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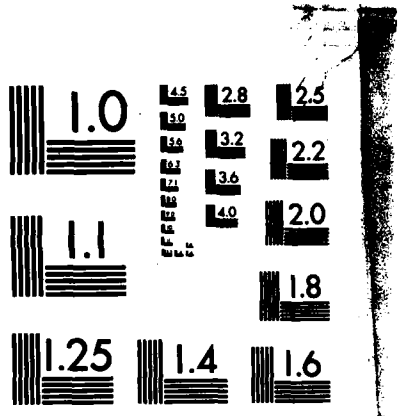

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FOREIGN TECHNOLOGY DIVISION

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($Gd_{3-x}Ca_xGa_{5-x}Zr_xO_{12}$)

by

Z. Luohui, B. Naizhi, et al

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EDITED TRANSLATION

FTD-ID(RS)T-1090-83 10 August 1983

MICROFICHE NR: FTD-83-C-000969

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English pages: 11

Source: Guisuanyan Xuebao, Vol. 10 Nr. 3, September 1982, pp. 332-337

Country of origin: China
Translated by: LEO KANNER ASSOCIATES
F33657-81-D-0264
Requester: FTD/TQTR

PREPARED BY:

TRANSLATION DIVISION
FOREIGN TECHNOLOGY DIVISION
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THE GROWTH AND MEASUREMENT OF SINGLE-CRYSTAL DOPED GGG ($Gd_{3-x}Ca_xGa_{5-x}Zr_xO_{12}$)

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Submitted 25 September 1981

The article deals with the growth and perfection of single crystals GGG doped with calcium and zirconium [called GGG(Ca, Zr) for short] and the phenomena of its constitutional supercooling. By chemical analysis and X-ray lattice parameter determination of the grown crystals, the segregation coefficients of CaO and ZrO_2 from the melt and the influences of CaO and ZrO_2 contents on the lattice parameter of the crystal have been determined. In the meantime, the similarities and differences in the growth and some of the properties of the single crystals of pure and doped GGG have been found out.

Experimental results not only show that, during the growth, the control of perfection of GGG(Ca, Zr) single crystals is more difficult than that of pure GGG crystals but also indicate that doped GGG(Ca, Zr) are liable to produce colour center after irradiation.

I. Foreword

In recent years, some development[(1-3)] proceeded in large lattice single-crystal doped gadolinium gallium garnet (GGG) for making into base plates of magneto-optical materials. The paper is a follow-up of the work

[1]Hu Boqing, Zhou Tang and Zhang Youlong assisted in determination of optical transmissions of crystals; Che Guangcan assisted in determination of lattice sizes of samples; and Zhang Gannan was concerned with this work. The authors express gratitude to the above mentioned persons.

of D. Mateika et al[1], similarly using CaO to replace Gd_2O_3, and ZrO_2 to replace Ga_2O_3; in other words, this uses Ca to partially replace Ga at the dodecahedral position, and Zr to partially replace Ga at the octahedral position for the growth of single-crystal GGG doped with calcium and zirconium (briefly called GGG(Ca, Zr)). In addition, observations were made on the integrity, lattice size, segregation coefficients and other properties (such as optical transmission) with the purpose of further understanding single-crystal GGG(Ca, Zr). Moreover, studies were performed on growth of single-crystal doped GGG.

II. Experiments

(A) Crystal growth

The method used for growth of single-crystal GGG(Ca, Zr) is the same for growth of single-crystal GGG(Nd), including several steps of compounding materials, growth, etc.[4] The compounding ratios of raw materials were $Gd_{3-x}Ca_xGa_{5-x}Zr_xO_{12}$, primarily with x=0.45. Purities of raw materials were: Ga_2O_3 99.999 percent, Gd_2O_3 99.95 percent, and $CaCO_3$ and ZrO_2 are A.R. Raw materials were baked before weighing; then the materials were weighed in compounding gram-mole ratios. Later, the materials were ground and mixed thoroughly, compressed tightly, and clinkered.

The crystal growth was by the extraction method; the iridium crucible used for high frequency induction heating of fused materials was not much different from the crucible for growth of GGG single crystals. Generally, the growth rate was 2 to 3 mm/h; the segregation coefficients of CaO and ZrO_2 in fused materials at different growth rates were determined.

(B) Observation of crystals

Observations on integrity of the growth of single crystals (Fig. 1) were made, mainly in observing iridium inclusions under a microscope, and

the stress figures showing dislocations under perpendicular polarized light. Chemical analyses were made of samples of fused materials remaining in the crucible, head and tail portions of crystals, and raw materials; thus, the contents of CaO and ZrO_2 in the samples were determined. In addition, atomic absorption spectrum and spectrophotometric methods were used to determine the CaO and ZrO_2 contents.

Fig. 1. Grown single-crystal GGG(Ca, Zr) 1x

The powder X-ray diffraction method was used to determine lattice constants; samples of single crystals were ground into powder and a wide angle Guinier was used to photograph the powder using the symmetric back reflection method. Later, irradiation with CuK_{alpha} was conducted; the precision of determination was $\pm$0.0004Å. At the same time, the lattice sizes of these samples were determined using the X-ray diffraction method. The determination results of both methods were quite consistent with each other.

Determinations of optical transmission curves of single-crystal GGG(Ca, Zr) and pure GGG were made; the range of wavelengths was from 0.25 (mu)m (in the ultraviolet sector) to the visible light sector, and then continued to the long wave sector, until the infrared zone of 25 (mu)m. These determinations were conducted[2] using three different spectrophotometers. Then, the whole curve was connected.

[2]Data here were provided by Hu Boying, Zhou Tang and Zhang Youlong.

In addition, ultraviolet irradiations were performed on single crystals of GGG(Ca, Zr) and GGG. The irradiation was made by exposing the crystals for 1 hour under a 500-800W ultraviolet lamp. Then, the formation of color cores was observed before determination of transmission curves from ultraviolet to infrared zones. Similarly, gamma irradiation tests were conducted and post irradiation transmission curves determined on the two above-mentioned samples.

III. Experimental Results and Discussions

(A) Integrity of crystals

Two defects in GGG that are not easy to control are iridium inclusions and dislocations. In growth experiments, when the growth rate was 2.5 mm/h, single crystals with iridium inclusions were obtained; the reason is possibly that the slow growth rate GGG can envelop iridium particles of large linear dimensions, exceeding the critical dimension[5] of being enveloped. In addition, when ZrO_2 is used to replace Ga_2O_3, the decomposition and evaporation of Ga_2O_3 in fused materials may be reduced.

The observation result of dislocations in single-crystal GGG(Ca, Zr) is explained by the fact that the main method of controlling dislocation is similarly the elimination of inclusions and controlling of plane boundary growth. In addition, the observation results explain the fact that the overall integrity (including constitutional supercooling) is relatively more difficult to control for doped GGG than for pure GGG single crystals. While comparing under perpendicular polarized light (with microscope) the growth stripes of pure GGG and doped GGG, it was discovered that the lining degree of growth stripes of doped crystals was relatively greater.

(B) Analyses of crystal constituents and lattice constants

Based on Table 1, the relationship between the lattice constants of single crystals GGG(Ca, Zr) and contents of CaO and ZrO_2 is shown in Fig. 2. We can see from Table 1 and Fig. 2, on increasing the contents of CaO and

ZrO_2 in crystals, the lattice constants of crystals also increase; the lattice constants of the tail portion of a crystal increase approximately by 0.008Å. This is because the segregation coefficients of CaO and ZrO_2 are smaller than 1; in the case of low weight ratios between fused materials and crystals, relatively significant variation in constituents is induced. Therefore, in order to have small variation in doped constituents in crystals, larger capacity crucibles should be used for growth of crystals with smaller weights. Thus, during the initial growth period and the later period, the doped constituents are comparatively constant, thus ensuring the mixing homogeneity of crystals. Figure 2 is a coordinate diagram with contents of CaO and ZrO_2 as the abscissa and the lattice constants as the ordinate. In ideal cases, by using appropriate coordinate ratios of CaO/ZrO_2, the coordinate points of CaO can coincide with the corresponding points of ZrO_2; however, in real cases these two groups of coordinate points are unable to coincide. This indicates that there are errors in constituent analysis.

Table 1. Data of chemical composition and lattice constant of single-crystal $Gd_{3-x}Ca_xGa_{5-x}Zr_xO_{12}$.

Sample	CaO (%)	ZrO_2 (%)	Segregation coefficient		Corresponding lattice constant (Å)
			CaO	ZrO_2	
80-CZ 4					
Top of the crystal*	0.97	2.43	0.71	0.82	12.4090
Raw material	1.36	2.98			
End of the crystal*	1.26	2.91	0.68	0.77	12.4162
Residue of the melt	1.85	3.80			
80-CZ 5					
Top of the crystal*	0.99	2.37	0.73	0.80	12.4089
Raw material	1.36	2.98			
End of the crystal*	1.52	4.00	0.60	0.82	12.4169
Residue of the melt	2.52	4.86			

* Samples of the top and the end part of the crystal have been taken approximately 1cm from both ends.

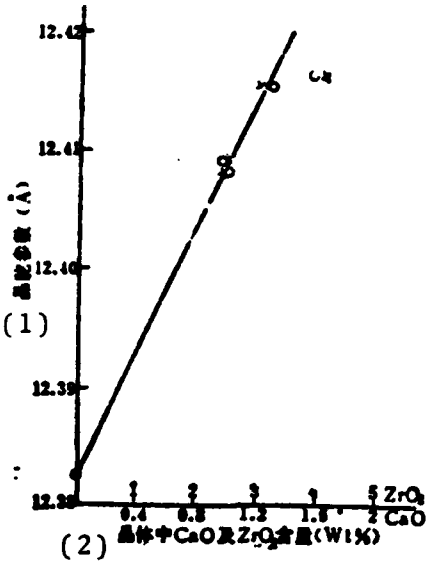

Fig. 2. Lattice constants and their corresponding CaO and ZrO_2 contents in GGG(Ca, Zr) Crystal: o - CaO; x - ZrO_2.
Key: (1) Lattice constants; (2) CaO and ZrO_2 contents in GGG(Ca, Zr) crystal.

(C) Effective segregation coefficients of crystals

Estimated calculations can be made of the initial constituents of the fused materials (compounded raw materials) and the analysis constituents of the head portion of constituents in the finally extracted crystals (tail portions) and the constituents in the remaining materials; the results are also listed in Table 1. The calculated segregation coefficients do not completely match. Primarily, there are two sources of errors: the first is deviation of sampling. In other words, there are deviations between the head and tail portions of samples and the initial and final crystal samples. The second error source is precision in analyses. Refer to segregation coefficients of CaO and ZrO_2 listed in Table 1; these coefficients are taken from crystal samples with a growth rate of 2.5 mm/h. For the case of different growth rates, of course the segregation coefficients of CaO and ZrO_2 are not the same; refer to Table 2 and Fig. 3. We can see from Fig. 3 and Table 2 that the segregation coefficients of CaO

and ZrO_2 increase with increase of growth rates. This is possibly because too fast growth rates cause the occurrence of constitutional supercooling. In Fig. 4, the opaque portions of the outer ring of the crystal indicate the situation of constitutional supercooling when the crystal diameters increase rapidly (abrup variation of diametral growth rates). By conducting chemical analyses on samples of opaque portions, contents of CaO and ZrO_2 are greater by about 1 percent than in the transparent portions. This indicates the phenomenon of constitutional supercooling. Based on the above-mentioned results, occurrence of constitutional supercooling in GGG(Ca, Zr) is easier during greater growth rates (V) at a definite temperature gradient (G); in other words, the occurrence of constitutional supercooling meets the criterion principle of smaller G/V[5].

Table 2. Variation of segregation coefficients in GGG(Ca, Zr) crystal with the crystal growth rate.

Sample	Growth rate (mm/h)	Segregation coefficient	
		CaO	ZrO_2
Top part	1.5	0.63	0.88
Top part	3.0	0.79	0.94
End part	4.0	0.85	0.87
End part	6.0	0.88	0.97
End part	10.0	0.85	1.00

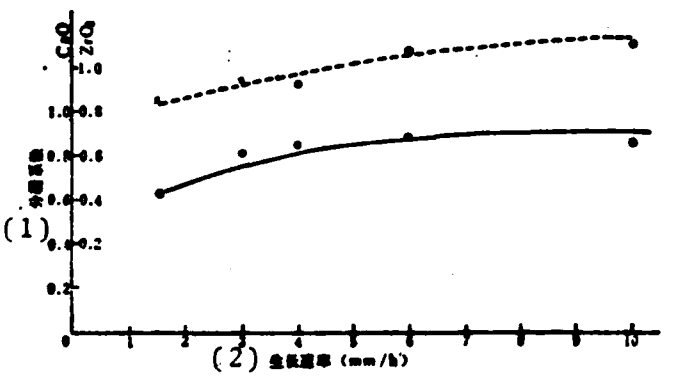

Fig. 3. Curves showing the variation of segregation coefficients of CaO and ZrO_2 with the growth rate: ___ CaO; --- ZrO_2.

Key: (1) Segregation coefficients; (2) Growth rate.

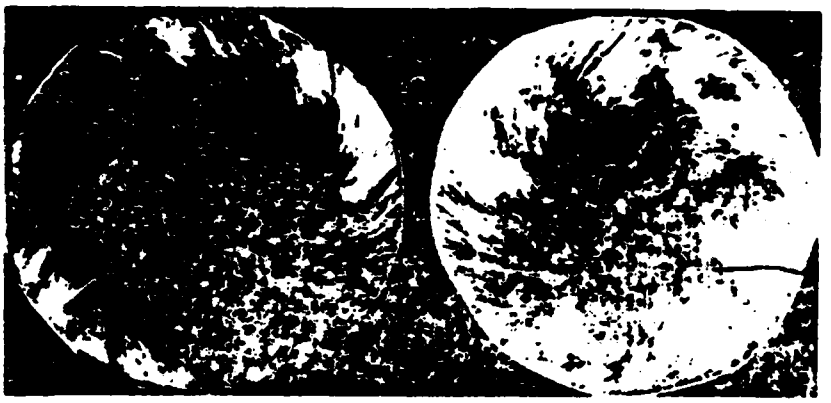

Fig. 4. Phenomena of constitutional supercooling occu d at the rapid increase of crystal diameter: 1.5 x.

Figure 5 shows the optical transmissions of GGG(Ca, Zr). From the figure, it is transparent for this type of crystals in the range of incident light wavelength (0.35 to 5 (mu)m) with transmission about 70 percent. The authors conducted the same determinations on pure GGG crystals. There was no obvious difference among these two types of crystals; same differences appear in the visible light range.

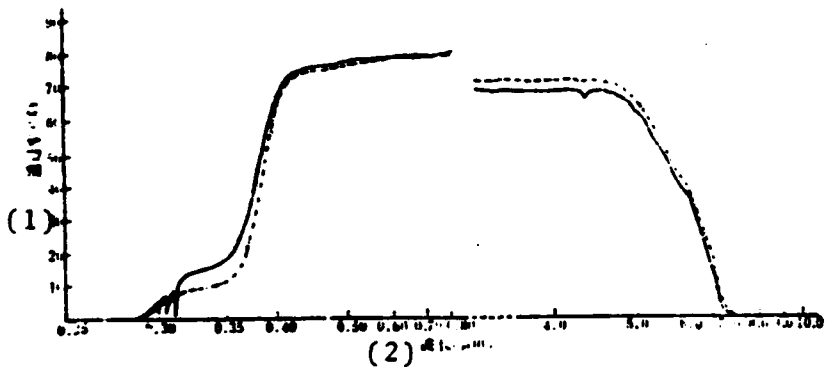

Fig. 5. Optical transmission curves of GGG(Ca, Zr) and GGG crystals: ___ GGG(Ca, Zr); -.-.- GGG.
Key: (1) Optical transmission; (2) Wavelength.

(D) Experimental results of irradiation

After 1 hour of irradiation of GGG(Ca, Zr) and pure GGG single crystals under ultraviolet lamp (power about 500W), it was discovered that the GGG(Ca, Zr) crystals became yellowish brown; for single crystals of GGG(Nd) and GGG(Nd, Cr), a slight color change was observed. In the case of pure GGG, there was no obvious color change. This indicates that color cores are very easily produced in single crystals of GGG(Ca, Zr). This is a supplement to results reached in the work conducted by R. Metselaar et al[7]. By conducting determinations of transmission at 0.35 to 0.80 (mu)m for the two above-mentioned crystals (GGG and GGG(Ca, Zr)), there were obvious variations in transmission curves of GGG(Ca, Zr) from those before irradiation with ultraviolet rays.

By using Co^{60} as the source, these two above-mentioned crystals (with the same thickness) were again irradiated in gamma rays with dosage of $2x10^{7}R$. These two types of crystals became brownish yellow; the color of GGG(Ca, Zr) was considerably deeper than that of GGG single crystals; same effect also occurred in GGG(Nd). Figure 6 shows the optical transmission curves following (the above mentioned) irradiations with ultraviolet rays and gamma rays and no irradiation for GGG(Ca, Zr) and pure GGG single crystals. By comparing curves, following irradiation the single crystals of GGG(Ca, Zr) displayed greater variations in optical transmission in the range of visible light. This means that in the color cores produced by irradiation, there are more intensive absorption belts in the wavelength range of visible light. While conducting gamma irradiation on single crystals of GGG(Ca, Zr) in an electron linear accelerator at 20MeV and $4x10^{8}R$, the effect of color cores produced was even more obvious. Therefore, the purpose of doping GGG single crystals can not only change the lattice constants, but also lead to new applications due to the occurrence of color cores.

IV. Conclusions

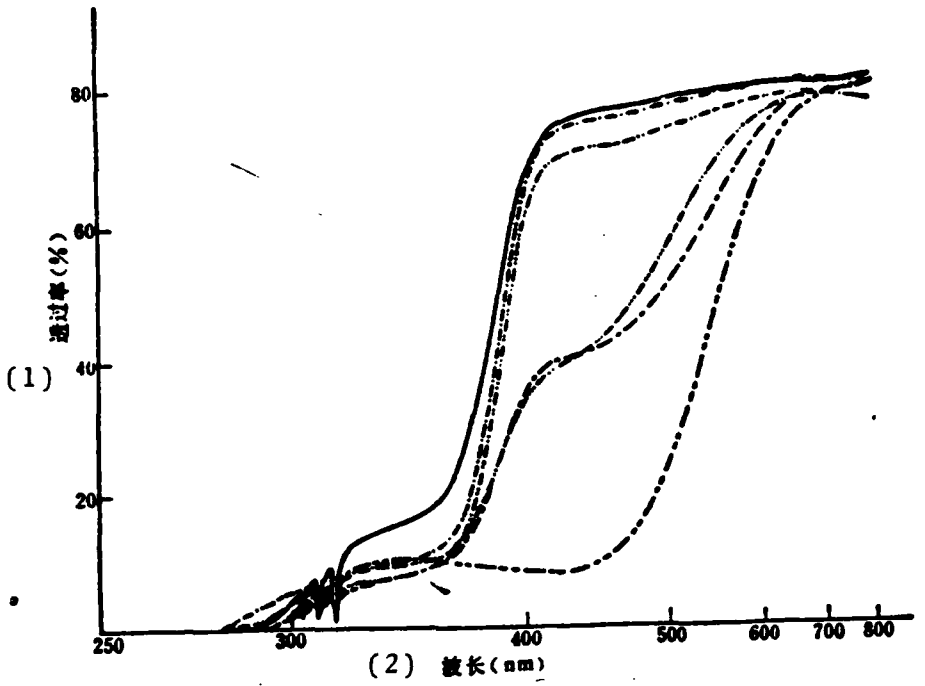

Fig.6 Optical transmission curves of GGG(Ca, Zr) and pure GGG crystals before and after irradiation

——GGG(Ca, Zr) before irradiation, ---GGG before irradiation, ----GGG after ultraviolet ray treatment(1h),·····GGG(Ca,Zr) after ultraviolet ray treatment(1h), —·—GGG after γ-irradiation (2×10^7R), ——·——GGG(Ca, Zr) after γ-irradiation (2×10^7R)

Key: (1) Optical transmission; (2) Wavelength.

(A) By doping constituents of CaO and ZrO_2 in GGG single crystals, the authors obtained single crystals of greater lattice constants than those of pure GGG; however, the control of integrity was more difficult than for the growth of single crystals of pure GGG.

(B) Generally, there were the same optical transmissions for GGG(Ca, Zr) single crystals and pure GGG single crystals. In the former case, color cores were easily produced with irradiations of ultraviolet rays or gamma rays. This phenomenon suggests new application prospects for doped GGG.

(C) The conditions for the occurrence of constitutional supercooling of GGG(Ca, Zr) single crystals meet the principle of a smaller G/V criterion.

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