マテリアル先端リサーチインフラ利用報告書
ARIM User's Report

【Release：2025.06.10】　【Update：2025.04.07】

課題データ / Project Data

課題番号 Project Issue Number	24NM5075
利用課題名 Title	Single Crystal Growth of Oxides and Fluorides
利用した実施機関 Support Institute	物質・材料研究機構 / NIMS
機関外・機関内の利用 External or Internal Use	内部利用（ARIM事業参画者以外）/Internal Use (by non ARIM members)
ARIM半導体基盤PF 関連課題 Related to ARIM-SETI	指定なし / No Designation
横断技術領域 Cross-Technology Area	計測・分析/Advanced Characterization
重要技術領域 Important Technology Area	高度なデバイス機能の発現を可能とするマテリアル/Materials allowing high-level device functions to be performed
キーワード Keywords	Optical single crystals, piezoeletric ceramics,光デバイス/ Optical Device,X線回折/ X-ray diffraction,センサ/ Sensor,電子顕微鏡/ Electronic microscope

利用者と利用形態 / User and Support Type

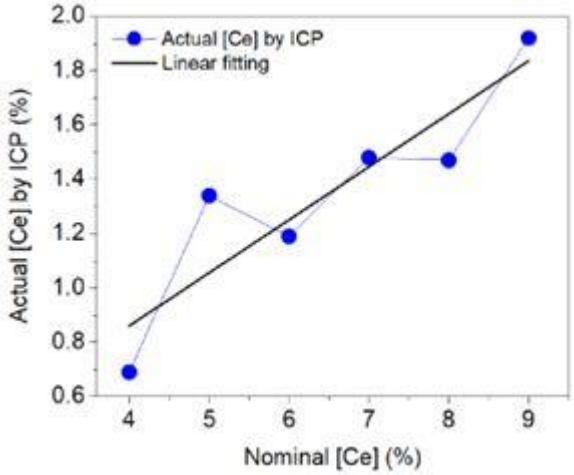
利用者名（課題申請者） User Name (Project Applicant)	ビジョラ ガルシア (VILLORA Garcia)
所属名 Affiliation	物質・材料研究機構
共同利用者氏名 Names of Collaborators Excluding Supporters in the Hub and Spoke Institutes	Shimamura Kiyoshi,Zhou Yueshen,Moreira Joel,Yuan Dongsheng
ARIM実施機関支援担当者 Names of Supporters in the Hub and Spoke Institutes	Yasufuku Hideyuki,Matsushita Yoshitaka,Iwanade Akio,Watanabe Eiichiro,FUJII Michiko
利用形態 Support Type	機器利用/Equipment Utilization,技術補助/Technical Assistance

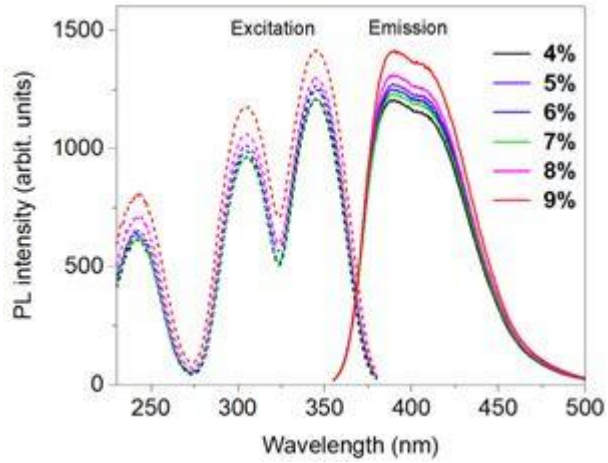
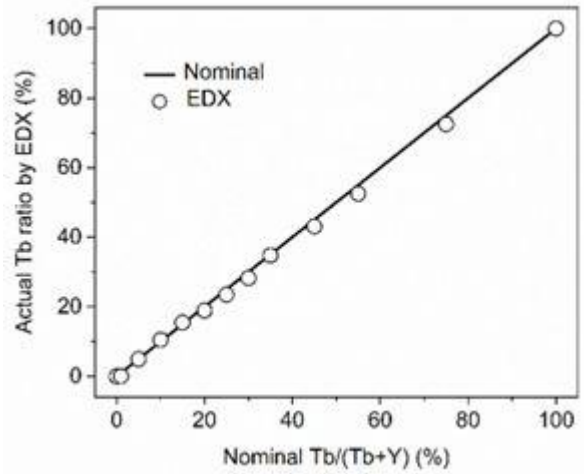
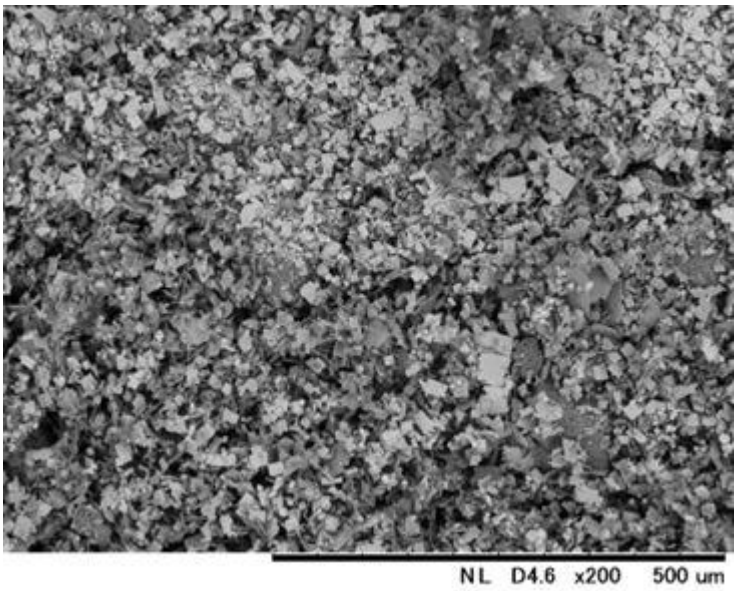
利用した主な設備 / Equipment Used in This Project

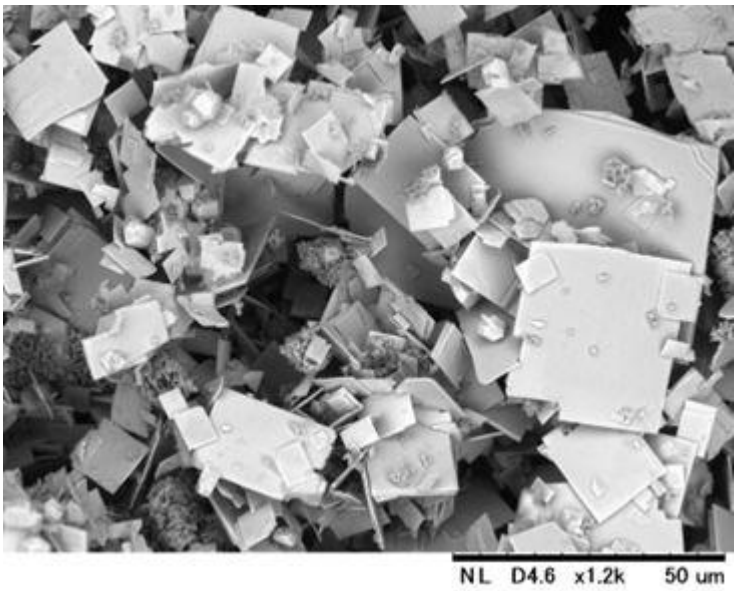
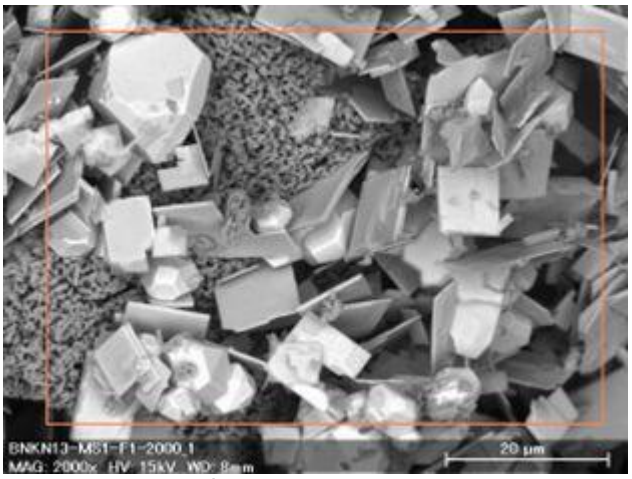
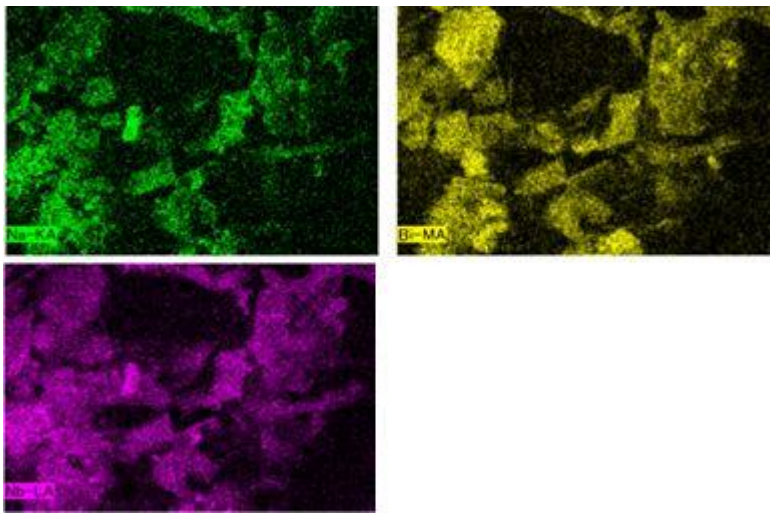
利用した主な設備 Equipment ID & Name	NM-650：卓上電子顕微鏡 [TM3000] NM-201：多環境場対応型X線単結晶構造解析装置 NM-203：誘導結合プラズマ発光分析装置群 NM-221：分光蛍光光度計（FP-8500DS）

報告書データ / Report

概要（目的・用途・実施内容） Abstract (Aim, Use Applications and Contents)	(1) Aiming at high-performance Ce:$Li_6Y(BO_3)_3$ (LYBO) single crystal for thermal neutron detection, photoluminescence dependence with high Cerium concentrations (nominal 4-9 mol% on Yttrium site) was studied. Here, inductively coupled plasma emission spectroscopy was used to measure the actual Cerium concentration in single-crystal samples and photoluminescence spectroscopy was used for excitation and emission characterization.(2) This research aims to develop high-performance single-crystal rare-earth tantalate scintillators for high-energy radiography application. The project, carried out in collaboration with the listed facilities, focuses on elemental composition, crystal structure analysis, and photoluminescence properties of the samples.(3) Scanning electron microscopy was used to observe bismuth sodium niobate oxides and evaluate their morphology, size, and aspect ratio. Moreover, energy-dispersive X-ray spectroscopy (EDX) was used to analyze the oxide's chemical composition.
実験 Experimental	(1) The elemental analysis was carried out by the inductively coupled plasma optical emission spectroscopy. The crystal samples were grinded in powder form and dissolved in a heated mixed acid solution (HCl: HNO_3 = 3: 1), then diluted with Milli-Q water at RT, and finally mixed with the same amount of Co standard solution. The spectrofluorometer FP-8500DS was employed to measure the photoluminescence spectra of the Ce:LYBO crystal samples with Cerium concentration increasing. In order to compare also their photoluminescence intensity, fine crystal powders in the same amount were used for the measurements. (2) • NM-650 Tabletop SEM+EDX [TM3000] Different Tb-concentration (1, 5, 10, 15, 20, 25, 30, 35, 45, 55, 75 and 100%) doped or mixed $YTaO_4$ single crystals were obtained by floating-zone technique. Single-crystal disks, cut from as-grown single-crystal rods, were analyzed using energy-dispersive X-ray spectroscopy (EDX) to determine the actual Tb doping concentration in the samples. The samples were mounted onto the sample holder with carbon tape, then placed in the chamber and evacuated. No electrode was sputtered on the surface. • Spectrofluorometer (FP-8500DS) To investigate changes in the luminescent center with increasing Tb doping concentration (1, 5, 10, 15, 20, 25, 30, 35, 45, 55, 75 and 100%) in $YTaO_4$, photoluminescence spectra were measured. The tested samples were prepared by grinding single crystals into powder. • 多環境場対応型X線単結晶構造解析装置(Single Crystal X-ray Diffractometer for Multiple Environments) The crystal structures of $YNbO_4$ and $TbTaO_4$ were determined through Rietveld refinement using transparent single crystals grown by the floating-zone method. A millimeter-sized single crystal was mounted on a thin glass fiber. Data were processed with the Rigaku Crystal-Clear suite (d*trek) and the structure was solved using the dual-space algorithm method (SHELXT). [1] (3) The sample was set on carbon tape and placed inside the chamber. For the scanning mode, the sample was observed using an acceleration voltage of 15 kV and magnification of x200, x1200, and x4000. For the spectroscopy mode, the sample was observed with a magnification of x2000.

結果と考察 **Results and Discussion**	(1) Ce:LYBO crystals with high nominal Cerium concentrations were investigated, here 4, 5, 6, 7, 8 and 9 mol%. With higher doping concentrations, from the perspective of the whole concentration range more Cerium activators were observed in the grown single crystals, as can be seen in Fig. 1. Despite certain experimental variations the trend can be described by a linear fitting with a slope of 0.2, which matches with the previous finding of the Cerium segregation coefficient in LYBO host. Unlike the Ce:LYBO crystals with low Cerium concentrations (below 4 mol%), which exhibit stronger photoluminescence when Cerium concentration increases, the samples here show comparable ones (Fig. 2). It seems that the photoluminescence starts to saturate but no obvious quenching was observed although the nominal Cerium concentration already reaches 9%. (2) • NM-650 Tabletop SEM+EDX [TM3000] As shown in Fig. 3, a very good correlation between the nominal and actual Tb concentration was found for all grown crystals, suggesting that both Tb and Y possess a similar segregation coefficient and, therefore, crystals with a uniform composition can be grown. • Spectrofluorometer (FP-8500DS) The results indicate that, with the substitution of Y^{3+} by Tb^{3+}, the intrinsic untra-violet (UV) photoluminescence from $YTaO_4$, stemming from the Ta-O complex, gradually decreases till only the intraionic Tb^{3+} emissions. With a 1% Tb concentration, both host and Tb emissions coexist, while for 5% Tb, the host emission is almost negligible. • 多環境場対応型X線単結晶構造解析装置(Single Crystal X-ray Diffractometer for Multiple Environments) They both exhibits a single monoclinic structure with a space group of I2/a. The unit cell parameters of $YNbO_4$: a = 5.0786 Å, b = 10.9550 Å, and c = 5.3029 Å; $TbTaO_4$: a = 5.0697 Å, b = 11.0187 Å, and c = 5.3830 Å. (3) On Fig. 4 and Fig. 5 most bismuth sodium niobate oxide particles have a platelike shape with high aspect ratio. This high aspect ratio is due to the crystallographic layered structure of bismuth sodium niobate oxide which favors growth along a and b axis. However, on Fig. 5 and Fig. 6 some well faceted grains and porous agglomeration of grains are visible. As we can see in Fig. 6 and Fig. 7, these parasitic phases correspond to respectively rich side bismuth and poor side bismuth.
図・表・数式 1 **Figures, Tables and Equations 1**	 Fig. 1: Actual Cerium concentration in as-grown Ce:LYBO single crystals.

図・表・数式 2 Figures, Tables and Equations 2	 Fig. 2: Excitation and emission photoluminescence spectra.
図・表・数式 3 Figures, Tables and Equations 3	 Fig. 3: Comparison between the Tb content measured by EDX and the nominal concentration.
図・表・数式 4 Figures, Tables and Equations 4	 Fig. 4: Sanning electron macroscopy image, magnification x200.

図・表・数式 5 Figures, Tables and Equations 5	 Fig. 5: Sanning electron macroscopy image, magnification x1200.
図・表・数式 6 Figures, Tables and Equations 6	 Fig. 6: Sanning electron macroscopy image, magnification x2000.
図・表・数式 7 Figures, Tables and Equations 7	 Fig. 7: Chemical mapping of the 2000-fold magnified image.
その他・特記事項（参考文献・謝辞等） Remarks(References and Acknowledgements)	[1] X. Fu, E. G. Villora, Y. Matsushita, Y. Kitanaka, Y. Noguchi, M. Miyayama, K. Shimamura and N. Ohashi. RSC Adv, 2017, 7 , 56697-56703.

成果発表・成果利用 / Publication and Patents

DOI（論文・プロシーディング）[1] DOI (Publication and Proceedings)	Yueshen Zhou, High Performance $Y_{1-x}Tb_xTaO_4$ Single-Crystal Scintillators for X-ray Detection, *Crystal Growth & Design*, **25**, 359-366(2024). DOI: 10.1021/acs.cgd.4c01391
口頭発表、ポスター発表および、その他の論文 Oral Presentations etc.	
特許出願件数 Number of Patent Applications	0件
特許登録件数 Number of Registered Patents	0件