

Structure defects and properties of fianites

*V.P.Pashchenko, A.M.Prudnikov, V.N.Varyukhin,
N.G.Kisel, G.N.Bogachova*, V.M.Ishchuk***

A.Galkin Donetsk Institute for Physics and Engineering,
National Academy of Sciences of Ukraine,
72 R.Luxemburg St., 83114 Donetsk, Ukraine

*M.Tugan-Baranovsky Donetsk University for Economics and Trade,

**Institute for Single Crystals, National Academy of Sciences of Ukraine,
60 Lenin Ave., 61001 Kharkiv, Ukraine

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X-ray structure examination and spectroscopy, as well as hydrostatic method and fluorescence have been used to investigate single crystals of fianites differing in colors, doped with yttrium and rare earth ions. The crystal lattice defects, microhardness, absorption spectra and fluorescence of those fianites have been determined. It is shown that mechanical (density, hardness) and optical (color, absorption, fluorescence) properties of fianites depend on rare-earth microimpurities (Ce, Eu) and structure defects.

Рентгеновскими структурным и спектральным, гидростатическим и флюоресцентным методами исследованы легированные иттрием и редкоземельными ионами фианитовые монокристаллы, отличающиеся цветом. Определена дефектность кристаллической решетки этих фианитов, их микротвердость, спектры поглощения и флюоресценции. Показано, что механические (плотность, твердость) и оптические (цвет, поглощение, флюоресценция) свойства фианитов зависят от редкоземельных микропримесей (Ce, Eu) и дефектности структуры.

Among modern materials for electronics and jewelry technology, fianites (single crystals on the ZrO_2 basis) are of great importance. The usage field of these metal oxides is broadened continuously due to special mechanical (high strength and hardness), thermal (refractoriness), electric (ionic conduction), optical (color, transparency, fluorescence) properties thereof. Recently, fianites find use in microelectronics, in particular, in laser engineering. Zirconia of cubic modification is known for its improved complex of properties; it is doped with CaO, Y_2O_3 or rare-earth elements to stabilize the cubic modification [1–3]. In contrast to the majority of works that were done on polycrystal ceramic samples which do not allow to research the materials deeply enough, we have studied the single crystals. In spite of numerous investiga-

tions of doped ceramic and even single crystal samples of ZrO_2 , the nature of the doping effect with ions of different valence on the structure defects and properties of such metal-oxide solid solutions is still open for discussion. The purpose of this work is to study the crystal lattice defects and its effect on physical properties of fianites doped with yttrium and containing rare-earth impurities.

The fianite single crystals were got at the "Fianite" works of the "Ferroceram" scientific and production company (Belaya Tserkov). The single crystals were grown using an improved technology in the "Fianite" unit at 2000°C using the garnissage method in a cool container under argon atmosphere, the raw blend being heated by an electron-plasma beam up to 2600–2700°C. Three series of samples were obtained doped with yttrium (8 % mol.) and differing in

their admixture composition and color (1 — colorless, 2 — pale pink, 3 — red). The coloration was obtained by Eu (Sample 2) and Ce (Sample 3) microdopants.

The following methods were used in the investigation:

1) x-ray structure examination using a DRON-3 unit to determine the phase composition (3 % error), the type of crystal lattice, its parameters (0.05 % error) and x-ray density ρ_r (0.5 % error);

2) x-ray microanalysis using a JSM-820 scanning microscope with the Link-10000 extension to determine the chemical composition (0.5 % error);

3) hydrostatic weighing to determine the sample hydrostatic density ρ_h (0.3 % error);

4) optical spectroscopy using an DFS-24 automated spectrometer with LPM-11 laser as the excitation source ($\lambda = 441.6$ nm) to record the absorption and luminescence spectra;

5) hardness determination by the Vickers method using a diamond pyramid.

According to the x-ray structural data, all the samples were single-phase ones with cubic lattice, the lattice parameters being changed slightly within a limits of 5.151 to 5.153 Å. For the three single crystals differing in color and composition the Table below presents the values of x-ray (ρ_r) and

hydrostatic (ρ_h) densities. The molar formula calculated basing on comparison of these densities for different defect models, taking into account the composition determined by x-ray microanalysis, and electric neutrality of the unit cell containing 4 formula units are given in the Table.

The electric neutrality and defects of crystal lattice for molar formula and unit cell at different-valence substitution by Y^{3+} ions for Zr^{4+} , taking impurities into account, were calculated for three models:

1) formation of anion vacancies — $Zr_{1-2x}^{4+} Y_{2x}^{3+} O_{2-x}^{2-} V_x^{(a)}$;

2) cation inclusion — $Zr_{1-3y}^{4+} Y_{4y}^{3+} O_2^{2-}$;

3) combined defects, when the lattice is incomplete in both the cation and anion sublattices.

From comparison of the x-ray density with the density experimentally measured by hydrostatic method follows obviously that the model where the lattice contains only anionic vacancies (model 1) is invalid. The model with the lattice containing only included cations without anion vacancies (model 2) is even more unacceptable.

All experimental and calculated data are found to be compatible in the frame of third, combined, model, where the real structure contains mostly anion vacancies (V^a), formed during the single crystal growth because of thermal dissociation and

Table. Densities and molar formulae of defect crystal structure of fianites

Sample No.	Color	Hydrostatic density, ρ_h , g/cm ³	x-ray density, ρ_r , g/cm ³	Molar formulae for different types of crystal lattice defects
1	Colorless	6.00	5.86	1) $Zr_{0.76}^{4+} Y_{0.24}^{3+} O_{1.88}^{2-} V_{0.12}^{(a)}$
			6.24	2) $Zr_{0.81}^{4+} Y_{0.26}^{3+} O_{2.00}^{2-}$
			6.03	3) $Zr_{0.78}^{4+} Y_{0.25}^{3+} O_{1.93}^{2-} V_{0.07}^{(a)}$
2	Pale pink	5.92	5.86	1) $Zr_{0.76}^{4+} Y_{0.24}^{3+} O_{1.88}^{2-} V_{0.12}^{(a)}$
			6.24	2) $Zr_{0.81}^{4+} Y_{0.26}^{3+} O_{2.00}^{2-}$
			5.92	3) $Zr_{0.77}^{4+} Y_{0.24}^{3+} O_{1.90}^{2-} V_{0.10}^{(a)}$
3	Red	5.95	5.84	1) $Zr_{0.69}^{4+} Y_{0.20}^{3+} Ce_{0.07}^{4+} O_{1.86}^{2-} V_{0.14}^{(a)}$
			6.33	2) $Zr_{0.74}^{4+} Y_{0.22}^{3+} Ce_{0.08}^{4+} O_{2.00}^{2-}$
			5.95	$Zr_{0.70}^{4+} Y_{0.21}^{3+} Ce_{0.06}^{4+} Ce_{0.01}^{3+} V_{0.02}^{(c)} O_{1.85}^{2-} V_{0.15}^{(a)}$

Variants of of structure defect types:

1) anion vacancies ($V^{(a)}$);

2) included cations;

3) combined defects — incompleteness of the anion ($V^{(a)}$) and cation ($V^{(c)}$) lattices.

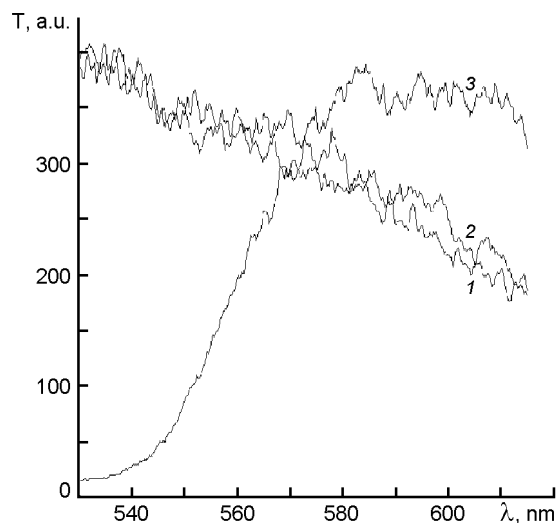


Fig. 1. Fragments of optical absorption spectra for fianite samples Nos. 1, 2, 3 at $T = 300$ K.

partially included cations because of cyclic changes of gas and thermal conditions at heating, annealing and cooling of samples [2, 4, 5]. In those conditions, the oxygen non-stoichiometry changes as well as the valence of ions, for example, of cerium in the third sample. The specific peculiarity of the second, pale pink, sample in comparison with the first, colorless, one is the fact that the lattice of the second sample contains a higher concentration (5 %) of anion (oxygen) vacancies and a lowered one of cation defects. The lower concentration of defects (3.5 %) in the colorless fianite lattice and absence of other admixtures seems to be the transparency thereof. As to the pale pink fianites, the increased number of defects in the lattice and probably microadmixture being not revealed by the x-ray method determine the color.

These explanations, however, are to be confirmed additionally and the causes of higher amount of defects in the lattice of these fianites and of their pale pink color are to be found. For this purpose, we have studied additionally the light absorption and luminescence [6]. Fig. 1 presents the fragments of absorption spectra of the three single crystals at $T = 300$ K. It is seen that the spectra of the first two samples are similar to one another and no absorption band is observed in the 520–620 nm region at the usual testing geometry. As to third sample, an intense absorption is observed at $\lambda < 560$ nm. Nevertheless, the higher number of defects in the crystal lattice of the

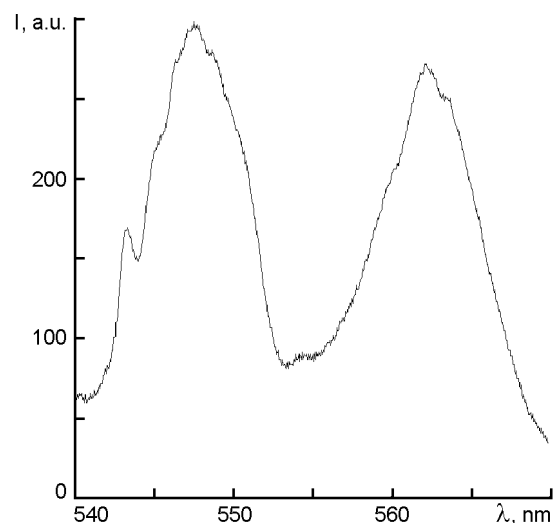


Fig. 2. Eu^{3+} luminescence spectrum for fianite sample No.2 at $T = 300$ K (${}^5D_1 \rightarrow {}^7F_0$ transition).

second sample is insufficient to explain its pale pink color. It can be supposed that the color can be associated with the admixture of erbium, europium, or holmium [7, 8]. But according to the x-ray microanalysis data, these rare-earth elements (error being taken into consideration) were not detected.

The photoluminescence investigation has shown an intense luminescence in this sample. Fig. 2 presents the photoluminescence spectrum in the 540–570 nm region. In this field both the Er^{3+} and Eu^{3+} ions are radiating. To elucidate the nature of luminescence in the sample No.2 and the element causing it, the absorption spectra presented in Fig. 1 and 3 have been analyzed. As Fig. 1 shows that, at the usual testing geometry, the line being characteristic of Er^{3+} and Eu^{3+} is not observed, the more accurate compensation method was employed [9]. It allowed to detect the low-intensity lines. Using this method, we detected a weak band characteristic of the Eu^{3+} ion in the absorption spectrum of the sample No.2 (Fig. 3). So, the fianite sample No.2 contains a small amount (~1 %) of Eu^{3+} impurity which causes its pale pink color and higher number of defects in the crystal lattice, which was formed because of the probable valence changes ($\text{Eu}^{3+} \rightarrow \text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$) during the single crystal growth [7, 9, 10].

The complex absorption spectrum of the red sample No.3 (Fig. 1) agrees completely with Ce^{4+} presence therein. Then the higher number of defects in the crystal lattice of

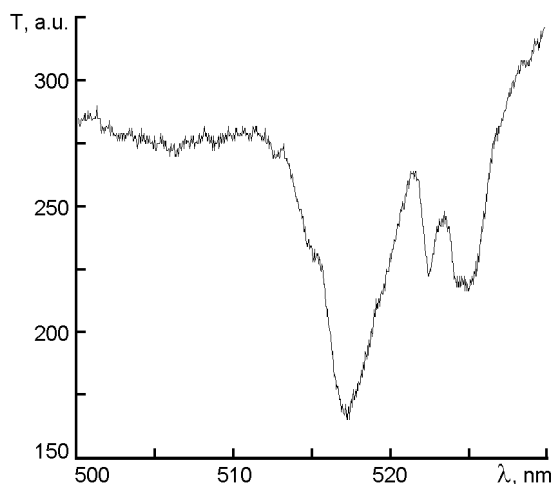


Fig. 3. Fragment of Eu^{3+} absorption spectrum for fianite sample No.2 at $T = 300$ K (${}^7F_0 \rightarrow {}^5D_1$ transition).

this sample is caused by the present Ce^{4+} ions which were found in the amounts shown in the Table by x-ray microanalysis and optical spectroscopy. The ability of cerium ions to change the valence ($\text{Ce}^{4+} \rightarrow \text{Ce}^{3+} \rightarrow \text{Ce}^{4+}$) in the course of heating, growing, and cooling of the single crystals causes the increased number of defects, the cation ones in our case, but mainly the anion vacancies, the concentration thereof attaining 7.5 %.

The effect of impurities and defects on the mechanical properties of fianites is of a special interest. The Vickers hardness measurements have shown that the rare-earth impurities results in the fianite microhardness increase while passing from the first sample to the third one: for the first sample, $\text{HV} = 13000$ mH/mm^2 , for the second, $\text{HV} = 14000$ mH/mm^2 , and for the third, $\text{HV} = 18000$ mH/mm^2 . This effect of rare-earth impurities on hardness is consistent with the data from [1, 2]. Then the reduction of transparence and especially increase of hardness accompanying the growing concentration of rare-earth impurities and structure defects can be explained by the dislocation hardening [11, 12]. Less essential differences in crystal lattice parameters ($\Delta a/a = 0.4$ %) for the three investigated samples, as compared to differences in the average ionic radius [13] of cations ($\Delta r/r = 0.8$ %) allow to assume that there is a deviation of the ion and vacancy distribution from the statistical one resulting in formation of chains or in-plane nanostructure defects [14]. The formation possibility of such

mesoscopic defects in non-stoichiometric metal oxides has been confirmed in [15, 16].

Thus, by the complex investigation of yttrium-doped fianites of different composition and color, the intrinsic and extrinsic composition, defects of crystal lattice and the properties thereof have been determined. It has been shown that the color of fianites, microhardness, absorption spectra and luminescence depend on impurities and structure defects caused thereby. The defects and impurities have been supposed to interact under formation of cluster type nanostructure inhomogeneities.

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Дефектність структури та властивості фіанітів

***В.П.Пащенко, А.М.Прудніков, В.М.Варюхін,
М.Г.Кисіль, Г.М.Богачова, В.М.Іщук***

Рентгенівськими структурним і спектральним, гідростатичним і флюоресцентним методами досліджено леговані ітрієм і рідкісноземельними іонами фіанітові монокристали, які відрізнялися кольором. Визначено дефектність кристалічної ґратки цих фіанітів, їх мікротвердість, спектри поглинання та флюоресценції. Показано, що механічні (густина, твердість) та оптичні (колір, поглинання, флюоресценція) властивості фіанітів залежать від рідкісноземельних мікродомішок (Ce, Eu) і дефектності структури.