

## A RAMAN SPECTROSCOPIC STUDY OF DEFECTS IN $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ CRYSTALS

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We performed spatially resolved polarized Raman measurements on a Czochralski grown  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  crystal, and observed significant spot-dependent changes in the relative scattering intensity of some  $A_1$ , E and  $F_2$  modes. In view of the different selection rules for these modes, such behaviour implies that there are regions with different crystal orientations. We ascribe this to the presence of two-dimensional structural defects with high concentrations and strongly non-uniform distributions.

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### 1. Introduction

$\text{Bi}_4\text{Ge}_3\text{O}_{12}$  is a basic material for scintillation detectors. It also has a range of potential future applications, due to its remarkable physical properties such as the photochromic effect [1], the electro-optic effect [2], etc. In particular, Mn-doped  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  crystals form transient spatial gratings when illuminated with modulated green light, due to an optically-induced redistribution of electrons and holes between impurity levels [3]. In order to better understand the influence of doping on the electronic properties and the lattice dynamics of  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ , the effects caused by its own lattice defects must be known. Here, we present polarized and spatially resolved Raman spectra that give evidence concerning the nature and location of the defects in  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  crystals.

### 2. Experimental details

A transparent and optically homogeneous  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  ingot was grown by the Czochralski method from melts consisting of approximately stoichiometric quantities of  $\text{Bi}_2\text{O}_3$  and  $\text{GeO}_2$ ; the pulling direction being along the [110] direction. The examined sample was cut nearly lengthwise from the ingot, with an approximately  $15^\circ$  inclination with reference to the growth axis. It thus comprises peripheral as well as central areas of the ingot. The Raman measurements were done on a polished surface approximately coinciding with the (110) plane, which ranges from the central part to the periphery of the ingot. The Raman spectra were measured on a Dilor multichannel spectrometer with entrance slits set to a  $2.5 \text{ cm}^{-1}$  spectral width. The 488 nm line of an Ar/Kr-laser was used for excitation; the absolute accuracy being  $1 \text{ cm}^{-1}$ . The laser beam, with a power of 25 mW, was focused to a spot of about  $30 \mu\text{m}$  in a backscattering geometry, using crossed polarizations.

The space group symmetry of  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  is  $T_d^6$  with two formula units per primitive cell [4]. According to a factor group analysis, there are  $4A_1+9E+14F_2$  Raman active modes [2]. The  $F_2$

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modes are also infrared active, and LO-TO splitting should occur. We chose the scattering geometry  $Y'(ZX')Y'$  with  $Y' = [-110]$  and  $X' = [110]$ , where only  $F_2$  modes are allowed by symmetry. The  $F_2$  modes were preferred because their scattering intensity has the most complicated angular (orientational) dependence, and along with the TO/LO intensity ratio they should provide the most comprehensive information on the local structure and orientation. Furthermore, the  $A_1$  modes in a parallel geometry overshadow any other spectral features because of their high intensity.

We performed spatially resolved Raman measurements along several differently oriented lines over the sample's surface of approximately  $2.5 \times 2$  cm<sup>2</sup> lateral dimensions. All spectra were recorded in the same scattering geometry and the same crystal orientation, with a step of 0.5 mm.

### 3. Results and discussion

Fig. 1 (uppermost trace) comprises the usual Raman spectrum as recorded from the majority of the examined sample spots. The  $F_2$  modes are close to their maximum intensity. However, peaks originating from the  $A_1$ - and E- modes are also present, possibly due to slight imperfections in the polarization analysis. All of the Raman spectra contain the same lines, with very small or no changes in frequency and line width, which indicates a high purity  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  crystal. Nevertheless, on some spots we detected significant deviations in the lattice orientation and order. The observed effects can be summarized as follows:

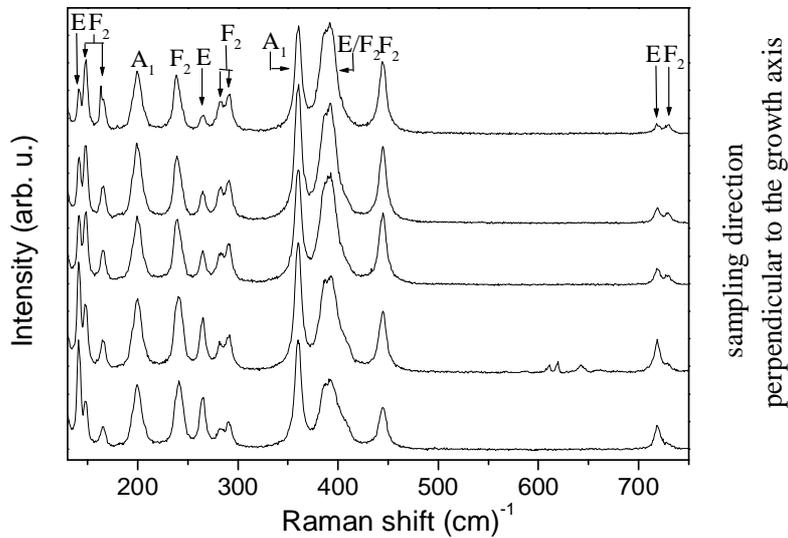


Fig. 1. Raman spectra of  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ , showing a continuous decrease in the  $F_2$  intensity and increase in the E intensity along the sampling line.

I. Some parts of the crystal, lying predominantly in the periphery of the examined surface and away from the growth axis, exhibit a high intensity from the E-modes and a low intensity from the  $F_2$  modes. The transition to such an abnormal intensity distribution takes place either smoothly (as can be appreciated from Fig. 1) or abruptly (as seen in the lowest two traces in Fig. 2). On the other hand, in a cubic symmetry, the intensities of the E- and  $F_2$ -modes are complementary: by parametrizing an arbitrary  $xy$ -set by  $x = \sin i$  and  $y = \cos i$  one obtains Raman intensities  $I$  of these modes of  $I_E \sim \sin^2 2i$  and  $I_F \sim \cos^2 2i$ . Hence, the observed intensity redistribution between the E- and  $F_2$ -modes can be understood assuming local deviations of up to 45 degrees in the directions of the crystallographic axes. These defects occur mostly in the periphery of the crystal, with a strongly non-uniform concentration.

II. Variations in the intensity ratio of the LO/TO-components of the  $F_2$  modes, as exemplified in Fig. 2. Here, we distinguish strong variations (see the two lowest traces in Fig. 2) that

are accompanied by an E- $F_2$  intensity redistribution and are obviously due to deviations in the lattice orientation, and smaller variations (see the top two traces in Fig. 2) that do not correlate with changes in other mode intensities. The TO/LO splitting in  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  is particularly strong, and is ascribed to the long-range interactions of O-atoms in the  $\text{GeO}_4$ -tetrahedra. It is assumed that these interactions are due to the local O-atom environment; this being composed of three cations which is untypical for oxygen [2]. Therefore, we ascribe the smaller TO/LO intensity variations to local disorder in the octahedral Bi sites, and probably to the random occurrence of Bi-ions with untypical valence, as is the case in  $\text{Bi}_{12}\text{SiO}_{20}$  crystals [6].

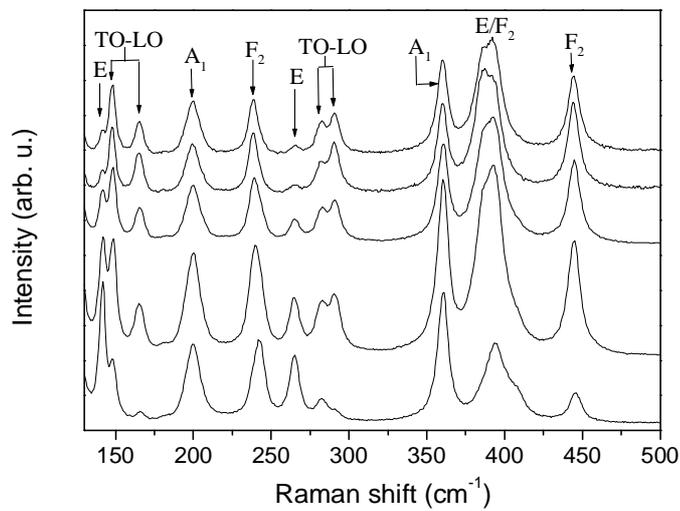


Fig. 2. Raman spectra from selected spots of the  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  crystal, showing variations in the TO/LO intensity ratio of the  $F_2$  modes. The top two spectra were taken from a sampling series along the growth axis, and the lower three spectra from one with a sampling direction perpendicular to the growth axis.

III.  $A_1$  modes are generally suppressed by symmetry in crossed polarization, and show up with “forbidden” intensities about 50 times smaller than those for parallel polarization. However, on some locations in the periphery of the crystal, the E- $F_2$  intensity redistribution is accompanied by a strong enhancement (up to five times) of the “forbidden”  $A_1$ -mode intensities, as depicted in Fig. 3.

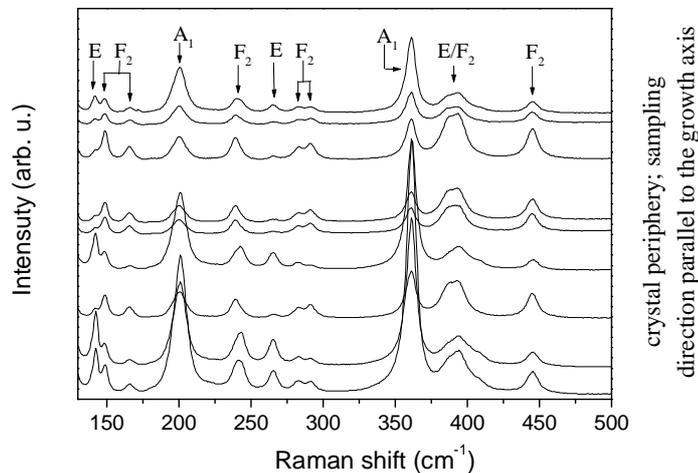


Fig. 3. Raman spectra from the periphery of the  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  crystal, showing sporadic enhancement of the  $A_1$  intensity along the sampling line.

This enhancement is particularly puzzling because in crossed polarization,  $A_1$ -modes cannot be enhanced by any deviations in the sample orientation. We therefore argue that the defects could form some kind of superlattice-like arrangement, which could change the local symmetry and hence the character of the  $A_1$  modes.

#### **4. Conclusions**

Our Raman scattering results provide evidence for various lattice defects in the examined  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ -crystals. We also found evidence for local misorientations in the crystal lattice and occasional disorder in the octahedral Bi positions. These imperfections were distributed mostly in the periphery of the crystal, with a strongly non-uniform concentration. They are possibly due to two dimensional structural defects.

#### **Acknowledgements**

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