

Luminescent properties of Cr-doped $(\text{Gd}_X, \text{Y}_{1-X})_3\text{Al}_5\text{O}_{12}$ infra-red scintillator crystals



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ABSTRACT

Cr-doped $(\text{Gd}_X \text{Y}_{1-X})_3\text{Al}_5\text{O}_{12}$ ($X = 0, 0.25, 0.50$) crystals prepared by the micro-pulling down method were investigated to develop an infra-red scintillator for implantable patient dosimeter in radiation therapy. In order to evaluate their optical and scintillation performance, the following properties were measured: (i) transmittance between ultra-violet and near-infra red region, (ii) photoluminescence spectra under Xe-lamp excitation, and (iii) X-ray excited radio-luminescence spectra. $\text{Cr:Y}_3\text{Al}_5\text{O}_{12}$ and $\text{Cr:}(\text{Gd}_{0.25}\text{Y}_{0.75})_3\text{Al}_5\text{O}_{12}$ crystals showed increased transmittance of 80%, while $\text{Cr:}(\text{Gd}_{0.50}\text{Y}_{0.50})_3\text{Al}_5\text{O}_{12}$ had a lower transmittance of 40% due to its polycrystalline structure. In addition, all the $\text{Cr:}(\text{Gd}_X \text{Y}_{1-X})_3\text{Al}_5\text{O}_{12}$ crystals showed sharp scintillation luminescence peaks ascribed to Cr^{3+} d–d transitions. Therefore, these results suggested that $\text{Cr:Y}_3\text{Al}_5\text{O}_{12}$ and $\text{Cr:}(\text{Gd}_{0.25}\text{Y}_{0.75})_3\text{Al}_5\text{O}_{12}$ crystals can be candidate materials for the dosimeter use.

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1. Introduction

Scintillation materials are widely used in various applications such as medical imaging, homeland security and resource exploration. Although a lot of scintillators emit in the UV or visible region, infra-red scintillators can find application in new field of patient dosimetry in radiation therapy [1]. Especially, an implantable scintillator with an emission wavelength of 650 nm and 1200 nm (which is a transparency region of human tissue [2]) is required in order to obtain real-time dose information and reduce the serious radiation accidents [3] in the radiation therapy. Nakata et al. [1] reported that the implantable dosimeter system can be realized with an infra-red scintillator $\text{Cr:Al}_2\text{O}_3$. However, the emission region of the $\text{Cr:Al}_2\text{O}_3$ is around 694 nm [4], and long-wavelength emission materials are more suitable for this application due to the higher transmittances of human tissue in the near infra-red region

[2]. Moreover, Al_2O_3 has small detection efficiency due to a small effective atomic number of 11.28 [5], while conventional scintillators have over 45. Therefore, optimization of the infra-red scintillators for this application is required.

For the infra-red scintillators for patient dosimetry, the following requirements need to be fulfilled: (i) emission wavelength between 650 nm and 1200 nm, (ii) high X-ray stopping power due to their small size required for the implantation, (iii) non-hygroscopic nature, and (iv) absence of background radiation from host material.

Cr-doped $(\text{Gd}_X \text{Y}_{1-X})_3\text{Al}_5\text{O}_{12}$ ($0 \leq X < 1$) crystal was widely used for high-intensity laser materials, and it can be one of the candidates for the described application because of the following reasons: (i) X-ray higher stopping power compared with Al_2O_3 , (ii) non-hygroscopic nature, (iii) non-intrinsic background from radio-active isotopes such as ^{176}Lu . In addition, the emission wavelength of Cr-doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ (Cr:YAG) is favorably placed around 700 nm [6,7], and thus similar characteristics can be expected also for Cr-doped $(\text{Gd}_X \text{Y}_{1-X})_3\text{Al}_5\text{O}_{12}$ ($0 \leq X < 1$). However, scintillation properties of these garnet crystals have still remained unknown. In this paper, we reported the optical and scintillation properties of Cr-doped $(\text{Gd}_X \text{Y}_{1-X})_3\text{Al}_5\text{O}_{12}$ ($0 \leq X < 1$) for the first time.

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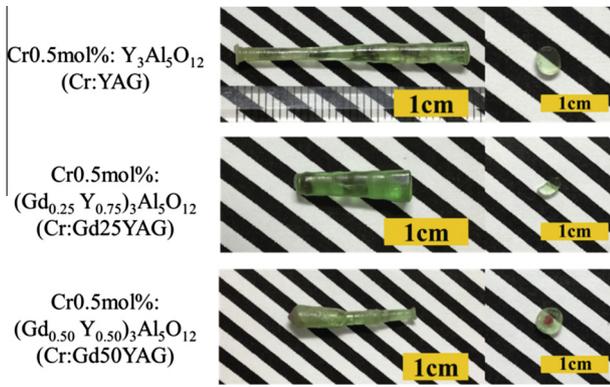


Fig. 1. Photographs of the $\text{Cr}:(\text{Gd}_x \text{Y}_{1-x})_3\text{Al}_5\text{O}_{12}$ ($0 \leq x < 1$) crystals.

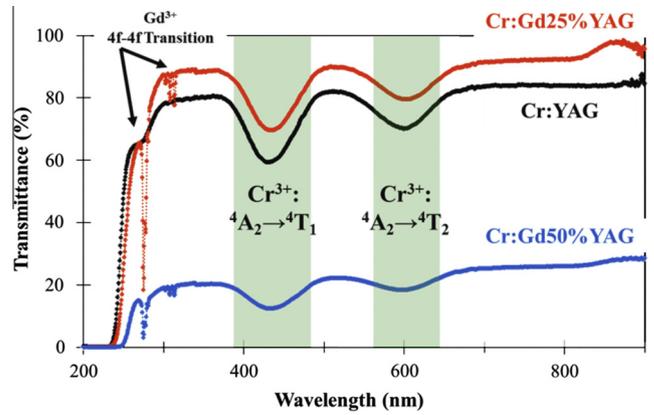


Fig. 3. Transmittance spectra of the $(\text{Gd}_x \text{Y}_{1-x})_3\text{Al}_5\text{O}_{12}$ samples from the ultra-violet to near-infra red region.

2. Materials and methods

Cr-doped $(\text{Gd}_x \text{Y}_{1-x})_3\text{Al}_5\text{O}_{12}$ ($0 \leq x < 1$) crystals were grown by the micro-pulling down method (μ -PD [8]) under nitrogen atmosphere. These grown crystals had their nominal compositions of $\text{Y}_3(\text{Al}_{0.995} \text{Cr}_{0.005})_5\text{O}_{12}$ (further denoted as Cr:YAG), $(\text{Gd}_{0.25} \text{Y}_{0.75})_3(\text{Al}_{0.995} \text{Cr}_{0.005})_5\text{O}_{12}$ (further denoted as Cr:Gd25YAG) and $(\text{Gd}_{0.50} \text{Y}_{0.50})_3(\text{Al}_{0.995} \text{Cr}_{0.005})_5\text{O}_{12}$ (further denoted as Cr:Gd50YAG). The starting materials were 99.99% purity Cr_2O_3 , Gd_2O_3 , Y_2O_3 and $\alpha\text{-Al}_2\text{O}_3$ powders. The mixtures were set in an iridium crucible. All the growth rates were kept constant at the value of 0.05 mm/min for the whole growth process. After the growth, the as-grown crystals were cut and mirror-polished.

Powder X-ray diffraction measurements were performed on the as-grown crystals with a diffractometer (RIGAKU: RINT-2000, X-ray: Cu $K\alpha$), and their crystal structures were determined by the comparison between the obtained XRD patterns and the data of JCPDS cards.

In order to evaluate its optical properties, transmittance spectra were obtained with a spectrophotometer (JASCO: V-550) on crack-free parts of the samples in the wavelength between 200 nm and 900 nm. Photoluminescence spectra of these samples were also measured with a photoluminescence measurement system (Hamamatsu: C9920-03G). The excitation lights were generated by a Xe lamp (Hamamatsu: L9799-02), and all the excitation wavelengths was approximately 450 nm.

X-ray excited radio-luminescence spectra were collected with a spectrometer (Andor: DU420-OE) and an X-ray generator (RIGAKU: RINT-2000). The X-ray power in all the measurements was approximately 400 W (40 kV, 10 mA).

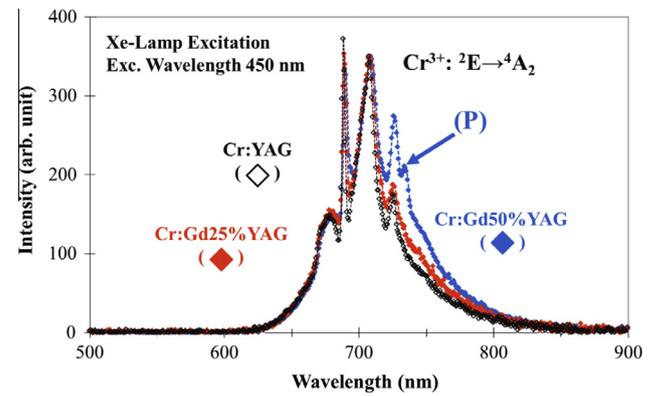


Fig. 4. Photoluminescence spectra of the $(\text{Gd}_x \text{Y}_{1-x})_3\text{Al}_5\text{O}_{12}$ crystals under the Xe-lamp excitation at 450 nm.

3. Results and discussions

Photographs of Cr-doped $(\text{Gd}_x \text{Y}_{1-x})_3\text{Al}_5\text{O}_{12}$ crystals are shown in Fig. 1. Powder X-ray diffraction patterns of these as-grown crystals are depicted in Fig. 2. In the cases of the Cr:YAG and Cr:Gd25YAG crystals, all the diffraction peaks approximately corresponded with the data of $\text{Y}_3\text{Al}_5\text{O}_{12}$ (JCPDS No. 33-0040). The small 2-theta shift in the Cr:Gd25YAG compared to the JCPDS data was observed. This shift was related to the expansion of the lattice due to the substitution of Gd for Y, because the crystal radius of Gd (1.193 Å) is larger than that of Y (1.159 Å) in the dodecahedral site

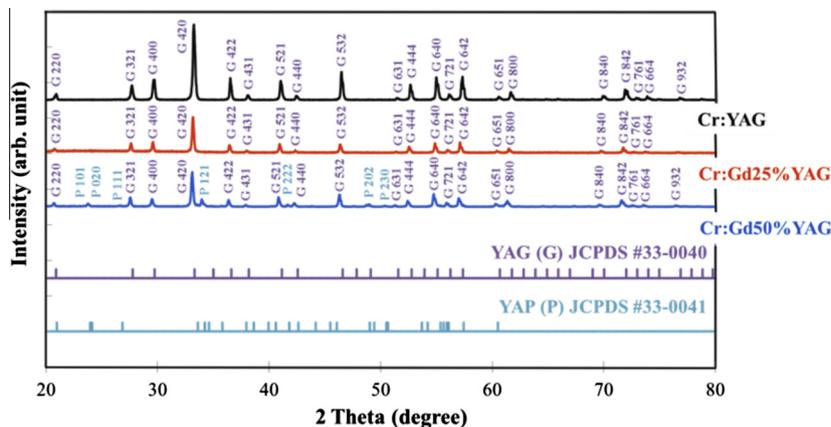


Fig. 2. Powder X-ray diffraction patterns of Cr-doped $(\text{Gd}_x \text{Y}_{1-x})_3\text{Al}_5\text{O}_{12}$ ($0 \leq x < 1$) crystals.

[9]. We confirmed that the crystal structure of the Cr:YAG and Cr:Gd25YAG crystals corresponded with the typical garnet structure (space group: $Ia3d$). On the other hand, the comparison on powder-XRD patterns of between Cr:Gd50YAG and reference crystals ($Y_3Al_5O_{12}$: JCPDS No. 33-0040, $YAlO_3$: JCPDS No. 33-0041) revealed presence of perovskite phase (space group: $Pnma$) in the Cr:Gd50YAG crystal. The Cr:YAlO₃ (perovskite phase) was observed as a red¹ part in the photograph of Gd50YAG in Fig. 1. This result implicated that an upper limit of the substitution of Gd for Y in the $(Gd_x Y_{1-x})_3Al_5O_{12}$ system was located between the values of X of 0.25 and 0.50 in the case of the μ -PD growth.

Transmittance spectrum of the $(Gd_x Y_{1-x})_3Al_5O_{12}$ crystals between 200 and 900 nm is shown in Fig. 3. All the spectra included two Cr³⁺ absorptions around 450 nm and 600 nm, and these bands were ascribed to the Cr³⁺ d–d transitions, i.e. from its ground state 4A_2 to its excited states 4T_1 and 4T_2 , respectively. In addition, two Gd³⁺ absorption bands were also detected around 280 and 310 nm, and they were ascribed to Gd³⁺ 4f–4f transitions, i.e. from its ground state 8S to the other excited states [10,11].

Cr:YAG and Cr:Gd25YAG showed higher transmittance than 70%, while Cr:Gd50YAG had lower transmittance of around 40%. Its low transmittance can be related to its perovskite phase. Cr:Gd50YAG was a polycrystalline material because the crystal had some perovskite parts, and there were a great number of grain boundaries between the grains of the perovskite and garnet phases. Therefore, scintillation photons would be scattered by these boundaries, and this will result in lowering the transmittance below the values for Cr:YAG and Cr:Gd25YAG crystals. Polycrystalline material was not appropriate for a scintillator, because its low transmittance causes a high loss of scintillation photons when emitted from inside of the material.

Photoluminescence spectra of these crystals under the Xe lamp excitation at 450 nm are shown in Fig. 4. All the samples showed a sharp luminescence around 700 nm due to Cr³⁺ d–d transition from its excited state of 2E to 4A_2 [6,7]. In the spectra of Cr:YAG and Cr:Gd25YAG, four emission peaks were observed around 680, 690, 700 and 730 nm, which are related to the luminescence of Cr³⁺ ion incorporated into the garnet phase. On the other hand, different weak peak (described as (P) in Fig. 4) was observed around 740 nm in the spectra of Cr:Gd50YAG, which is related to the emission of Cr³⁺ incorporated into the perovskite phase [12].

The shape of Cr³⁺ luminescence spectrum depends on the surrounding crystal field [13]. However, in this research, there were no large differences in these spectra except for the luminescence peak from a perovskite phase. Therefore, this result implicated that the substitution of Gd for Y in the $(Gd, Y)_3Al_5O_{12}$ system has little effect on the change of the surrounding crystal field.

X-ray excited radio-luminescence spectra of the $(Gd_x Y_{1-x})_3Al_5O_{12}$ crystals are shown in Fig. 5. Typical Cr³⁺ luminescence peaks were also observed in all the spectra, which corresponds to the above described photoluminescence emission spectrum. They can be again ascribed to the Cr³⁺ d–d transition from its 2E to 4A_2 states [6,7]. In addition, elevated emission intensity around 740 nm in the Gd50YAG was also observed as well as in its photoluminescence spectrum.

As shown in Fig. 3, transmittance higher than 80% for Cr:YAG and Cr:Gd25YAG samples suggested that the reabsorption of these scintillation photons is negligible around their emission wavelength of 700 nm. Moreover, these photons can penetrate the human tissue more easily when compared with those emitted by Al₂O₃, because their scintillation emission wavelength was located within the tissue optical window region. Thus, Cr:YAG and

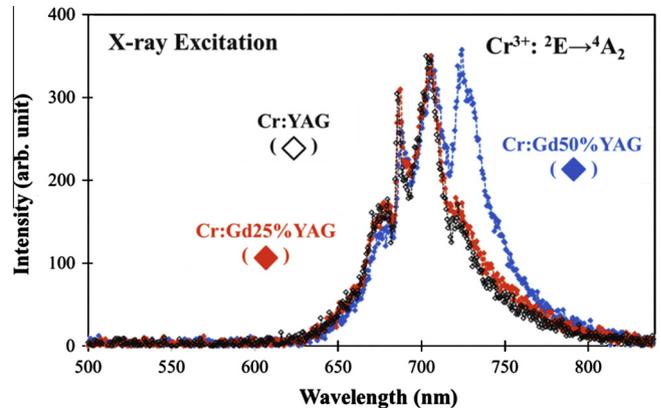


Fig. 5. Radioluminescence spectra of the Cr: $(Gd_x Y_{1-x})_3Al_5O_{12}$ ($0 \leq X < 1$) crystals under X-ray excitation.

Cr:Gd25YAG crystals can be used for the patient dosimetry, while Cr:Gd50YAG cannot be applied due to its degraded transmittance. Cr:YAG and Cr:Gd25YAG crystals have high effective atomic numbers and non-hygroscopic nature. Therefore, these two crystals can be the candidates for new implantable dosimeters.

4. Conclusion

Cr-doped $(Gd_x Y_{1-x})_3Al_5O_{12}$ ($0 \leq X < 1$) crystals were prepared using the micro-pulling down method. Powder XRD measurements determined that a crystal structure of Cr:YAG and Cr:Gd25YAG corresponded to a garnet phase, while Cr:Gd50YAG contained a perovskite phase. In addition, the transmittance measurements showed that Cr:YAG and Cr:Gd25YAG were highly transparent from 650 to 1200 nm, while Cr:Gd50YAG had a transmittance lower than 40% due to its secondary perovskite phase. The photoluminescence peaks were detected around 700 nm under the 450 nm excitation with a Xe lamp. The X-ray excited radioluminescence spectra showed sharp scintillation peaks around 700 nm related to Cr³⁺ d–d transitions. Cr:YAG and Cr:Gd25YAG crystals can be possible candidates for an implantable dosimeter material in the radiation therapy.

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References

- [1] E. Nakata, Y. Hosokai, H. Kanzaki, T. Shikama, S. Nakata, H. Matsuki, K. Ishii, Y. Ogawa, H. Ariga, S. Yamada, *Radiological Soc. North Am.* (2008).

¹ For interpretation of color in Fig. 1, the reader is referred to the web version of this article.

- [2] Y.Y. Huang, A.C.H. Chen, J.D. Carroll, M.R. Hamblin, *Dose-Response* 7 (2009) 358.
- [3] International Atomic Energy Agency, *Lessons Learned from Accidental Exposures in Radiotherapy*, IAEA Safety Reports Series No. 17, IAEA, Vienna, 2000.
- [4] T. Teichmann, M. Sommer, J. Henniger, *Radiat. Meas.* 56 (2013) 347.
- [5] A.J.J. Bos, *Nucl. Instrum. Methods Phys. Res., Sect. B* 184 (2001) 3.
- [6] J.P. Hehir, M.O. Henry, J.P. Larkin, G.F. Imbusch, *J. Phys. C: Solid State Phys.* 7 (1974) 2241.
- [7] K. Fujioka, T. Saiki, S. Motokoshi, Y. Fujimoto, H. Fujita, M. Nakatsuka, *J. Lumin.* 130 (2010) 455.
- [8] A. Yoshikawa, M. Nikl, G. Boulon, T. Fukuda, *Opt. Mater.* 30 (2007) 6.
- [9] R.D. Shannon, *Acta Cryst. A* 32 (1976) 751.
- [10] G.H. Dieke, H.M. Crosswhite, *Appl. Opt.* 2 (1963) 675.
- [11] K. Kamada, T. Yanagida, J. Pejchal, M. Nikl, T. Endo, K. Tsutumi, Y. Usuki, Y. Fujimoto, A. Fukabori, A. Yoshikawa, *J. Cryst. Growth* 352 (2012) 84.
- [12] M. Sugiyama, T. Yanagida, D. Totsuka, Y. Yokota, Y. Futami, Y. Fujimoto, A. Yoshikawa, *J. Cryst. Growth* 362 (2013) 157.
- [13] S.M. Borisov, K. Gatterer, B. Bitschnau, I. Klimant, *J. Phys. Chem. C* 114 (2010) 9118.