

## Features of YAG crystal growth in Ar+CO reducing atmosphere

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### Abstract

The influence of the reducing Ar+CO atmosphere on the stages of starting raw material preparation, growth and post-growth annealing of yttrium aluminium garnet,  $Y_3Al_5O_{12}$  (YAG) crystals was studied. The chemical reactions involving CO atmosphere and its impact on the raw material, melt, and crystal composition are determined. Modification of YAG optical properties under the reducing annealing is discussed.

### Introduction.

The majority of artificial crystals are grown from melts in protective atmospheres because of chemical activity of crystallized substances and addition of crucible materials to oxidation under high temperatures. A protective atmosphere, apart of protection of growth crucible, is capable to affect the properties of grown crystals. Oxidation and reduction reactions during the growth process create variety of defects of different types, which influence optical and mechanical properties of crystals [1, 2]. The choice of protective atmosphere is of special importance at crystallization of high melting point oxides from molybdenum (Mo) or tungsten (W) crucibles. Usage of Mo and W crucibles gives a potentially big advantage in crystal production cost compared to those made of iridium (Ir) or platinum (Pt). Usually protective atmospheres consist of argon (Ar), nitrogen ( $N_2$ ), hydrogen ( $H_2$ ), helium (He), carbon oxide (CO), or their mixtures.

Any reactions involving the growth atmosphere are affected by dissociation and evaporation of the melt. The products of melt dissociation are capable to interact with crucible and heat insulation. In many crystal growth processes the graphite heat insulation or graphite heaters are used. The presence of carbon significantly complicates the gas-transport reactions in the Al-O-C system [7, 8, 9, 10].

Among the oxide crystals the behavior of  $\text{Al}_2\text{O}_3$  melt at high temperatures and the role of its dissociation products in gas-transport reactions are the most studied [3, 4, 5, 6]. The influence of atmosphere composition on the growth process and properties of yttrium aluminum garnet,  $\text{Y}_3\text{Al}_5\text{O}_{12}$  (YAG) crystals is less known compared to  $\text{Al}_2\text{O}_3$ . YAG is a widely used host for laser, optical, and scintillation materials. YAG, as well as  $\text{Lu}_3\text{Al}_5\text{O}_{12}$  (LuAG)-based crystals are produced for decades by Czochralski [11, 12] and Bridgman [13, 14] techniques in Mo crucibles or ampules under the reducing  $\text{H}_2$  atmosphere. Recently, the methods to produce rare-earth garnets under the reducing Ar+CO atmosphere by the Horizontal Gradient Freezing (HGF) technique [15] and Czochralski method [16] have been proposed. Luminescent and scintillation properties of YAG:Ce crystals grown from melt under different atmospheres by the HGF technique were analyzed in [15, 17]. The influence of growth atmosphere on the YAG properties was illustrated in [18, 19, 20] and many other works. Meanwhile, there are few data on the interaction of the atmosphere with melt and products of its dissociation.

This work is focused on study of interaction of YAG crystal and melt with the reducing Ar+CO atmosphere with the aim to find the causes of structure defects formation and changes of optical absorption, thus making it possible to improve the properties of various crystals with the garnet structure.

## **Experimental**

Mixture of yttrium oxide ( $\text{Y}_2\text{O}_3$ ) powder and crushed sapphire ( $\alpha\text{-Al}_2\text{O}_3$ ) crystals in the stoichiometric ratio 3:5 was taken as the starting raw materials for YAG crystal growth. To densify the  $\text{Y}_2\text{O}_3$  it was pressed into tablets and sintered inside the graphite thermal insulation under Ar atmosphere at  $1900^\circ\text{C}$  and 0,1 MPa pressure. Crystal growth and further post-growth annealing of YAG was carried out in a conventional RF-heating growth furnace with a graphite heater under Ar+CO atmosphere. Initially the growth camera was filled with ultrapure (6N) Ar. YAG crystals of length up to 80 mm were grown by the Czochralski technique at the rate of 1.5-3 mm/hour from W crucibles. The reducing Ar+CO atmosphere was being formed by the interaction of the graphite heater with residual oxygen adsorbed on growth camera walls and heat insulation, as well as with oxygen evolving from the melt.

The surface composition of studied samples was controlled using a JSM 6390 LVX scanning electron microscope with the MAX<sup>N</sup> X-ray microanalysis system. Structure and phase composition of samples were determined using a Siemens D500 diffractometer. The phases were identified using «EVA» and «SEARCH» software and PDF-1 database.

Absorption spectra of crystals were measured with a Specord 40 spectrophotometer.

## Results and Discussion

### Interaction of CO with Y<sub>2</sub>O<sub>3</sub>.

After the calcination, the Y<sub>2</sub>O<sub>3</sub> tablets shrunk by up to 50% and their surface darkened. The coloration inside the tablets was not uniform and penetrated in different depths. The element composition analysis of dark (1) and light (2) parts of tablet cuts is presented in Table 1. According to the XRD diffraction pattern (Figure 1), the dark parts consist of Y<sub>2</sub>O<sub>3</sub>, and yttrium oxycarbides YO<sub>0,7</sub>C<sub>0,3</sub> and YO<sub>0,45</sub>C<sub>0,55</sub>. This means that Y<sub>2</sub>O<sub>3</sub> intensively interacts with CO atmosphere during the calcination with formation of the stable oxycarbides.

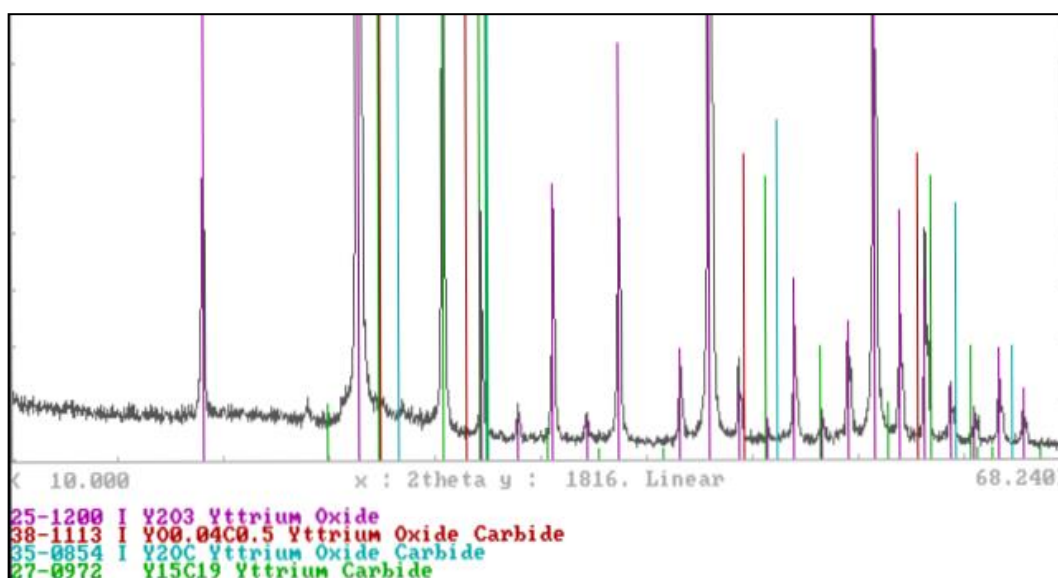


Fig. 1. XRD spectra of dark area in the sintered Y<sub>2</sub>O<sub>3</sub> tablet.

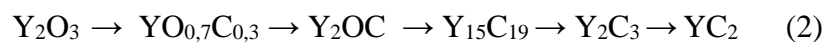
Table 1. Element composition of dark area in the sintered Y<sub>2</sub>O<sub>3</sub> tablet.

	C % at.	O % at.	Y % at.
1	32,4	44,6	23,1
2	17,8	60,6	21,6

Some features of interaction of high-melting point oxides with carbon are summarized in [6]. It is shown that oxides of the IIIa and IIIb subgroups of the Periodic table possess the high thermodynamic stability at elevated temperatures. Under P<sub>CO</sub>=0,1 MPa the temperature of their notable interaction with graphite is above 1900°C. In these conditions the different reactions involving CO occur at the surface of metal oxides: chemisorption, CO disproportionation into CO<sub>2</sub> and C with subsequent partial substitution of oxygen of rare earth oxide by carbon and formation of oxycarbide and carbide phases. The same processes we observed at Y<sub>2</sub>O<sub>3</sub> sintering in CO atmosphere with formation of yttrium oxycarbides in the surface layer:

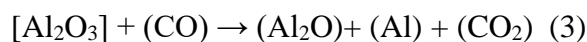


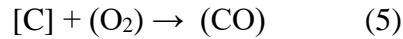
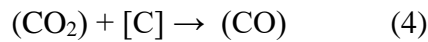
At higher temperatures over 2000°C the kinetic interaction of Y<sub>2</sub>O<sub>3</sub>-CO is more intense with full substitution of oxygen with carbon and formation of yttrium carbide YC<sub>2</sub> phase. Some intermediate phases of this process were determined by XRD analysis (PDF cards NN 41-1105, 38-1114, 35-854, 27-972, 22-988, 11-602):



#### **Interaction of CO with YAG melt.**

Reactions (2) are evidently the basic origin of melt contamination with carbon. YAG melt partially dissociates under the Ar+CO atmosphere. The dissociation products interact with atmospheric CO and form compounds, which are deposited on the thermal insulation and the chamber walls. It is known [6] that during evaporation of Al<sub>2</sub>O<sub>3</sub> in vacuum at 1330 °C without direct contact with carbon the atmosphere contains Al, AlO, Al<sub>2</sub>O, Al<sub>2</sub>O<sub>2</sub>O, O<sub>2</sub>, CO, CO<sub>2</sub>. The ratio between basic molecular forms Al:AlO:Al<sub>2</sub>O of gas is 100:3:62. The interaction with CO follows the reactions:





Without direct contact of aluminium oxide with carbon under  $P_{\text{CO}} = 0,1 \text{ MPa}$  and  $1900 \text{ }^\circ\text{C}$  the  $\text{Al}_4\text{C}_3$  phase is deposited at the graphite surface as the product of the graphite interaction with vapors of aluminium and its higher oxides [5].

Analysis of the deposit reveals the sequence and the mechanisms of these reactions, and their influence on the crystal and melt properties. In our experiments the crystal growth process takes about 100 hours. Over this period the deposit with dendritic morphology containing 9-15% wt% of C, 9-26% wt% of Al, 5-30% wt% of Si, and  $55 \div 60$  wt% of oxygen was formed (the spread of values corresponds to different experiments). The silicon contamination was attributed to alumina ceramics containing 0.1 wt% of silicon. Yellow dendrites and needles consisting of 55 % of Al and 45 % of C (composition nearly corresponds to silicon carbide) were deposited at graphite thermal insulation.

The yttrium compounds were not found in condensates and deposits species. This confirms the results [5] pointing to the absence of gaseous Y-containing products of  $\text{CO}-\text{Y}_2\text{O}_3$  interaction. Hence, while yttrium oxide is in mixture with alumina, only more active  $\text{Al}_2\text{O}_3$  interacts with CO.

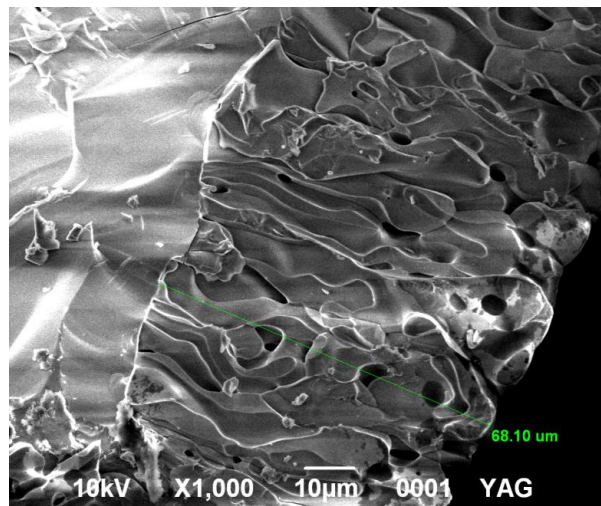


Fig. 2. Electronic microscope view of the porous  $\text{Y}_2\text{O}_3$  layer formed on YAG surface.

Surface layer of melt recrystallized at the crucible walls became porous with crystalline YAG phase underneath (Fig. 2). This layer was formed by interaction with CO atmosphere. For the period of 100 hours its thickness reached  $68 \text{ } \mu\text{m}$ . The Al:Y ratio in this layer is 3,8:4,2 pointing at the significant lack of Al. In the crystalline phase under the porous layer the Al:Y

ratio is stoichiometric (5:3). The rate of this process depends on temperature and CO concentration. CO not reacts with  $Y_2O_3$  under the  $Al_2O_3$  presence, because the first is more stable thermodynamically. Therefore, the melt stoichiometry during the crystal growth shifts to yttrium oxide excess due to evaporation of alumina and its interaction with CO atmosphere.

### Interaction of CO with YAG crystal.



Fig. 3. Photo of as-grown YAG crystal.

The crystals were grown over the period of several days under  $\sim 1800$  °C and Ar+CO atmosphere. As the result, the mat porous film was formed on the crystal upper parts, which are longer exposed to such conditions (Fig. 3).

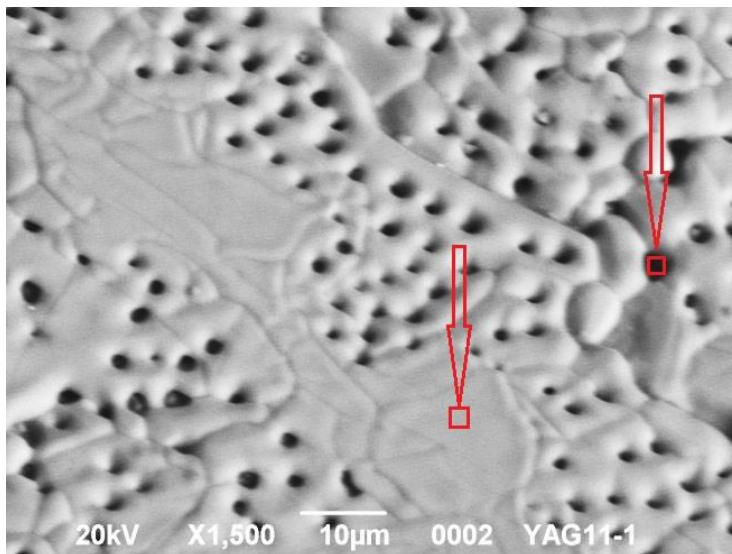


Fig. 4. Mat surface of as-grown YAG crystal. The arrows and squares depict the light and dark areas where elements composition was determined.

Table 2. Element composition of crystal surface.

	O at.%	Al at.%	Y at.%
light area in Fig. 4	58	25,3	16,7
dark area in Fig 4	62,5	19,8	17,7
stoichiometric YAG	60	25	15

The element composition of crystal upper part surface (Fig. 4) is presented in Table 2. The surface after the interaction with CO contains less Al compared to the stoichiometric garnet composition. The decrease of Al concentration may result in formation of  $YAlO_3$  perovskite phase with another lattice parameters and in appearance of cracks.

Therefore, the prolonged interaction of CO with crystal surface results in the etching of oxygen and aluminum and the change of element composition and morphology of the surface layer. These effects in combination with diffusion processes affect crystal bulk composition and its optical properties.

#### **Thermal annealing in the reducing atmosphere**

The specific feature of YAG crystals grown in CO atmosphere is the yellow-brown coloration becoming gradually deeper towards the bottom of crystals (see Fig. 3). The strongest absorption bands peaked at 255, 300, and 375 nm (Fig. 5) are attributed to various defects (impurities, antisite defects, etc) [21, 22, 23]. The crystal coloration was eliminated and the absorption bands were diminished by several times after the thermal annealing of polished samples under the Ar+CO atmosphere (0,1 MPa pressure) and temperature 1350-1450°C. Herein the visible band absorption was decreased down to  $0.2 - 0.7 \text{ cm}^{-1}$  (the light reflection at the sample surfaces is not deduced from these values). So the additional thermal annealing in CO atmosphere significantly improves YAG optical characteristics. The causes of absorption decrease after annealing in the reducing atmosphere need for further study.

Meanwhile, the prolonged thermal treatment under the high temperature resulted in crystal surface etching, the same as at crystal growing. After the longer (20 hours) thermal treatment under higher temperature (1700°C) the sample surface became mat. The defect film with the composition  $Y_{4.4}Al_{3.6}O_{12}$  was formed at the polished surface and looked like that observed at the as-grown crystal surface (see Figs. 3, 4). According to XRD data, in the process of interaction with CO the crystal surface was depleted with Al and oxygen so heavily that the film containing

YAlO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> was formed at the surface. So the high temperature accelerates the chemical reactions (3) – (5) at the crystal surface with formation of CO<sub>2</sub>, Al<sub>2</sub>O, and their evaporation.

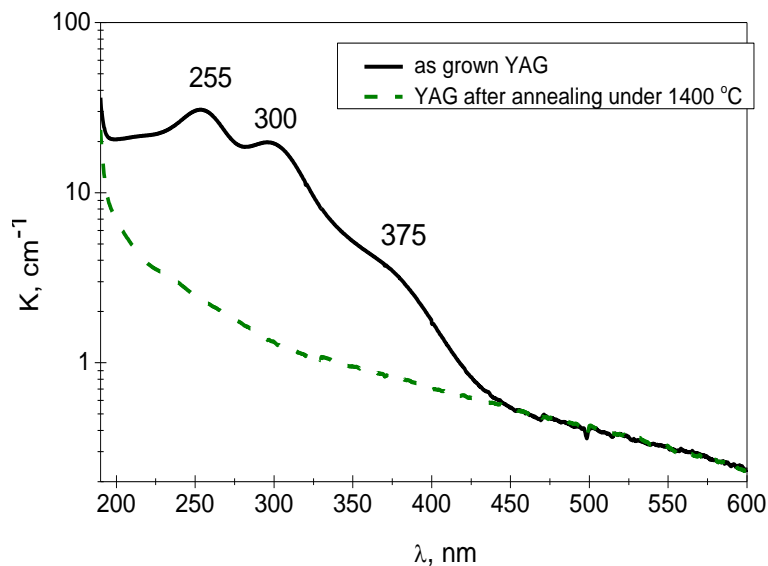


Fig. 5. Absorption spectra of as grown and heat treated YAG crystal.

## Conclusions

The reducing CO atmosphere actively participates in gas transport reactions proceeding during the raw material sintering, crystal growth, and post-growth thermal treatment of YAG crystals. During the raw material high-temperature sintering of the stoichiometric mixture of Y<sub>2</sub>O<sub>3</sub> powder and ground parts of Al<sub>2</sub>O<sub>3</sub> crystal, CO interacts with yttrium oxide with substitution of oxygen by carbon and formation of non-volatile yttrium oxycarbides and carbides. At crystal growth, CO interacts with YAG melt with formation of carbides and oxycarbides depositing on the thermal insulation. The absence of yttrium-containing compounds in the deposits certifies a better chemical stability of Y<sub>2</sub>O<sub>3</sub> under these conditions. While Al<sub>2</sub>O<sub>3</sub> remains in YAG raw material, melt, or crystal, yttrium oxide not reacts with CO and does not form any chemical products.

The prolonged interaction of CO results in surface depletion with oxygen and aluminum, and the change of morphology and structure of the surface layer. Meanwhile, the colorated YAG crystal grown under the Ar+CO atmosphere unexpectedly bleaches after post-growth annealing under the same atmosphere. The latter effect should be studied in more detail by comparison of YAG crystals grown under different conditions.



## *Examples:*

Reference to a journal publication:

[1] J. van der Geer, J.A.J. Hanraads, R.A. Lupton, The art of writing a scientific article, *J. Sci. Commun.* 163 (2010) 51–59.

## **References**

- [1] Kh. Bagdasarov, The problems of high-temperature crystallization, *Prog. in Cryst. Growth and Charact.* 16 (1988) 59–80.
- [2] S. Nizhankovskiy, E. Krivonosov, V. Baranov, A. Budnikov, V. Kanishchev, L. Grin', G. Adonkin, Optical homogeneity of Ti:Sapphire crystals grown by horizontal directional solidification, *Inorg. Mater.* 48 (2012) 1111-1114.
- [3] A. Vodop'yanov, G. Kozhevnikov, S. Baranov, Interaction of refractory metal oxides with carbon, *Russian Chem. Rev.* 57 (1988) 1419-1433.
- [4] Yu. Folomeikin, I. Demonis, E. Kablov, S. Lopatin, V. Stolyarova, Mass spectrometric study of evaporation of alumina in the presence of carbon, *Doklady Chem.* 399 (2004) 257–260.
- [5] Yu. Folomeikin, S. Lopatin, V. Stolyarova, Vaporization of aluminum oxide in neutral and reductive conditions, *Russian J. Gen. Chem.* 76 (2006) 1693-1697.
- [6] P. Sitnikov, S. Lopatin, Yu. Ryabkov, V. Grass, Thermal stability of aluminum oxycarbides, *Russian J. Gen. Chem.* 74 (2004) 989 – 992.
- [7] D. Kostomarov, Kh. Bagdasarov, S. Kobzareva, E. Antonov, Chemical processes and composition of the gas and solid phases in the Al<sub>2</sub>O<sub>3</sub>–Mo system in the temperature range 2327–2500 K, *Cristallogr. Rep.* 53 (2008) 663–670.
- [8] D. Kostomarov, Kh. Bagdasarov, S. Kobzareva, E. Antonov, The chemical action of oxygen on a heater during growth of refractory oxide crystals from melt, *Cristallogr. Rep.* 54 (2009) 89-93.
- [9] A. Dan'ko, M. Rom, N. Sidelnikova, S. Nizhankovsky, A. Budnikov, L. Grin, Transformation of the corundum structure upon high-temperature reduction, *Cristallogr. Rep.* 53 (2008) 1112-1118.
- [10] D. Kostomarov, Kh. Bagdasarov, S. Kobzareva, E. Antonov, Thermodynamic analysis of the W-Al<sub>2</sub>O<sub>3</sub> system near the melting temperature of Al<sub>2</sub>O<sub>3</sub>. I. Evolution of the system in the pressure range of 10<sup>-1</sup>÷10<sup>-4</sup> bar, *Crystallogr. Rep.* 55 (2010) 318-323.

- [11] Ji. Kvapil, Jo. Kvapil, B. Perner,  $O^-$  centre formation in YAG crystals doped with rare earth ions, *Cryst. Res. and Technol.* 10 (1975) 161-165.
- [12] Ji. Kvapil, Jo. Kvapil, B. Manek at all, Czochralski growth of YAG:Ce in a reducing protective atmosphere, *J. Cryst. Growth.* 52 (1981) 542.
- [13] A. Petrosyan, Crystal growth of laser oxides in the vertical Bridgman configuration, *J. Cryst. Growth.* 139 (1994) 372-392.
- [14] A. Petrosyan, K. Ovanesyan, R. Sargsyan, G. Shirinyan, D. Ablter, E. Auffray, P. Lecoq, C. Dujardin, C. Pedrini, Bridgman growth and site occupation in LuAG:Ce scintillator crystals, *J. Cryst. Growth.* 312 (2010) 3136–3142.
- [15] S. Nizhankovsky, A. Danko, V. Puzikov, Yu. Savvin, A. Trushkovsky, S. Krivonogov, Optical and luminescence characteristics of YAG Ce crystals grown by horizontal directed crystallization in reducing gas medium, *Func. Mat.* 15 (2008) 546-549.
- [16] P. Arhipov, S. Tkachenko, S. Vasyukov, M. Biatov, O. Sidletskiy, P. Mateychenko, E. Bryleva, Features of YAG Czochralski growth in Mo crucibles, *Func. Mat.* 19 (2014) 472-475.
- [17] Yu. Zorenko, V. Savchin, V. Gorbenko, T. Voznyak, T. Zorenko, V. Puzikov, A. Dan'ko, S. Nizhankovsky, Luminescence and scintillation properties of Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce single crystals and single-crystal films, *Phys. of the Solid State.* 53 (2011) 1620-1625.
- [18] Y. Dong, G. Zhou, J. Xu, G. Zhao, F. Su, L. Su, H. Li, J. Si, X. Qian, X. Li, J. Shen, Color centers and charge state change in Ce:YAG crystals grown by temperature gradient techniques, *J. Cryst. Growth.* 286 (2006) 476–480.
- [19] Ji. Kvapil, Jo. Kvapil, B. Manek, B. Perner, Czochralski growth of YAG:Ce in a reducing protective atmosphere, *J. Cryst. Growth.* 52 (1981) 542-545.
- [20] D. Zhang, L. Su, H. Li, X. Qian, J. Xu, Characteristics and optical spectra of V:YAG crystal grown in reducing atmosphere, *J. Cryst. Growth.* 294 (2006) 437–441.
- [21] M. Springis, A. Pujats, J. Valbis, Polarization of luminescence of colour centres in YAG crystals, *J. Phys. Condens. Matter.* 3 (1991) 5457-5462.
- [22] H. Tippins, Charge-transfer spectra of transition-metal ions in corundum, *Phys. Rev. B.* 1 (1970) 126-135.
- [23] J. Blum, H. Tuller, R. Coble, Temperature dependence of the iron acceptor level in aluminum oxide, *J. Am. Ceram. Soc.* 65 (1982) 379-382.