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GROWTH AND CHARACTERIZATION OF $Bi_4Ge_3O_{12}$ SINGLE CRYSTALS*

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Experiences obtained in the growth of $Bi_4Ge_3O_{12}$ single crystals together with characteristic data on the crystals are described. The tail of the self-absorption near the absorption edge is shown to depend sensitively on crystal quality. This property can be used for crystal characterization.

1. Introduction

In the fifties one of the predecessors of our Laboratory was engaged in developing NaI(Tl) scintillators, and introduced the manufacturing of these crystals at the Gamma Works, where they are now being produced on large scale in excellent quality. However, the techniques of nuclear measurement are steadily developing and require scintillators of various properties. Miniaturization raised the need for scintillators having large atomic numbers. Furthermore, the development of computed tomography (CT) demands scintillators of short afterglow in order to increase the signal processing rate. In Table I we have selected the most important scintillators and presented some of their characteristic data. The first column presents the density, the second the effective atomic number, the third the index of refraction (measured at the wavelength of the emission maximum), the fourth the afterglow (which is the emitted energy after the first 3 milliseconds relative to the total emitted energy of scintillation), the fifth the wavelength of maximum emission, the sixth the decay time (defined as the time in which the decreasing light intensity attains the e-th fraction of the initial intesity), finally in the last column the light output relative to that of NaI(Tl) is presented. These data clearly show the advantage of bismuth germanate manifested by its great density, large effective atomic number and short afterglow. The density and atomic number determine the high absorption coefficient. This enables one to decrease 9—16 times the volume of the crystal which is of considerable advantage for example in

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* Dedicated to Prof. I. Tarján on his 70th birthday.

Table I

Characteristic data of scintillators

	Density $[g/m^3]$	Z_{eff}	n at λ_{Emax}	Afterglow % >3 ms	$\lambda_{E_{max}}$	Decay time $[\mu s]$	Rel. light output [%]
NaI(Tl)	3.67	49.8	1.85	0.5–5	410	0.23	100
CaF(Eu)	3.18	16.6	1.44	0.3	435	0.94	50
CsJ(Tl)	4.51	54.0	1.80	0.5–5	565	1.00	45
$Bi_4Ge_3O_{12}$	7.13	71.7	2.15	0.005	480	0.30	8
$CdWO_4$	7.90	61.2	2.3	.0.005	540	5	38

geophysical measurements. Taking into account that bismuth germanate, because of the $^3P_1 \rightarrow {}^1S_0$ transition of the Bi^{3+} ion, is an intrinsic scintillator, no problems arise due to activator distribution. Moreover, the crystal is chemically inert, nonhygroscopic, its afterglow is short, consequently it is reasonable to state that bismuth germanate is one of the best scintillators for CT application.

2. Products of crystals

The first paper on bismuth germanate crystal growth was published by Nitsche [1] in 1965. His crystals were still yellow. After this growth work started at several places and in 1971 Philipsborn [2] reported already on colourless crystals. In 1975 Nestor and his coworkers [3] had measured the scintillator properties of the crystal that led to CT applications. Literature is poor in describing growth techniques of practically important materials, so we have made some effort to arrive at a result in a short time by realizing our own conception.

The tasks that had to be solved are summarized as follows:

a) First it was necessary to test the basic materials of various purity and origin. We have found that in order to get colourless crystals substances of the purity of at least 5N are required. However, in order to preserve the Pt crucible the use of Bi_2O_3 and GeO_2 of 6N purity is more advantageous. With 4N purity the crystals have a yellow tinge.

b) It became necessary to develop the optimal rate of the solid state reaction in order to maintain stoichiometry. This was obtained by a special temperature program.

c) In connection with the Czochralski method a series of furnace constructions had to be tested and for every furnace construction the optimal rate of pulling and rotation had to be established. This was rather difficult because in the literature one finds extreme values ranging from 0 to 100 rpm. It was found that at medium rotation rates the crystal tends to form inclusions due to the flow system appearing in the melt. Further on it has also been established that inclusions diminish at low rotation rates.

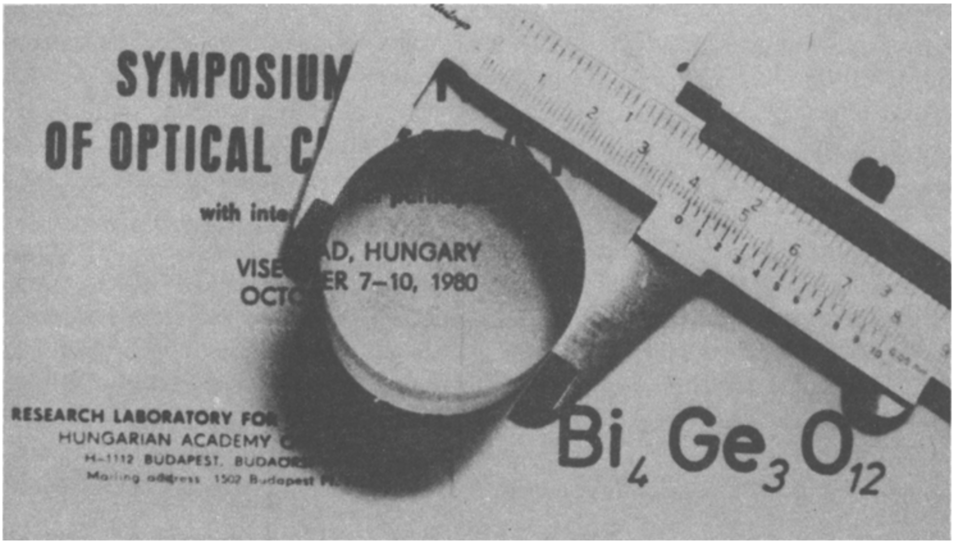

Fig. 1. $Bi_4Ge_3O_{12}$ single crystal

(Transition to Kyropoulos growth). They also diminish on passing over to higher rotation rates where the convexity of the growing front decreases. The crystals were generally grown on seeds of ⟨100⟩ orientation.

d) Most of our experiments have been carried out by means of some temperature control. It was necessary to work out an optimal program for a given furnace construction in order to grow crystals close to the required uniform diameter. Since we did not always succeed we tried our invention developed for the growth of TeO_2 and to be patented presently, which is a simple balance control system. In this way we succeeded to pull $Bi_4Ge_3O_{12}$ single crystals with a uniform and predetermined diameter of 40 mm and a length also of 40 mm. The processed crystal is depicted in Fig. 1.

e) For scintillation purposes the crystals must be processed. It was found that the crystals can be processed by simple turning, whereas the optical window for the scintillation light output can be prepared by the usual polishing technique applied to glasses of smaller hardness. Finally the crystals are capsulated and provided with a light reflector in a way used for NaI(Tl).

3. Characterization of crystals

a) Visual observation

Observing visually the as-grown crystal boule after cooling some statements can be made. There are ridges on the crystal surface starting from the seed, their perfectness proves the single-crystal character of the crystal and their symmetry shows the crystallographic directions. The ridges tend to extend to facets, so that the crystal takes a typical habit, especially if the thermal gradient is small due to furnace construction. By visual observation the colour and inclusions of the crystal become directly apparent. Both are connected to impurities. Pulling with high rate gives rise to a very large number of inclusions so that the crystal is non-transparent, with a dark grey colour. Slow pulling results in a better purification effect, the crystal is generally colourless and transparent, however, because of the large index of refraction there is hardly any way to observe the inside of the crystal through its curved surfaces. Thus it is useful to polish two flat faces of optical quality on both ends of the crystal perpendicular to the rotation axis. In this way the inside of the crystal can be investigated. In some cases an ordered inclusion structure forms starting from the cylinder jacket around the rotation axis. This may be probably connected to the growth front having some unfavourable shape and to the flow structure of the melt. The melt frequently contains well observable rotating flow cells. We succeeded to produce inclusion-free crystals of small diameter only from materials purified by pre-pulling, using low pulling and high rotation rates.

b) Absorption measurement

Absorption has been measured using polished samples cut from crystals in dimensions of 10 × 20 × 5 mm, near the selfabsorption edge applying a Perkin-Elmer 554 type spectrophotometer. In Fig. 2 the wavelength is recorded on the horizontal and the absorption coefficient on the vertical axis. The curves show rather well that the

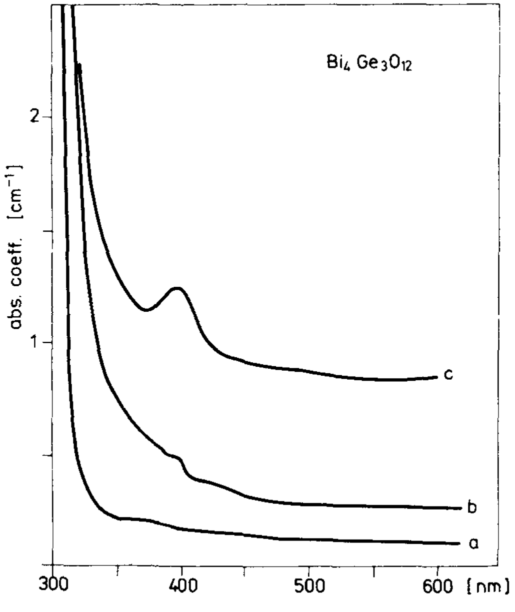

Fig. 2. Absorption curves

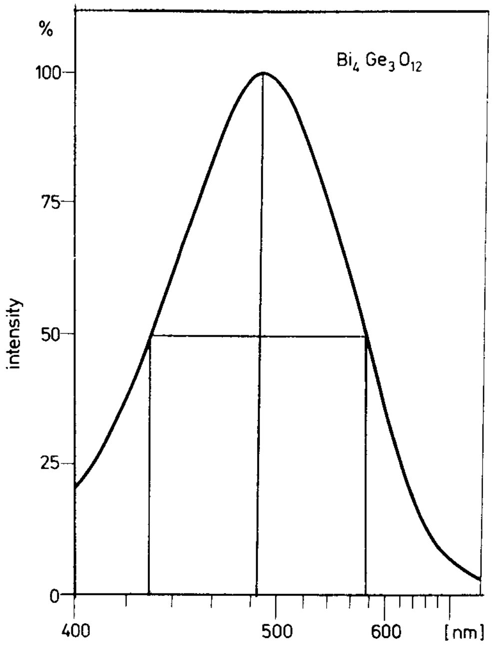

Fig. 3. Luminescence emission spectrum

absorption changes sensitively with impurities and inclusions. Curve "a" shows the absorption of an inclusion-free colourless crystal, curve "c" belongs to a crystal of yellow colour and containing inclusions, whereas curve "b" belongs to a crystal having intermediate properties. Attempts at the identification of the impurity responsible for the maximum at 400 nm have been up to now unsuccessful. Research work in this direction is still in progress.

c) Luminescence measurement

The luminescence emission spectrum has also been measured on samples prepared for absorption measurement using a measuring system developed in our Laboratory [4]. The crystals have been excited by X-rays. Fig. 3 shows a typical emission spectrum where the emitted intensity is given in relative units. The maximum is near to 480 nm. This is close to the value published in the literature (Table I). In the case of yellow crystals the maximum is shifted towards longer wavelengths, which can be partly explained by the self-absorption of such crystals.

d) Measurements of scintillator characteristics

The resolution of our best crystal of 25 mm diameter and 25 mm length has been measured in the Gamma Works using the 0.661 MeV line of ^{137}Cs. The spectrum is shown in Fig. 4. The channel number is recorded on the horizontal axis whereas the

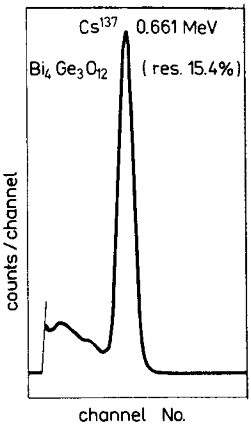

Fig. 4. The γ-spectrum of ^{137}Cs

vertical axis displays the number of impulses per channel. The resolution, which is defined as the halfwidth relative to the maximum position, is in this case 15.4%. The value given in the literature is 15% (Table I). The resolution is rather sensitive to changes of crystal quality. We have measured values as large as 43% on yellow crystals full of inclusions. The light output as related to NaI(Tl) has also been measured, in the case of our best crystal it proved to be 7.2% which is in good agreement with the value 8% given in the literature (Table I).

4. Conclusion

As shown by the above discussion bismuth germanate possesses properties making this material rather important from the practical point of view. Though activator distribution problems do not arise, experiments carried out so far indicate a strong inclination to form inclusions as well as a susceptibility to impurities, requiring a proper growth technology to be worked out reproducing the dimensions and quality of the crystals. Absorption measurements appear to be useful for the characterization of crystals because the tail of the self-absorption near the absorption edge shows sensitive changes due to impurities and inclusions. A separate investigation of the influence of various impurities on the scintillation properties would be of interest. A better knowledge of our material resulting from such investigations would help to produce more perfect crystals by either improving the purification methods or by applying dopants positively influencing the crystal properties.

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