd complexes.

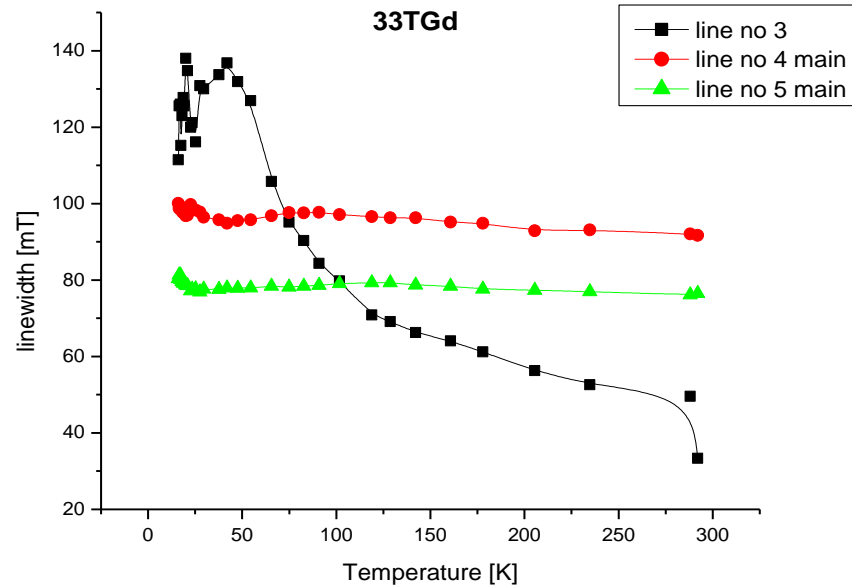


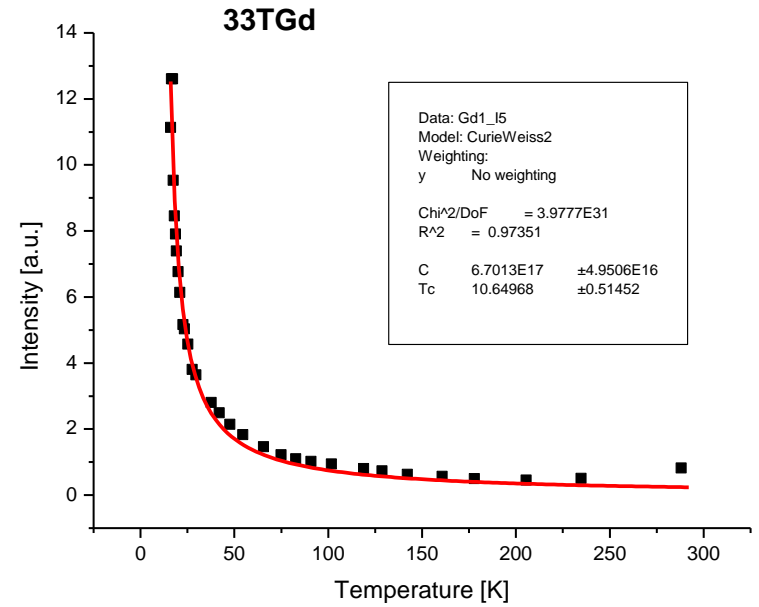
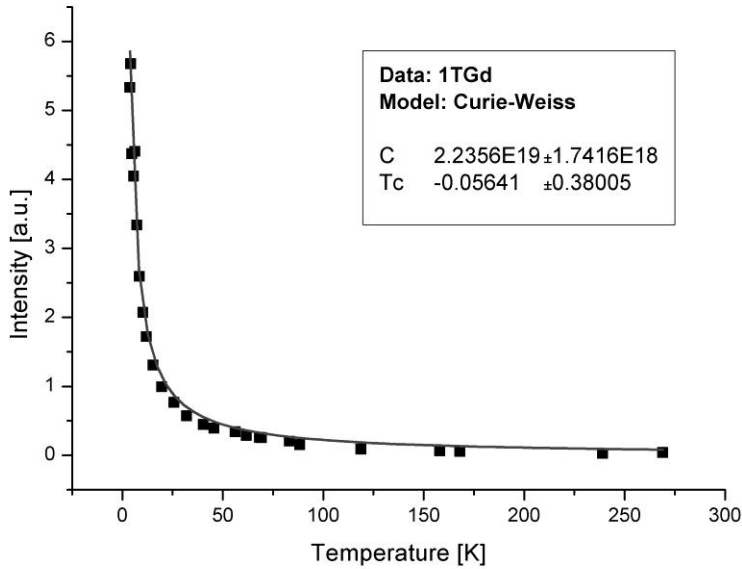






Peak-to-peak linewidths





Weak antiferromagnetic interaction of ion pairs with  $S=7/2$ .

$$H = H_{\text{Zeeman}} = g_0 \beta B \cdot S$$

$$g=1.99$$

$$\mu_{\text{eff}}^2 = 3Ck / \mu_B^2 N$$

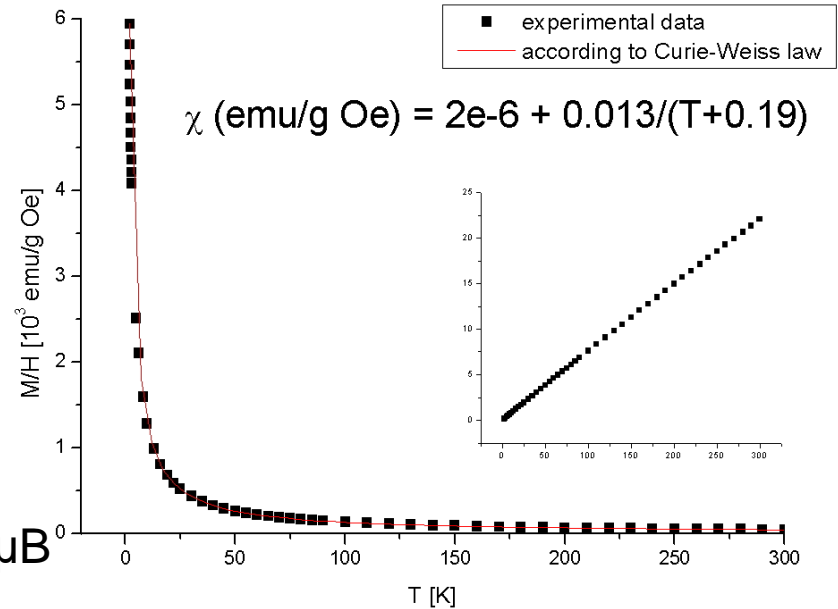
$$\chi = C / (T - \Theta)$$



33TGd

Magnetic momentum  $\mu_{\text{eff}} = 8,46 \mu_B$

$p = g[S(S+1)]^{1/2} = 7,94 \mu_B$



The differences in spectra observed between 1TGd and 33TGd are presumably due to different neighbourhood of the rare-earth ion. The molecule of macrobicyclic (1TGd) is much bigger than the macrocyclic one (33TGd). The gadolinium ion is placed inside the 1TGd complex and enough good isolated from another gadolinium ion. In this case the spin-spin interactions between ions are small and distances between them are much bigger, the consequences of that is the 1TGd spectra are better resolved than the 33TGd spectra.

The peak-to-peak linewidth of 1TGd complex is not clear, but the linewidth of 33TGd complex does not change in the full temperature range.

The structure with no water molecules in the inner sphere complexation of  $Gd^{3+}$  is characterized by one strong line of  $g=1.95-1.99$  [8]. In proper fig. two lines were seen in a superposition at  $g=2.11$  and  $g=1.86$ , what suggests appearing the water molecule in the inner sphere of the 33TGd complex.

The susceptibility of magnetic ion follows the Curie-Weiss type behaviour for the 33TGd complex. The best fitting parameters are determined to be  $\Theta=-0.19$  and  $C=0.013$ . The effective magnetic moment per gadolinium ion is higher than the magnetic moment of the free gadolinium ion. This indicates some weak antiferromagnetic interaction of Gd ions and strong crystal field of ligands. Both the EPR measurement and magnetic susceptibility results agree well and show that  $Gd^{3+}$  ion is scarcely affected by the crystal field in this compound [9].



[8] A. Szczyzewski, S. Lis, Z. Kruczynski, S. But, M. Elbanowski, J. Pietrzak, J. Alloys Comp. 275-277, 349-352, 1998

[9] G. Leniec, S.M. Kaczmarek, B. Kołodziej, E. Grech, to be published

[10] G. Leniec, J. Typek, L. Wabia, B. Kołodziej, E. Grech, N. Guskos, „Electron paramagnetic resonance of Schiff base copper (II) complex, with poly(propylene imine)tetramine dendrimer (DAB – AM-8)”, *Molecular Physics Reports*, 39 (2004) 154-158

[11] G. Leniec, J. Typek, L. Wabia, B. Kołodziej, E. Grech, N. Guskos, „Electron paramagnetic resonance study of two copper (II) complexes of Schiff base derivatives of DAB AM-4”, *Molecular Physics Reports*, 39 (2004) 159-164

## 2. Synthesis and characterization of new compounds

$\text{Ni}_2\text{CrV}_3\text{O}_{11}$ ,  $\text{Mg}_2\text{CrV}_3\text{O}_{11}$  and  $\text{Zn}_2\text{CrV}_3\text{O}_{11}$  MSc A.

Worsztynowicz

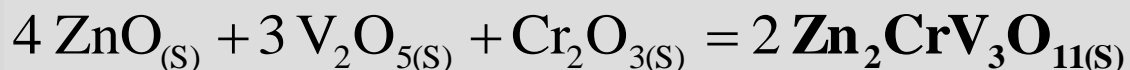
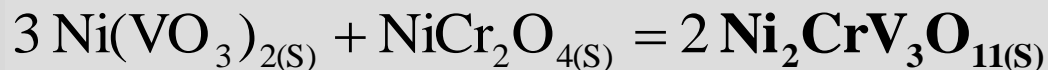
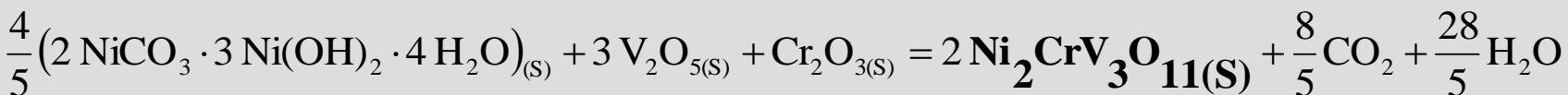
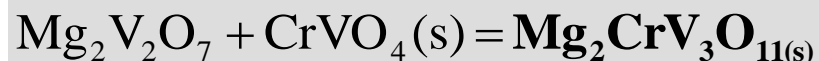
Transition metal oxides as well as their multicomponent systems have been objects of numerous investigations for many years, first of all because of their catalytic properties enabling their more and more comprehensive use in industrial practice as active and selective catalysts in many processes of oxidative dehydrogenation of lower alkanes [1]. Literature information implies that there exists a series of compounds of a general formula  $\text{M}_2\text{FeV}_3\text{O}_{11}$  in the three-component metal oxide systems of  $\text{MO} - \text{V}_2\text{O}_5 - \text{Fe}_2\text{O}_3$  type where  $\text{M} = \text{Co}, \text{Mg}, \text{Ni}, \text{Zn}$  [2, 3]. What is more, also compounds of  $\text{M}_3\text{Fe}_4(\text{VO}_4)_6$  type are formed in some of these systems [4]. Compounds of  $\text{Mg}_2\text{CrV}_3\text{O}_{11}$  type being formed in the  $\text{MO} - \text{V}_2\text{O}_5 - \text{Cr}_2\text{O}_3$  ( $\text{M} = \text{Ni}, \text{Zn}, \text{Mg}$ ) systems have recently been obtained [5].



- [1] E.Tempesti, A.Kaddouri and C.Mazzochia: Appl. Catal. A, Vol. 166 (1998) p. L 259
- [2] I.Rychlowska-Himmel and A.Blonska-Tabero: J. Therm. Anal. Cal. Vol. 56 (1999) p. 205
- [3] X.Wang, D.A.Vander Griend, Ch.L.Stern and K.R.Poeppelmeier: J. Alloys Comp., Vol. 298 (2000) 119
- [4] M.Kurzawa and A.Blonska-Tabero: Mater. Res. Bull. (in press)
- [5] M.Kurzawa, I.Rychlowska-Himmel, A.Blonska-Tabero, M.Bosacka and G.Dabrowska: Solid State Phenom.

# Compounds of $M_2CrV_3O_{11}$ (M=Mg, Ni, Zn) were obtained for the first time as a result of solid state reactions

The reagents used for research were:  $V_2O_5$ , p. a. (Riedel-de Haën, Germany),  $Cr_2O_3$ , p. a. (Aldrich, Germany),  $3 MgCO_3 \cdot Mg(OH)_2 \cdot 3 H_2O$ , p.a. (POCh, Gliwice, Poland),  $2 NiCO_3 \cdot 3 Ni(OH)_2 \cdot 4 H_2O$ , p.a. (POCh, Gliwice, Poland),  $ZnO$ , p. a. (Ubichem, UK). The reacting substances were weighed in appropriate portions, thoroughly homogenised by grinding, formed into pellets and heated in cycles by means of a syllite furnace in the atmosphere of air. After each heating cycle the samples were gradually cooled down to ambient temperature, ground and subjected to examinations by the XRD and DTA methods; thereafter they were shaped into pellets again and heated, these procedures being repeated until monophase preparations were obtained.



No.	Composition of initial mixtures	Preparation conditions	Results of XRD analysis
1.	16.67 [2 NiCO <sub>3</sub> ·3 Ni(OH) <sub>2</sub> ·4 H <sub>2</sub> O] 62.50 V <sub>2</sub> O <sub>5</sub> 20.83 Cr <sub>2</sub> O <sub>3</sub>	500 °C (24h) + 600 °C (24h) + 650 °C (24h) + 750 °C (24h) + 800 °C (24h)	Ni <sub>2</sub> CrV <sub>3</sub> O <sub>11</sub>
2.	50.00 CrVO <sub>4</sub> 50.00 Ni <sub>2</sub> V <sub>2</sub> O <sub>7</sub>	700 °C (24h) + 800 °C (24h)	
3.	25.00 NiCr <sub>2</sub> O <sub>4</sub> 75.00 Ni(VO <sub>3</sub> ) <sub>2</sub>	700 °C (24h) + 800 °C (24h)	
4.	50.00 ZnO 37.50 V <sub>2</sub> O <sub>5</sub> 12.50 Cr <sub>2</sub> O <sub>3</sub>	550 °C (24h × 2) + 570 °C (24h)	Zn <sub>2</sub> CrV <sub>3</sub> O <sub>11</sub>
5.	50.00 CrVO <sub>4</sub> 50.00 Zn <sub>2</sub> V <sub>2</sub> O <sub>7</sub>	550 °C (24h × 2) + 570 °C (24h)	
6.	20.00 [3 MgCO <sub>3</sub> ·Mg(OH) <sub>2</sub> ·3 H <sub>2</sub> O] 60.00 V <sub>2</sub> O <sub>5</sub> 20.00 Cr <sub>2</sub> O <sub>3</sub>	690 °C (24 h) + 750 °C (24 h) + 820 °C (24 h)	Mg <sub>2</sub> CrV <sub>3</sub> O <sub>11</sub>
7.	50.00 CrVO <sub>4</sub> 50.00 Ni <sub>2</sub> V <sub>2</sub> O <sub>7</sub>	700 °C (24h) + 750 °C (24h) + 820 °C (24h)	



The DTA measurements were conducted by using the F.Paulik–L.Paulik–L.Erdey derivatograph (MOM, Budapest, Hungary). The measurements were performed in the atmosphere of air, in quartz crucibles, at a heating rate of 10°/min in the range of 20-1000°C. The mass of investigated samples amounted always to 500 mg.

The XRD examination was always performed by using the diffractometer DRON-3 (Bourestnik, Sankt Petersburg, Russia) and by applying the radiation  $\text{CoK}\alpha/\text{Fe}$ . The identification of the individual phases was based on the accordance of obtained diffraction patterns with the data contained in JC PDF cards [6].

The unit cell parameters of the obtained compound were calculated by means of the program POWDER [7], belonging to the crystallographic programs library of X-Ray System 70. Exact positions of diffraction lines were determined by the internal standard method. The internal standard used was  $\alpha\text{-SiO}_2$  (space group P3121,  $a = b = 0,49133(1)$  nm,  $c = 0,54044(3)$  nm).

The density of the compound was measured by a method described in the work [8].

The IR spectrum was recorded in the wave-number range of 1100-250  $\text{cm}^{-1}$  by means of the SPECORD M 80 (Carl Zeiss, Jena, Germany). A technique of pressing pellets with KBr at a weight ratio of 1 : 300 was applied.

A sample of the new compound was examined using scanning electron microscope (JSM-1600, Joel, Japan) linked to an X-ray microanalyser (ISIS 300, Oxford).

The electron paramagnetic resonance (EPR) spectra were recorded for both non-annealed in the air and annealed samples, using a Bruker E 500 X-band spectrometer. During the annealing the samples were held at the temperature of 750 K for two hours in oxidizing atmosphere. The temperature dependence of EPR spectra we registered in the temperature range of 4 to 300 K using Oxford helium gas flow cryostat.

Magnetic measurements were carried out using a MPMS-5 SQUID magnetometer. Zero-field-cooled and field-cooled magnetization measurements were performed in the temperature range of 2-300 K at constant magnetic field. The isothermal magnetization was measured versus temperature and magnetic field up to 50 kOe.

[6] Powder Diffraction File, International Center for Diffraction Data, Swarthmore (USA), File Nos.: 10-351, 34-13, 36-309, 4-829, 38-1479.








[7] D.Taupin: J. Appl. Crystallogr. Vol. 6 (1973) p. 380

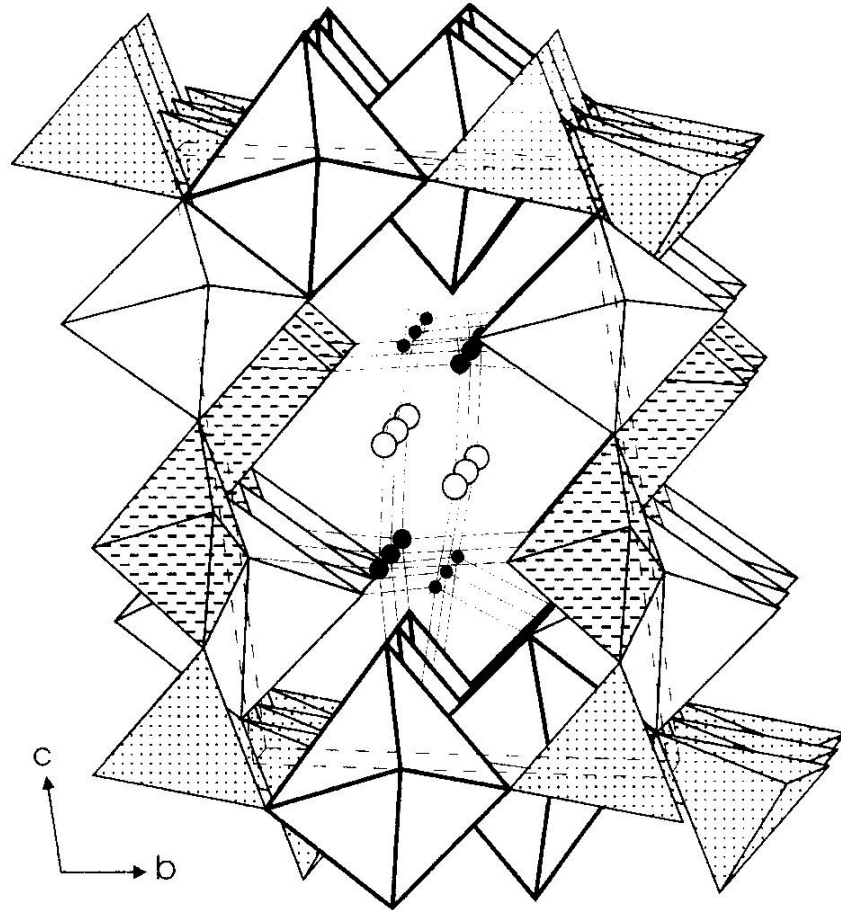
[8] Z.Kluz and I.Waclawska: Chem. Ann. Vol. 49 (1975) p. 839, in Polish





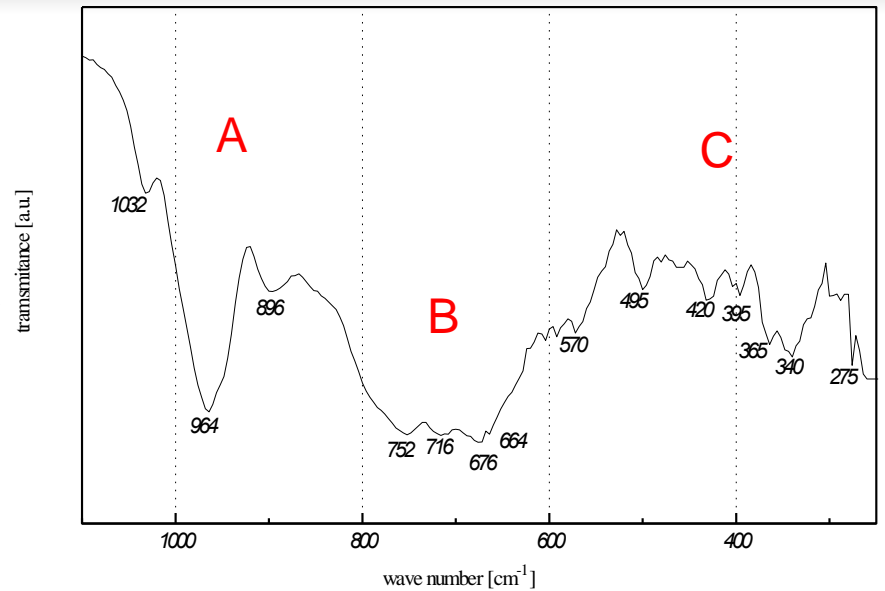
# $M_2FeV_3O_{11}$ (M= Zn, Mg) isostructural to $M_2CrV_3O_{11}$

-  O - jony tlenu
-  M - jony metalu (M = Zn,Mg,Ni)
-  V - jony wanadu
-  Oktaedry M06
-  Oktaedry M06
-  Trygonalne Bipiramidy V05
-  Tetraedry V04



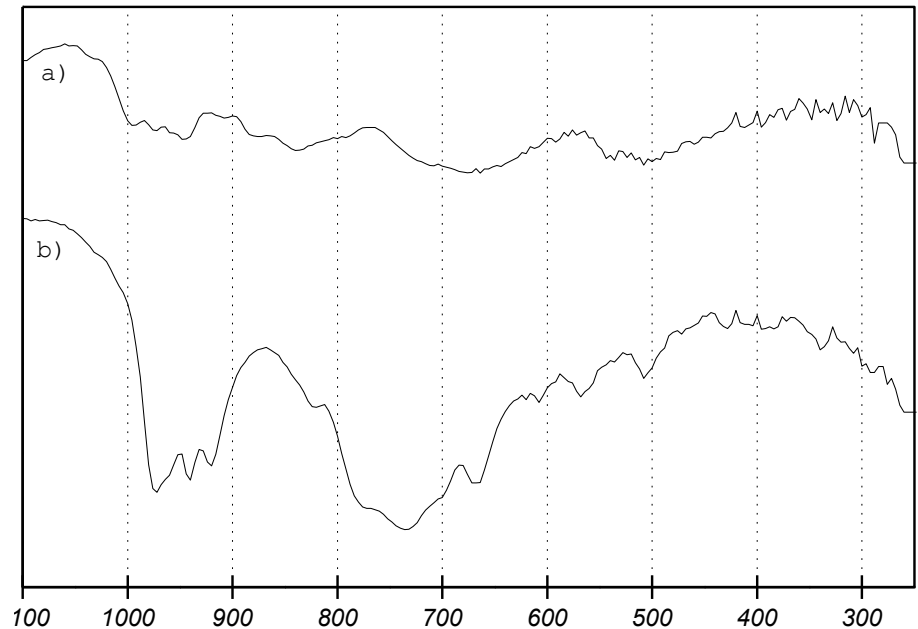
Composed of  $M(1)O_6$  i  $M(2)O_6$  octaheders,  $M(3)O_5$  i  $V(2)O_5$  trigonal bipyramides and  $V(1)O_4$  tetraheders

The IR spectrum of  $\text{Mg}_2\text{CrV}_3\text{O}_{11}$ . **A**: 1100 and 830  $\text{cm}^{-1}$  - stretching vibrations of the V–O bonds in the  $\text{VO}_4$  tetrahedra and in the  $\text{VO}_5$  trigonal bipyramids, **B**: 830 – 650  $\text{cm}^{-1}$  - stretching vibrations of the M–O bonds in  $\text{MO}_5$  trigonal bipyramids and in  $\text{MO}_6$  octahedra, where M = Cr, Mg, Zn, Ni **C**: 650 – 280  $\text{cm}^{-1}$  - bending vibrations of the V–O bonds in the  $\text{VO}_4$  tetrahedra and of the M–O bonds in the  $\text{MO}_5$  and  $\text{MO}_6$  polyhedra. It cannot be also ruled out that in this wave-number range the absorption bands could be ascribed to bending vibrations of M–O–V, Cr–O–Cr or to vibrations of a mixed nature.



SEM image of  $\text{Mg}_2\text{CrV}_3\text{O}_{11}$ . The analysis of the biggest grains, performed by means of an X-Ray microanalyser, proved that the molar ratio of Mg : Cr : V corresponded to the stoichiometric value of 2 : 1 : 3.

The IR spectra of  $\text{Ni}_2\text{CrV}_3\text{O}_{11}$  (curve a) and  $\text{Zn}_2\text{CrV}_3\text{O}_{11}$  (curve b).



## Space group P1, triclinic

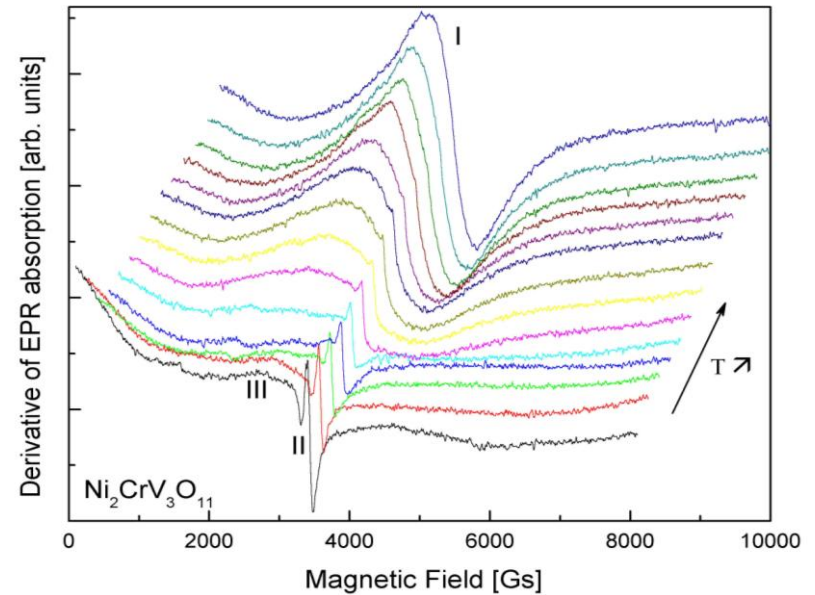
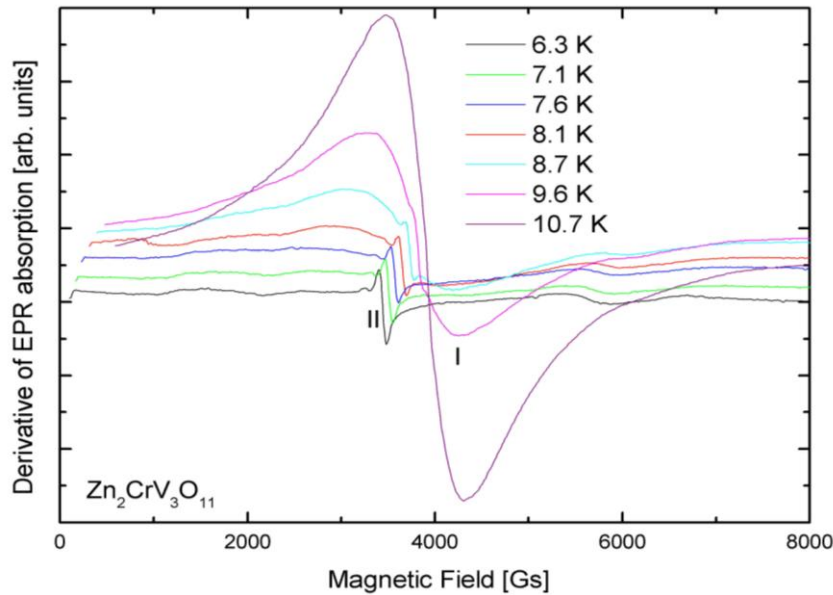
Compound	a [nm]	b [nm]	c [nm]	$\alpha$ [°]	$\beta$ [°]	$\gamma$ [°]	V [nm <sup>3</sup> ]	d [g/cm <sup>3</sup> ]
Ni <sub>2</sub> CrV <sub>3</sub> O <sub>11</sub>	0,6341(7)	0,8212(4)	0,8084(7)	90,82(3)	101,24(3)	110,34(9)	0,40345	3,54
Zn <sub>2</sub> CrV <sub>3</sub> O <sub>11</sub>	0,6277(2)	0,7038(9)	1,1006(2)	114,17(3)	101,27(5)	101,89(6)	0,4122	4,02
Mg <sub>2</sub> CrV <sub>3</sub> O <sub>11</sub>	0,6276(5)	0,6705(2)	1,123(2)	113,9	106,4	94,9	0,4102	3,53

Mg<sub>2</sub>CrV<sub>3</sub>O<sub>11</sub> is brown in colour and it melts at a temperature of  $900 \pm 5^\circ\text{C}$ , Ni<sub>2</sub>CrV<sub>3</sub>O<sub>11</sub> is dark brown in colour and it melts congruently at a temperature of  $940 \pm 5^\circ\text{C}$ , Zn<sub>2</sub>CrV<sub>3</sub>O<sub>11</sub> is light brown, melts congruently at  $680 \pm 5^\circ\text{C}$ . V - unit cell volume.

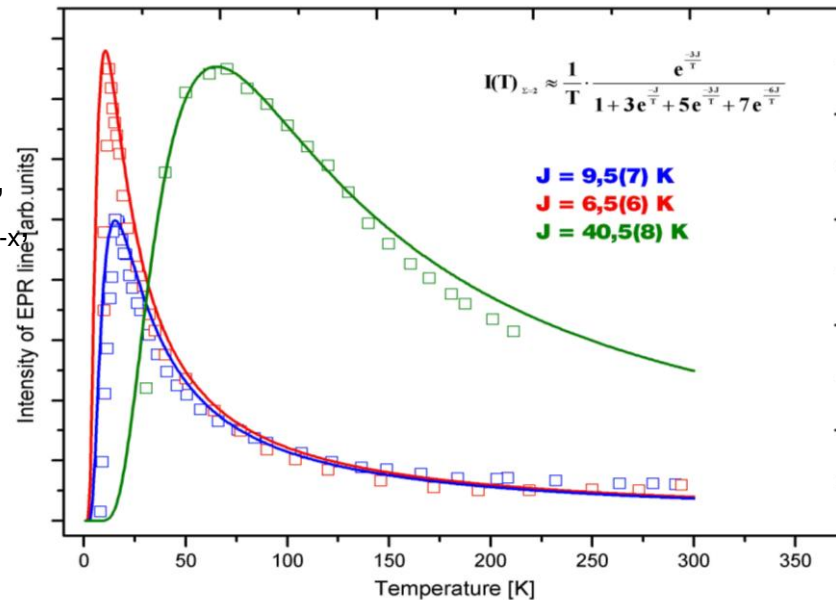
### EPR results

Two absorption lines with  $g \approx 2.0$  (type I) and  $g \approx 1.98$  (type II) we recorded in the EPR spectra, which can be attributed to V<sup>4+</sup> ions and Cr<sup>3+</sup> ion clusters (pairs) respectively. Volumetric titration confirmed distinctly the presence of vanadium V<sup>4+</sup> ions in the investigated compounds. Studies of EPR spectrum in glasses [9] have shown that EPR spectrum gradually changes with increase in the Cr<sub>2</sub>O<sub>3</sub> concentration, from an initial  $g \approx 4.0$  low field absorption assigned to isolated, octahedrally coordinated Cr<sup>3+</sup> ions, to another one at high field with a  $g \approx 2.0$ , attributed to exchange coupled pairs of Cr<sup>3+</sup> ions six-fold coordinated. They observed also Cr<sup>5+</sup> absorption line in EPR spectra with  $g=1.97$ .



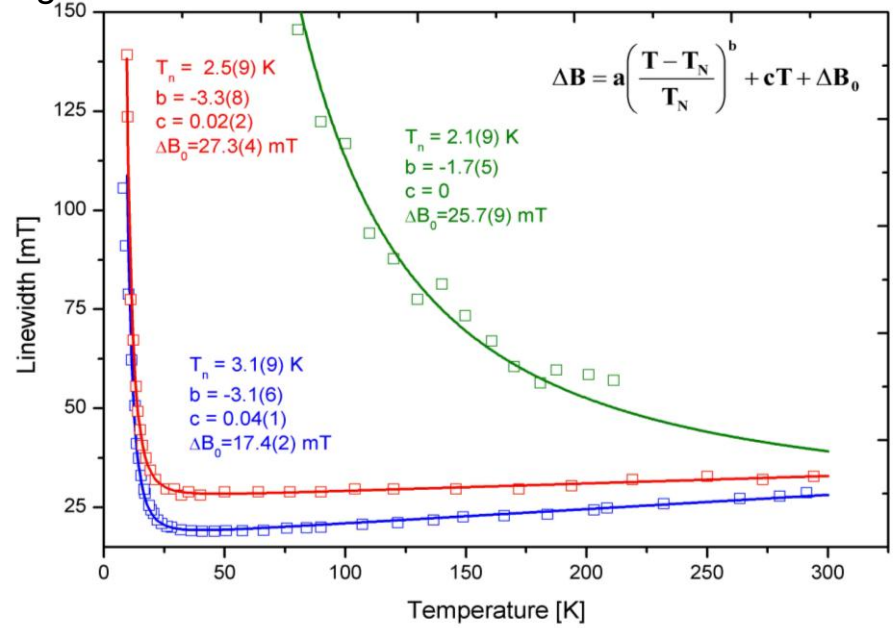


As the temperature increases, II ( $\text{VO}^{2+}$  centers) type line is not observed because is strongly overlapped by the broad and very intense I Type ( $\text{Cr}^{3+}$  clusters) Lorentzian line [10]. The I line could be clearly observed for higher temperatures, i.e.  $> 10$  K,  $> 15$  K,  $> 70$  K for  $(\text{Zn}, \text{Mg}, \text{Ni})_2\text{CrV}_3\text{O}_{11-x}$  respectively.

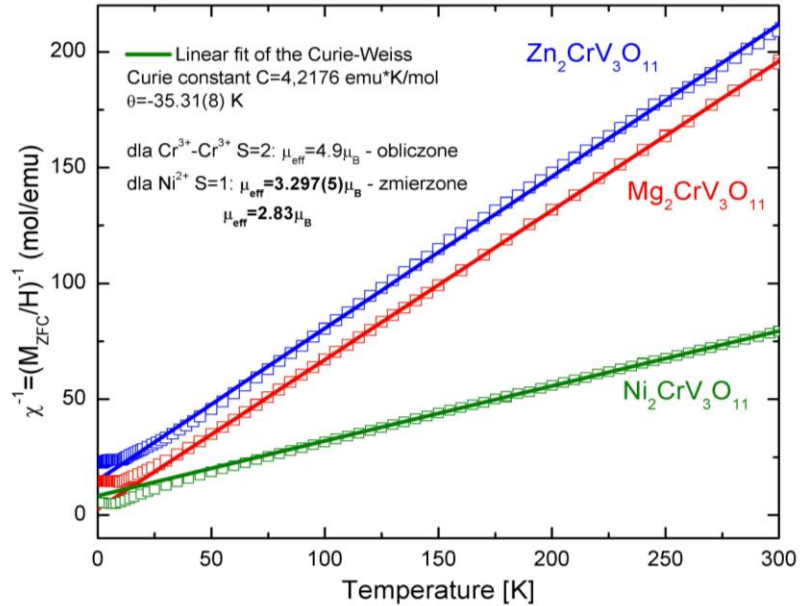


[10] A. Worsztynowicz, S.M. Kaczmarek, M. Kurzawa, M. Bosacka, "Magnetic study of  $\text{Cr}^{3+}$  ion in  $\text{M}_2\text{CrV}_3\text{O}_{11-x}$  ( $\text{M}=\text{Zn}, \text{Mg}$ ) compounds", *J. Solid State Chem*, 178 (2005) 2231-2236

In the same temperature range the peak-to-peak linewidth  $\Delta B_{\text{eff}}$ , increases substantially as the temperature is lowered (magnetically ordered state) while in high temperatures one can observe an interesting linear progress of the  $\Delta B_{\text{eff}}$ .



At low temperature, where the exchange coupling interactions between  $\text{Cr}^{3+}$  ions became stronger, spin-spin relaxation time decreases with decrease in temperature and hence sudden increase in the linewidth is observed.

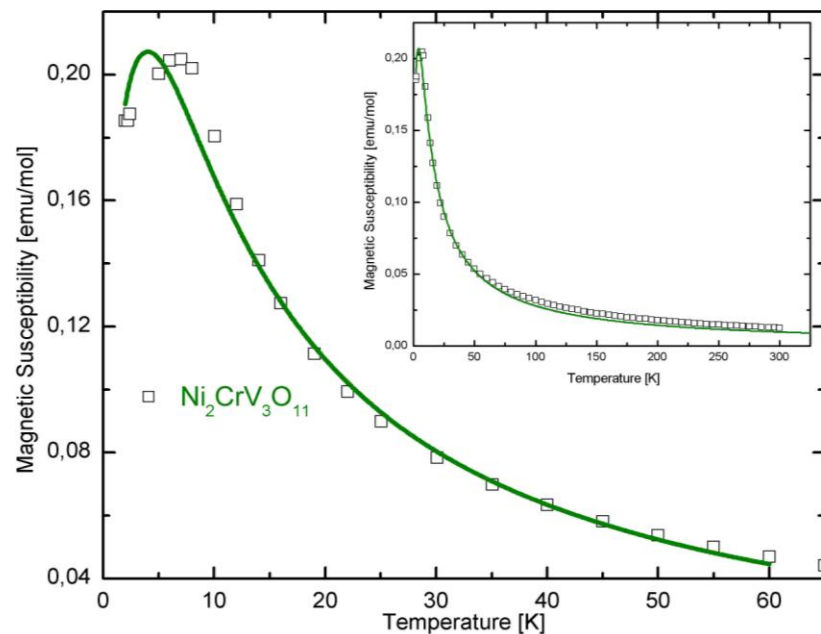
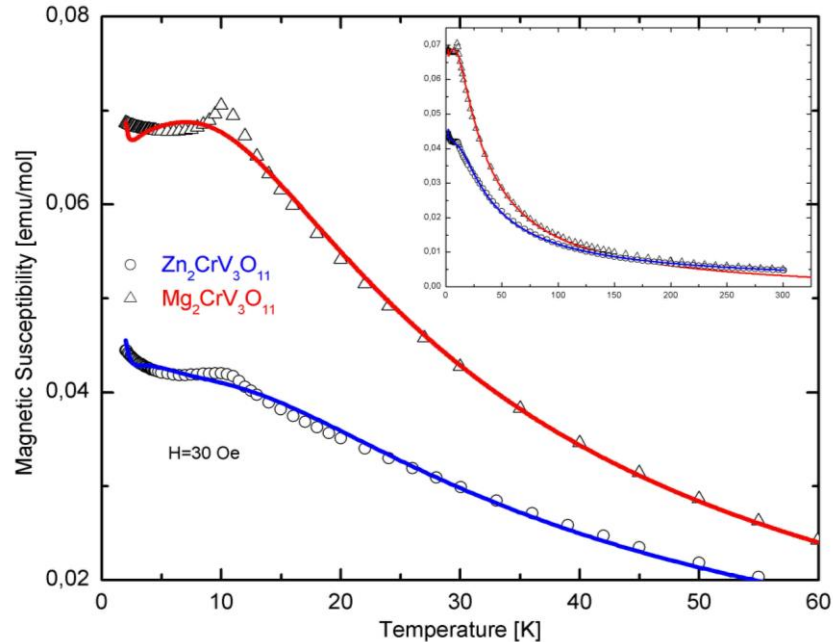


$$\chi(T) = A + \frac{C_1}{T} + \frac{C_2}{T} \frac{\exp(\frac{D}{T}) + 5\exp(\frac{3D}{T}) + 14\exp(\frac{6D}{T})}{1 + 3\exp(\frac{D}{T}) + 5\exp(\frac{3D}{T}) + 7\exp(\frac{6D}{T})} + \frac{C_3}{T - \theta}$$

$A$  - weik diamag.  
 $D = \frac{J}{k_B}$   
 $V^{4+}$   
 dimers  $\text{Cr}^{3+}\text{-O-Cr}^{3+}$   
 $\text{Ni}^{2+}$  ions (additional factor for  $\text{Ni}_2\text{CrV}_3\text{O}_{11}$ )  
 $C_{1,2,3} = \frac{N_A S(S+1) g^2 \mu_B}{3k_B}$

[11] J.C.M. Henning, J.H. Den Boef, G.G.P. van Gorkom, Phys. Rev. B 7 (1973) 1825

[12] D.L. Huber, Phys. Rev. B 6 (1972) 3180



Sample	A [emu/mol]	C1 [emu* K/mol]	C2 [emu* K/mol]	D [K]	$\mu_{\text{eff}}^{\text{Cr}3+}$	$\mu_{\text{eff}}^{\text{Cr}3+}$ teor. 1	$\mu_{\text{eff}}^{\text{V}4+}$	$\mu_{\text{eff}}^{\text{V}4+}$ teor. 1	C3 [emu*K/mol]	$\Theta$ [K]	$\mu_{\text{eff}}^{\text{Ni}2+}$	$\mu_{\text{eff}}^{\text{Ni}2+}$
Zn <sub>2</sub> CrV <sub>3</sub> O <sub>11</sub>	0.0007(3)	0.075(4)	1.387(9)	-8.39(12)	4.71	4.9	0.78	1.73	-	-	-	-
Mg <sub>2</sub> CrV <sub>3</sub> O <sub>11</sub>	0.00027(15)	0.061(9)	1.431(7) 1)	-6.46(24)	4.78	4.9	0.7	1.73	-	-	-	-
Ni <sub>2</sub> CrV <sub>3</sub> O <sub>11</sub>	0.00009(81)	~ 0	1,61(8)	-2.95(58)	5.07	4.9	-	1.73	1.002(5)	- 15.48	2.83	2.83

We suggest, that main contribution to total magnetic susceptibility arises from Cr<sup>3+</sup> ion pairs with total spin S=2. At low temperature, as the interactions between chromium pairs become AFM and non-Curie susceptibility goes to zero, V<sup>4+</sup> or other paramagnetic centers contribute to total magnetic susceptibility. Hence, a slight increase of  $\chi^{-1}$  as T→0 is predicted.

EPR and magnetic susceptibility on the recently synthesised vanadates  $M_2CrV_3O_{11-x}$  ( $M = Zn, Mg$ ) Provide experimental evidence that  $Cr^{3+}$  ions in the compounds form clusters, may be pairs. The exchange constant,  $J$ , calculated by EPR measurements was:  $J/kB = -9.5$  K and  $J/kB = -6.5$  K for  $(Zn, Mg)_2CrV_3O_{11-x}$ , respectively. The sign of  $J$  is negative and indicate antiferromagnetic interactions. Different lattice constants of Cr-Cr distance lengths between the compounds can cause different value of  $J$  constant. Accurate values of the Neel's temperatures obtained from EPR data are:  $T_N=3.1(9)$  K and  $T_N=2.5(9)$  K for  $(Zn, Mg)_2CrV_3O_{11}$ , respectively. Temperature dependence of the magnetic susceptibility shows also antiferromagnetic phase transition at  $T_N=10$  K and  $T_N=11$ K for  $(Zn, Mg)_2CrV_3O_{11}$ , respectively. The lack of decay of  $\chi(T)$  is caused by the presence of  $V^{4+}$  ions or other additional paramagnetic defects. The existence of  $V^{4+}$  ions suggests that indeed strong oxygen-deficient can be present in  $M_2CrV_3O_{11-x}$  ( $M = Zn, Mg$ ) compounds.



### 3. Growth and optical properties of $\text{Li}_2\text{B}_4\text{O}_7$ pure and Co doped single crystals MSc Danuta Piwowska [1]

$\text{Li}_2\text{B}_4\text{O}_7$  (LBO) crystal is a negative uniaxial crystal, which belongs to the 4 mm point group and  $I4_1cd$ . ( $C^{12}_{4v}$ ) space group of tetragonal symmetry ( $a=b=9.479 \text{ \AA}$ ,  $c=10.286 \text{ \AA}$ ). Its structure is determined by the  $\text{B}_4\text{O}_9$  net, the  $\text{Li}^+$  ions are localized in the special spaces in this net. B-O mean distance is equal to  $1.45 \text{ \AA}$ , O-O to  $2.38 \text{ \AA}$ , and  $\text{Li-O}$  to  $2.1 \text{ \AA}$ . The structure of the crystal along c axis is presented in Fig. 1.

LBO melts congruently at 1190 K at a composition of 1:2 of  $\text{Li}_2\text{O}$  and  $\text{B}_2\text{O}_3$ , so it may be grown by Czochralski and Bridgman methods. Rare-earth and transition metal ions may substitute for both octahedral  $\text{Li}^+$  and tetrahedral  $\text{B}^{3+}$  sites. It is expected that primarily the Li site should be occupied by all the dopant ions due to extremely small size of boron ion ( $0.23 \text{ \AA}$ ).

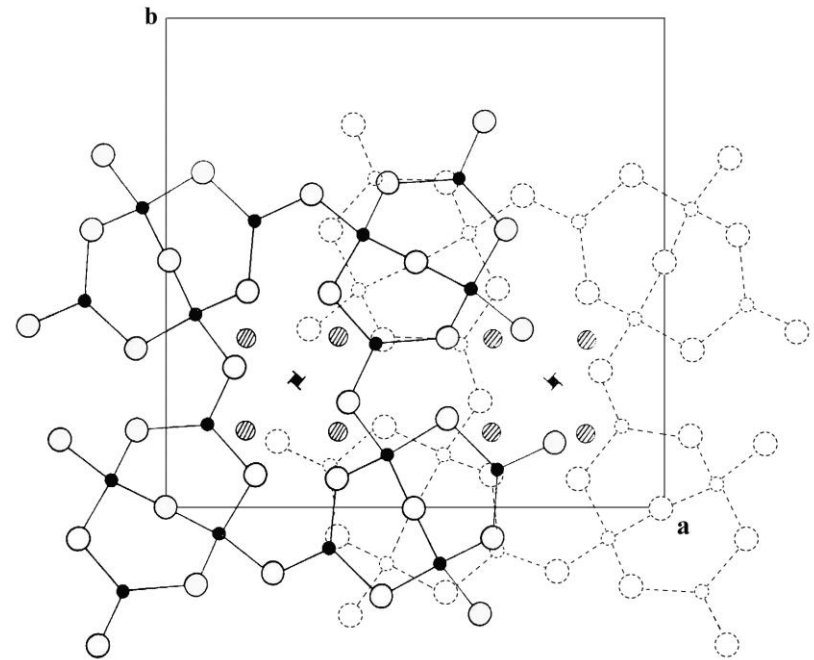


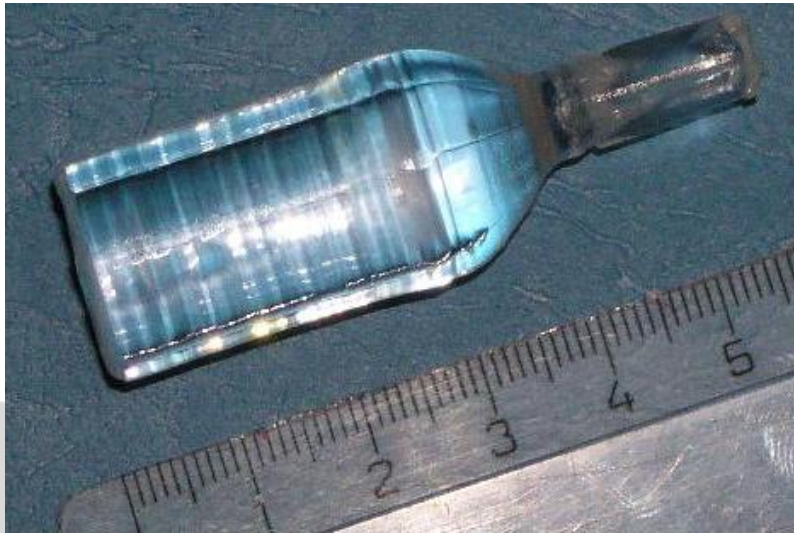
Fig. 1. Structure of LBO crystal along c-axis (● - B, ○ - O, ⊗ - Li)

[1] D. Piwowska, S.M. Kaczmarek, W. drozdowski, M. Berkowski, A. Worsztynowicz, „Growth and optical properties of...”, Acta Phys. Pol. A, 107 (2005) 507-516





- ✓ LBO is a piezoelectric material and has been studied as a substrate for surface acoustic wave (SAW) devices  
Microwave devices using surface acoustic waves are in common use for infrared filters for color television and under signal processing elements
- ✓ LBO have been also studied as promising non-linear crystal
- ✓ Nonlinear optical properties of LBO in the UV range were demonstrated and commented on the fourth and fifth harmonic generation of a YAG: Nd laser
- ✓ LBO is considered to be one of the useful materials for neutron detection because it contains Li and B, which possess large neutron capture cross-section isotopes



$\text{Li}_2\text{B}_4\text{O}_7$  Single crystals obtained by Czochralski method in the Institute of Physics, Szczecin University of Technology

a) pure LBO single crystal

b) LBO:Co (0.5 mol. %) single crystal

[2] R. Komatsu, T. Suagawara, K. Sassa, N. Sarukura, Z. Liu, S. Izumida, Y. Segawa, S. Uda, T. Fukuda and K. Yamanouchi, *Appl. Phys. Lett.*, 70 (1997) 3492

[3] Ya.V. Burak, B.V. Padlyak, V.M. Shevel, *NIMB* 191 (2002) 633



## Czochralski puller

In the Optoelectronics Head,  
Institute of Physics,  
Szczecin University of Technology



## Co doped $\text{Li}_2\text{B}_4\text{O}_7$ (1 mol. %) crystal

11:29.24 Czochralski growth. Date: 21/06/2004

11:29.24 Material: LBO:Co1% starting weight 151.00 g

11:29.24 Crucible: TPt50

11:29.24 Density 1.95 g/ccm

11:29.24 Expected parameters of the crystal:

11:29.24 \*\*\*\*\* Seed Cone Cylinder

11:29.24 Diameter [mm] 5.5 ----- 20.0

11:29.24 Length [mm] 10.0 13.6 100.0

11:29.24 Weight [g] 0.5 3.9 61.3

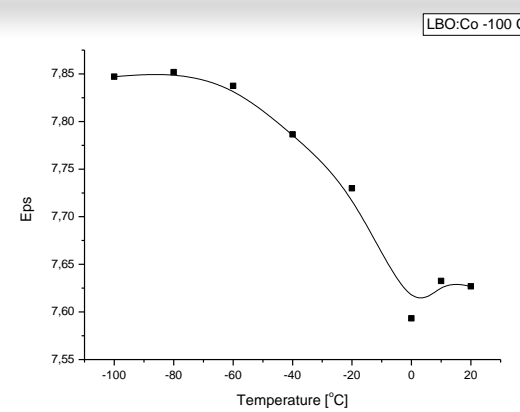
11:29.24 Time [h] 16.7 29.1 166.7

11:29.24 Cone gape [deg]: 80.0

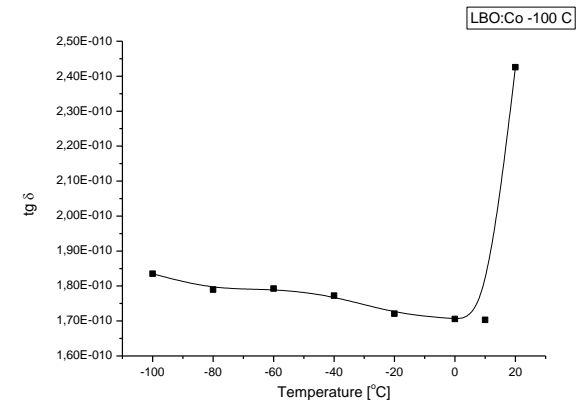
11:29.24 Crystallization front gape [deg]: 140.0

11:29.24 constant growth rate in the middle of the crystal

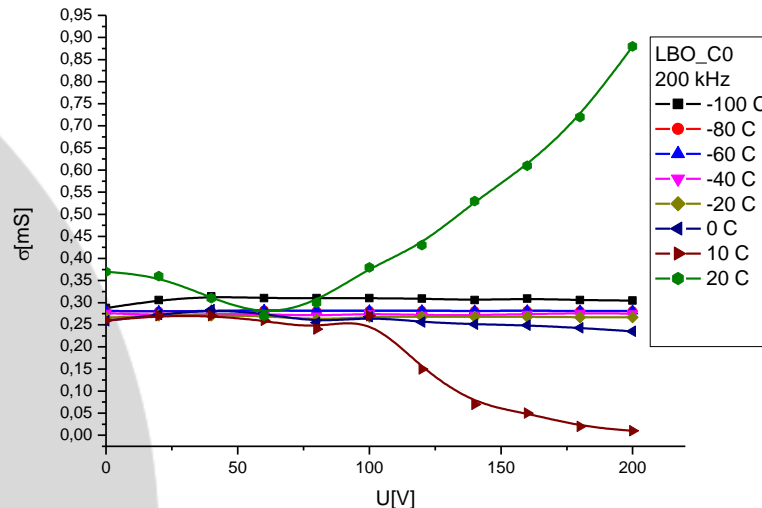
11:29.24 as high as 0.60 mm/h



## Dielectrical permissivity

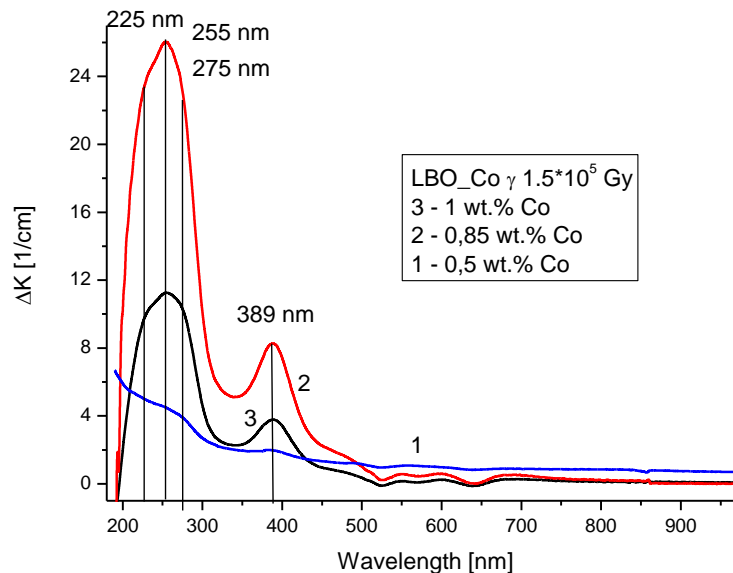
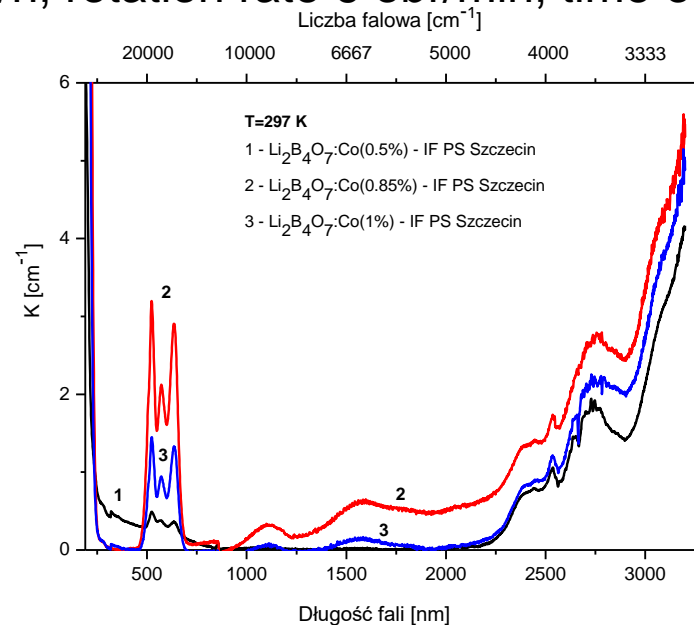
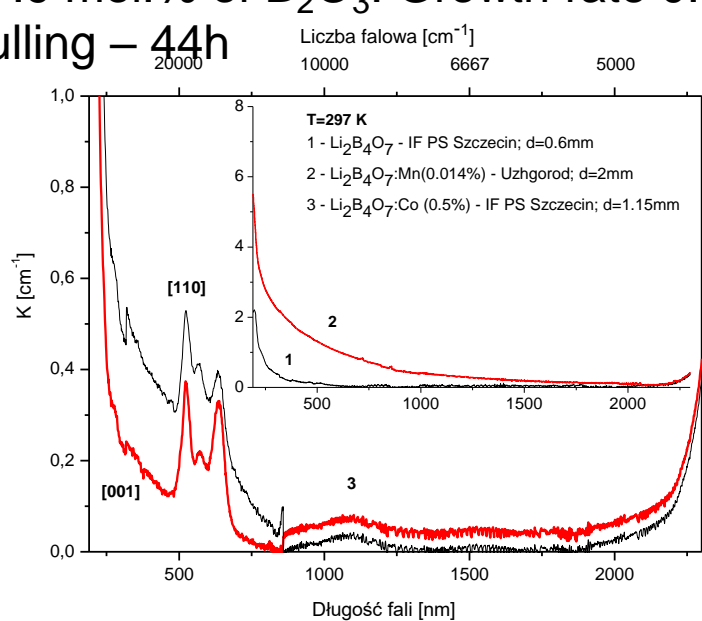


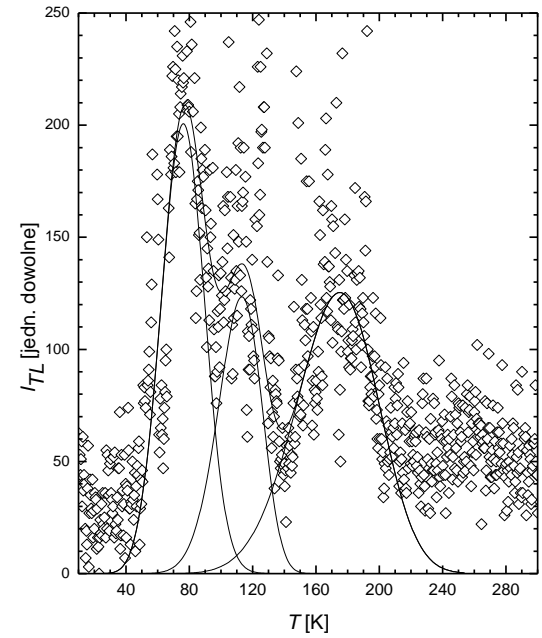
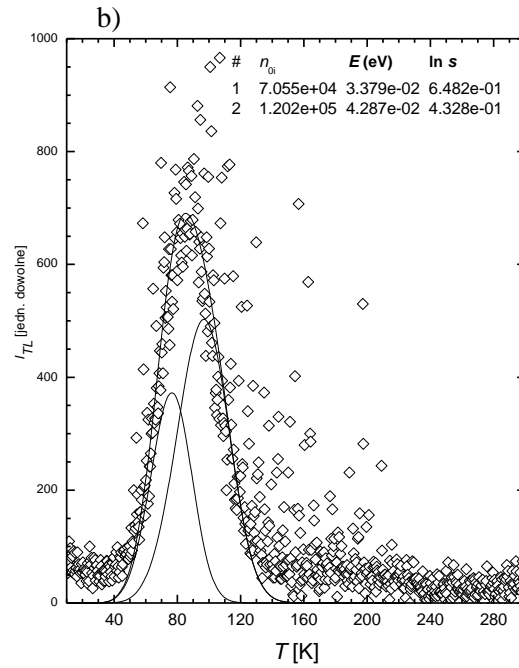
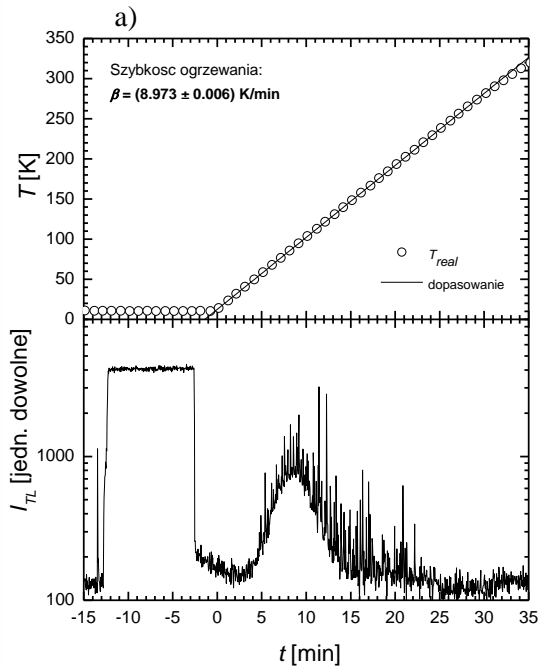
## Dielectrical losses



## Conductivity

The melt was prepared by melting in platinum crucible at first  $B_2O_3$  of 4N purity and gradually adding  $Li_2CO_3$  of 5N purity to reach starting composition with 67.9 mol.% of  $B_2O_3$ . Growth rate 0.6 mm/h, rotation rate 6 obr/min, time of the pulling – 44h

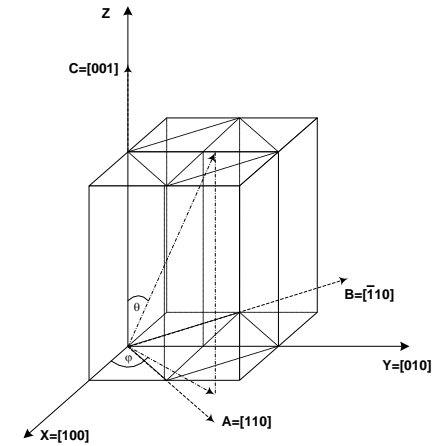
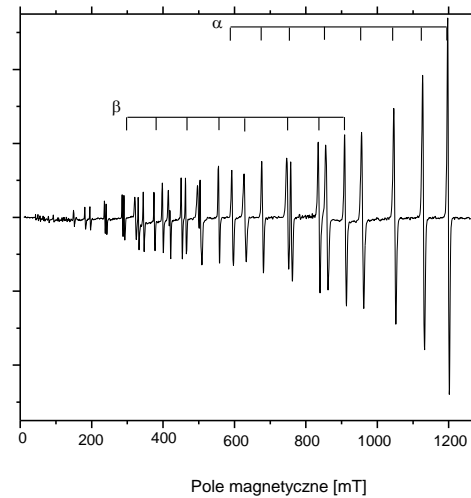




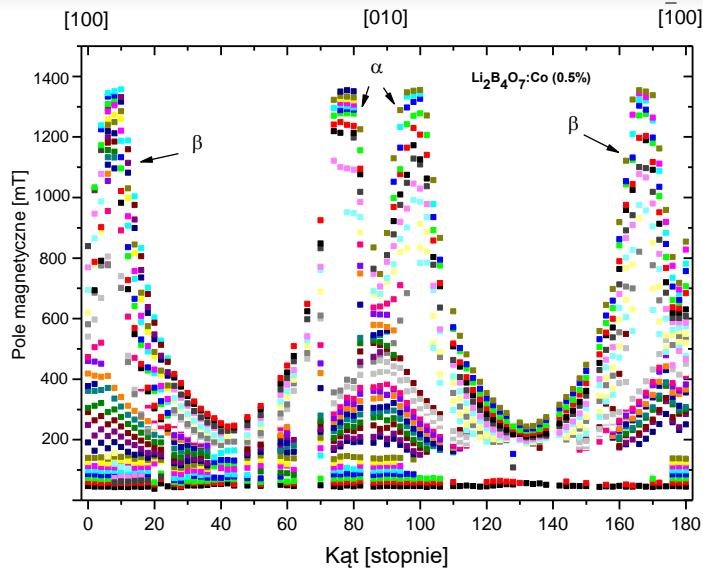
type	$n_0$	$E$ (eV)	$\ln s$
1	$3.903e+04$	$3.183e-02$	$3.436e-01$
2	$2.710e+04$	$7.226e-02$	$2.828e+00$
3	$4.969e+04$	$8.967e-02$	$7.465e-01$



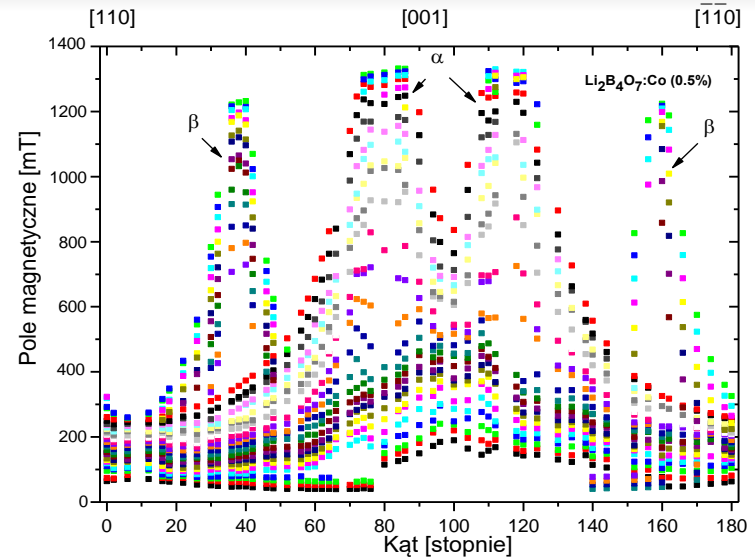
$T=12\text{K}$ ,  $B||[001]$



$A||[110]$ ,  $C||[001]$



Experimental anisotropy, XY plane (AB);  
( $T=4\text{K}$ ,  $\nu=9.45622\div 9.46365\text{ GHz}$ )



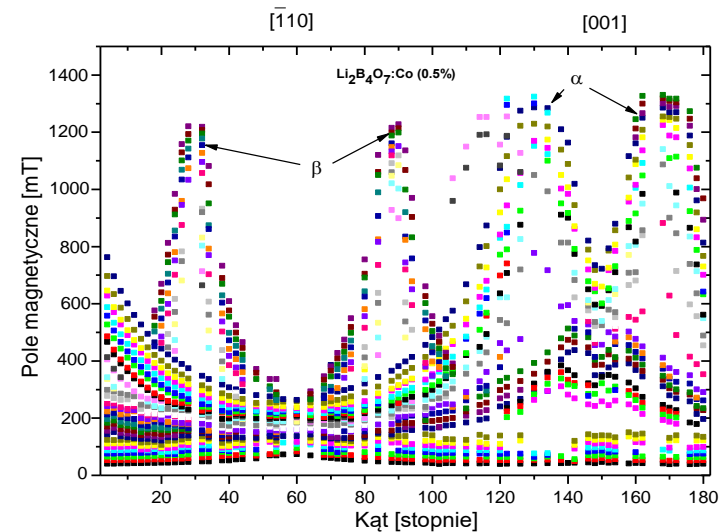
Experimental anisotropy, XZ plane (AC);  
( $T=4\text{K}$ ,  $\nu=9.45811\div 9.46137\text{ GHz}$ )

❖ Experimental anisotropy – two structural nonequivalent paramagnetic centers of  $\text{Co}^{2+}$  ions ( $\alpha$ ,  $\beta$ )

❖ Spin Hamiltonian:

$$H = \mu_B (g_x B_x S_x + g_y B_y S_y + g_z B_z S_z) + A_x S_x I_x + A_y S_y I_y + A_z S_z I_z$$

Experimental anisotropy, ZX plane (BC)  
( $T=4\text{K}$ ,  $\nu=9.45647\div 9.46008\text{ GHz}$ )



## Second-harmonic generation



## 4. Growth of strontium barium niobate: doping with chromium

### Students

Due to its outstanding photorefractive, electrooptic, nonlinear optic and dielectric properties  $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$  is one of the most interesting materials. Potential applications include pyroelectric detection, holographic data storage, surface acoustic wave devices, phase conjugation, quasi-phase-matched second-harmonic generation and electro-optic modulation. SBN crystallize in a tetragonal tungsten bronze structure over a wide solid solution range. All physical properties of SBN are composition dependent ( $x=0.5-0.61$ ).

[4] M.Ulex, R. Pankrath, K. Betzler, *J. Cryst. Growth* 271(2004) 128-133

Pure SBN crystal obtained in the Institute  
of Physics Szczecin University of Technology





## Pure SBN crystal

1:58.10 Czochralski growth. Date: 6/06/2005  
11:58.10 Material:  $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Nb}_2\text{O}_6$  starting weight 178.00 g  
11:58.11 Crucible: TIr40  
11:58.11 Density: 4.40 g/ccm  
11:58.11 Expected parameters of the crystal:  
11:58.11 \*\*\*\*\* Seed Cone Cylinder  
11:58.11 Diameter [mm] 5.5 ----- 20.0  
11:58.11 Length [mm] 10.0 13.6 100.0  
11:58.11 Weight [g] 1.0 8.9 138.2  
11:58.11 Time [h] 3.3 6.0 33.3  
11:58.11 Cone gape [deg]: 80.0  
11:58.11 Crystallization front gape [deg]: 140.0  
11:58.11 constant crystal growth in the middle of the crystal  
11:58.11 as high as 3.00 mm/h

## SBN crystal doped with Cr

10:50.15 Czochralski growth. Data: 7/07/2005  
10:50.15 Material: SBN:Cr0.02% starting weight 175.00 g  
10:50.15 Crucible: TIr40  
10:50.15 Density: 4.40 g/ccm  
10:50.15 Expected parameters of the crystal::  
10:50.15 \*\*\*\*\* Seed Cone Cylinder  
10:50.15 Diameter [mm] 5.5 ----- 20.0  
10:50.15 Length [mm] 10.0 13.6 100.0  
10:50.15 Weight [g] 1.0 8.9 138.2  
10:50.15 Time [h] 4.0 7.2 40.0  
10:50.15 Cone gape [deg]: 80.0  
10:50.15 Crystallization front gape [deg]: 140.0  
10:50.15 constant crystal growth in the middle of the crystal  
10:50.16 as high as 2.50 mm/h

