Glass-ceramics Phosphor

Development of Ce:YAG Glass-ceramics Phosphor for White LED Application

P. Nandi*, M. Goswami, Ashok K. Arya

Glass & Advanced Materials Division, Bhabha Atomic Research Centre, Mumbai 400085, INDIA

Demonstration of white light generation using Ce:YAG glass-ceramics phosphor

ABSTRACT

We report here successful synthesis of Ce:YAG glass-ceramic phosphor with improved thermal characteristics compared to polymer based phosphor used in conventional white LEDs. Composition of the base glass and subsequent heating schedule were fine tuned for optimum concentration of Ce:YAG phosphors with proper microstructure and optical properties. Understanding the crystal growth kinetics in the glass was essential to predict the time-temperature parameters for the required phase concentration. Isothermal predictions were derived and then applied to convert the glass to glass-ceramics by thermal activation. XRD analysis confirmed the development of single phase Ce:YAG phosphor crystals in glass-ceramics powder samples. Surface crystallization of ~50μm of phosphor layer was observed from the Scanning electron microscopy (SEM) study. Glass-ceramics disk with desired optical quality was prepared to demonstrate generation of the white light.

KEYWORDS: *Glass, Glass-ceramics, Phosphors, White LED*

Introduction

Conventional white LED devices has Ce:YAG ($Y_3Al_5O_{12}$) phosphor crystals dispersed in polymer matrix, and placed in front of a blue LED source. The blue light is partially absorbed by microscopic Ce:YAG phosphors and converted to yellow light which additively mix up with unabsorbed blue to generate white light. The working principle is shown schematically in Fig.1. The drawback of polymer matrix is that they degrade due to junction temperature of the semiconducting light emitting diode during continuous operation and thermal cycles, thus the performance quality decrease over time and usage. An improved thermal stability using Ce:YAG glass-ceramics phosphors were proposed in the literature[1-4]. Glass-ceramics is a material having crystalline phase embedded in a glass matrix. Starting from Ceria doped Yttria-Alumina-Silica (YAS) base glass one can derive the Ce:YAG glass-ceramics phosphor with suitable heat treatment. The advantage is they are thermally stable and have almost no degradation upon thermal cycles. There are reports about compositional dependence, structure property correlations, microstructure evolution and luminescent properties of Ce:YAG phosphor crystals in YAS glasses[1-4]. Crystallization kinetics of YAS glass compositions and evolution of mixed crystalline phases like Mullite ($Al_6Si_2O_{13}$), Crystoballite and Y-disilicate ($Y_2Si_2O_7$) are reported in literature[5-7].

In this work, we focused on fabrication and characterization of a glass compositions which can be devitrified into a single phase Ce:YAG glass-ceramics phosphor. Further, to optimize the white light generation, we systematically studied the phosphor crystal growth kinetics, microstructure and photoluminescence spectra. Knowledge of crystallization kinetics is important for controlled devitrification, which was extracted from non-isothermal DTA data. Crystallization kinetics and isothermal predictions were simulated for YAS glass using non-iosthermal data and AKTS software. This study helped us to develop the Ce:YAG glass-ceramics phosphor with required concentration, microstructure and photoluminescence for the demonstration of a white LED.

*Author for Correspondence: P. Nandi
E-mail: pnandi@barc.gov.in

Glass Synthesis

CeO_2 doped Y_2O_3-Al_2O_3-SiO_2 glasses were prepared with varying compositions. The aim was to derive the desired Ce:YAG phosphor phase in the glass matrix. Most of the time there were mixed phases like $Y_2Si_2O_7$, $Al_6Si_2O_{13}$ and $Y_3Al_5O_{12}$ in the glass-ceramics depending on the initial glass composition and heat treatment schedule. After several iterations glass composition 45.1 Y_2O_3 - 31.8 Al_2O_3 - 21.4 SiO_2 - 1.7 CeO_2 (wt %) suitable for the glass-ceramics phosphor was optimised. To prepare the glass, constituent oxides were weighed and mixed thoroughly. Each batch were melted in Pt-Rh crucibles at

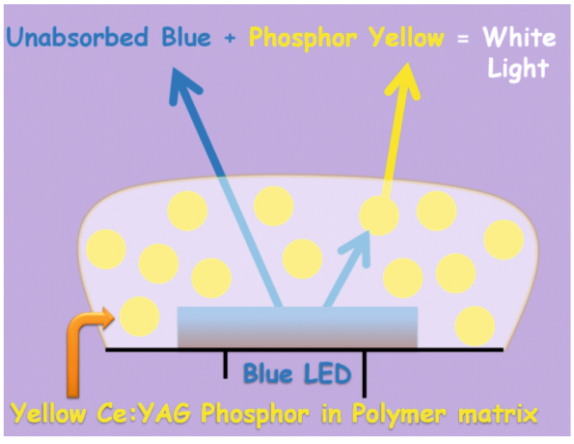

Fig.1: Schematic highlighting the working principle of white LED.

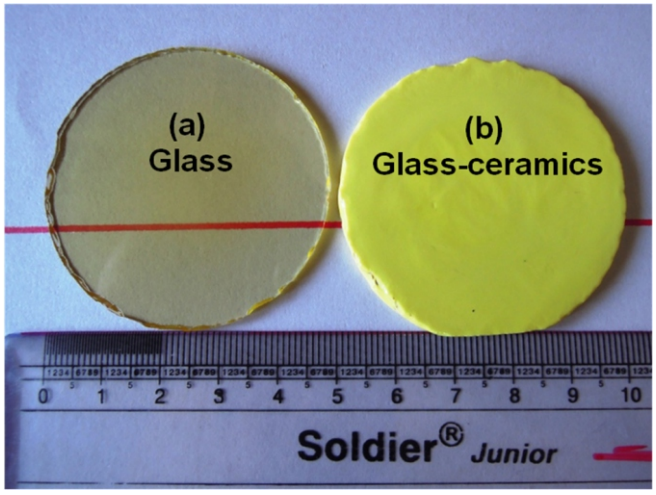

Fig.2: Polished YAS glass disk(a) and glass-ceramics phosphor(b).

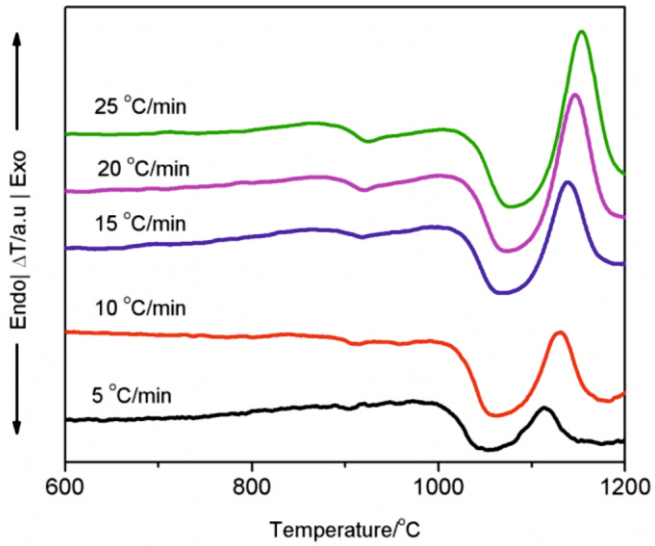

Fig.3: DTA plot of YAS glass powder at five different rates of heating.

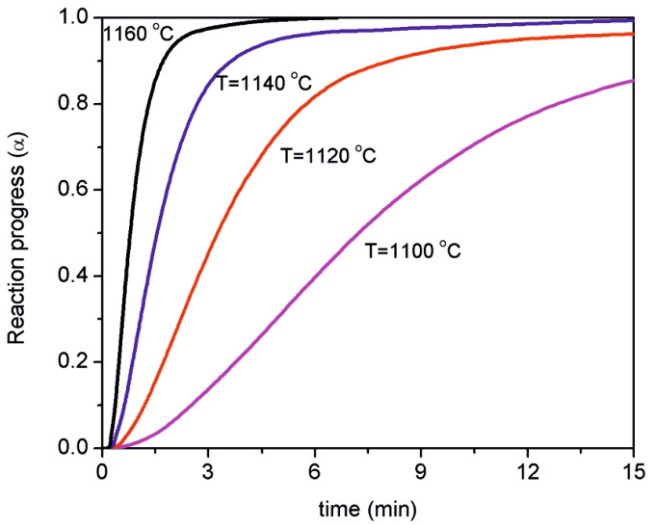

Fig.4: Isothermal predictions of the reaction progress(α) with time(min) at four temperatures (T °C).

~1650°C and held for two hours for homogeneous mixing before quenching the melt into a cylindrical mold. The same composition of the glass was prepared several times to check the repeatability and also to prepare glass cylinders in diameter range 10mm to 50mm. Prepared glasses were annealed at appropriate temperature to remove the thermal stresses. The glasses were cut into disks and polished before crystallization. Photographs of transparent and bubble free glass disk (left) and the yellow glass-ceramics (right) after suitable isothermal heat treatment are shown in Fig.2.

Thermal analysis

The differential thermal analysis (Labsys-SETARAM) was used to record the thermal changes of glass powder for five different heating rates: 5, 10, 15, 20 and 25°C per min shown in Fig.3. The data shows the glass transition (T_g) at around 875°C followed by exothermic peak in the temperature range of 1050-1200°C, indicating crystallization of glass. Because of high T_g, the glass-ceramics phosphors are thermal stable and not degrading as compared to polymer based phosphors at LED working temperature. The DTA data was used to derive the crystallization kinetics parameters by isoconversional method as reported elsewhere[8].

The isoconvertional principle is that reaction rate (dα/dt) at a constant reaction progress (α) is only a function of temperature (T). The activation energy E(α) was calculated without any particular form of the reaction model f(α). That is the reason it is also called 'model free' kinetics principle. Activation energy (E) of crystallization at reaction progress (α = 0.5) estimated 659 $kJmol^{-1}$. No specification of the reaction model f(α) is necessary for the kinetic prediction since the product term {A(α) f(α)} considered constant, which was also experimentally extracted along with E(α) from the isoconvertional data analysis. Then it is possible to simulate kinetic predictions at isothermal temperature (T) as given below.

$$t_\alpha = \int_{\alpha_0}^{\alpha} \frac{d\alpha}{\{A(\alpha) f(\alpha)\} e^{\frac{-E(\alpha)}{RT}}}$$

Four isothermal predictions of our interest simulated from above equation shown in fig.4. For fixed conversion α = 0.8, calculated time prediction for isothermals at 1160°C, 1140°C, 1120°C and 1100°C are approximately 1.4, 2.7, 5.7, and 12.9 min, respectively. Accordingly the glass samples were baked at isotherms for different holding times, for different fraction of crystalline phase. The yellow colored glass-ceramics disk (Fig.2) was obtained by isothermal heating at 1120°C for ~ 5 min.

Glassy/ Crystalline phase and microstructure analysis

X-ray diffraction of base glass and glass-ceramics powder are given in Fig.5. The characteristic broad hump confirms the amorphous nature of the glass sample. The diffraction pattern of glass-ceramics shows the crystalline peaks and a broad hump in the background at around 25–35 degrees indicating the residual glass. All the crystalline peaks can be attributed to cubic YAG as compared to JCPDS card #33-0040. Thus it confirms that single phase Ce:YAG phosphors present in the glass-ceramics sample.

The microstructure of glass-ceramics surface as observed under scanning electron microscope. Dendrite like crystal growth was observed on the glass-ceramics surface shown in Fig.6. These microscopic dendrites grew uniformly in glass matrix acting as yellow phosphors. Polishing quality of the

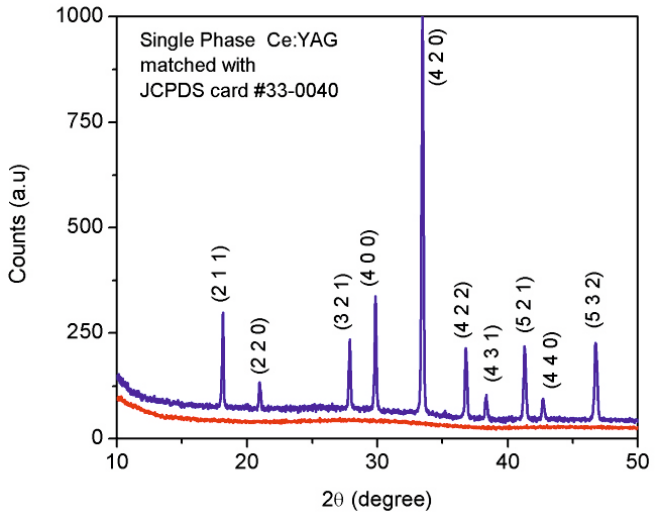

Fig.5: XRD pattern of as prepared YAS glass(red) and glass-ceramics phosphor(blue).

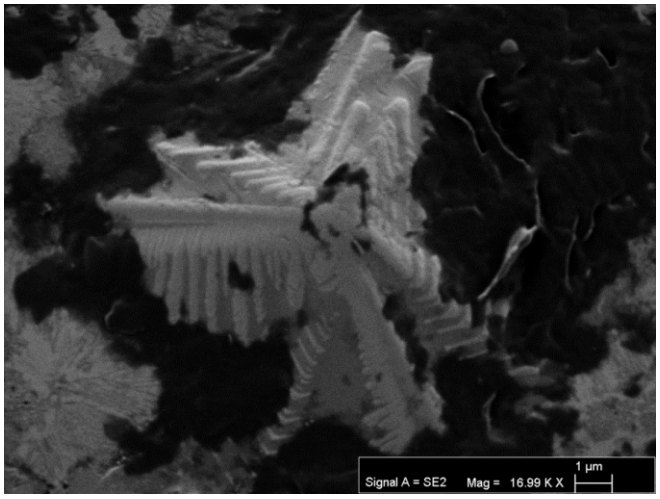

Fig.6: Micrograph of Ce:YAG dendrite at glass-ceramics surface.

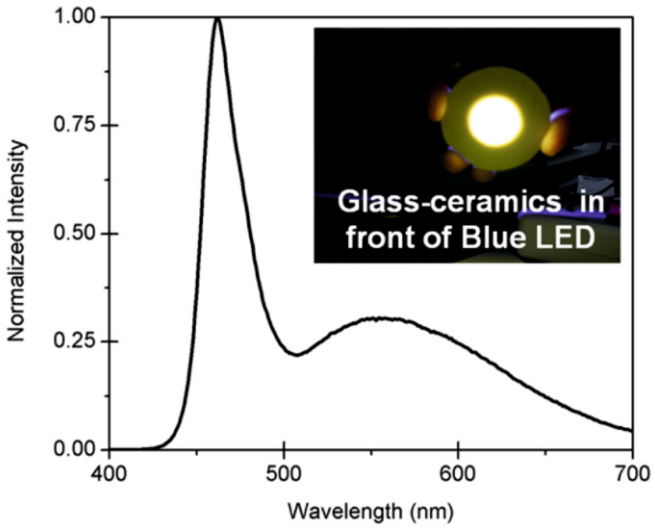

Fig.7: The illuminated glass-ceramics(inset) and the white light spectra as recorded by the PL spectrometer.

Fig.8: White light dispersed by a compact disk grating to create the rainbow.

surface before crystallization was important parameter to control the microstructures. Fine polished surface has less nucleation, hence shows less number of dendrite compared to the rough polished surface. Surface nucleation was particularly helpful to control the crystal growth only on the surface, therefore their optical properties suitable for generation of white light.

Optical properties of glass-ceramics phosphors

The photoluminescence experiments were done to test the optical quality of the material. The glass-ceramics sample shown in Fig.7 was illuminated against a blue LED. The spectrum was recorded in spectrometer (FLS 980-Edinburgh Instruments) using the remote fibre optic probe, and PMT detector. Two peaks are observed, one is the unabsorbed blue peaked at 465 nm and the other one is broad band Ce:YAG yellow fluorescence, ranging from 500 to 700 nm with a peak maximum at 570 nm as shown in Fig.7. The color co-ordinates of the spectrum found at (0.37, 0.39) which is nearest among the prepared samples to the theoretical white point at (0.33, 0.33). It was evident from the study that using appropriate heating schedule one can fine-tune the phosphor concentration, thickness and color of the resultant spectra. A device was assembled for white light generation using a commercially available blue light source and our laboratory made Ce:YAG glass-ceramics phosphor. The white light was again diffracted by a CD grating to disperse the light into rainbow colors shown in the Fig.8. This confirms the presence of red, green, and blue colors primarily required for white light spectrum.

Conclusions

We have developed an unique glass composition that can be converted to single phase Ce:YAG glass-ceramics phosphor. Processing parameters like, time and temperature dependent crystallization rate, polishing quality, microstructure and thickness of evolving phosphor layer are optimized to generate the white light. Isothermal predictions were used to crystallize the glass. Ce:YAG glass-ceramics with conversion factor (~ 0.75) was obtained by isothermal heating at 1120°C for ~5 min, found to generate the desired optical properties. XRD analysis of glass-ceramics confirms the evolution of Ce:YAG phase. Microstructure evolution showed surface nucleation and dendrite like growth of phosphor crystals, making ~50 µm thick phosphor layer. A device was setup using blue LED to demonstrate the white light generation using our laboratory made glass-ceramics phosphor.

Acknowledgements

Authors thank Madangopal Krishnan, Former Director, Materials Group, BARC for his role in conceiving and guiding the team of scientists involved in this work. We acknowledge thankfully Senthil Kumar, Yogesh Shirkar and P. A. Wagh for rendering technical assistance during preparation of glass and glass-based ceramics. Thanks to Abhijit Ghosh for carrying out FESEM experiments as part of this study.

References

[1] S. Fujita, S. Tanabe, Glass-Ceramics and Solid-State Lighting, International Journal of Applied Glass Science, 2015, 6, 356-363.

[2] S. Fujita, A. Sakamoto, S. Tanabe, Luminescence characteristics of YAG glass-ceramic phosphor for white LED, IEEE Journal of Selected Topics in Quantum Electronics, 2008, 14, 1387–1391.

[3] D. Chen, Xiang W, Liang X, Zhong J, Yu H, Ding M, Lu H, Z. Ji, Advances in transparent glass ceramics phosphors for white light emitting diode- A review, Journal of the European Ceramic Society, 2015, 35, 859–869.

[4] A. Keshavari, W. Wisniewski, R. Kloe, C. Russel, Surface Crystallization of yttrium aluminum garnet from a silicate glass, Crystal Engineering Communication, 2013, 15, 5425-5433.

[5] S. Ahmad, T. Ludwig, M. Herrmann, M. Mahmoud, W. Lippmann, H. Seifert, Phase evaluation during high temperature long heat treatments in the Y_2O_3 – Al_2O_3 – SiO_2 system, Journal of the European Ceramic Society, 2014, 34, 3835–3840.

[6] B. Roduit, W. Dermaut, A. Lunghi, P. Folly, B. Berger, A. Sarbach, Advanced Kinetics based simulation of time to maximum rate under adiabatic conditions, Journal of Thermal Analysis and Calorimetry, 2008, 93, 163–173.

[7] R. Muller, E. D. Zanotto, V. M. Fokin, Surface crystallization of silicate glasses: nucleation sites and kinetics, Journal of Non-Crystalline Solids, 2000, 274, 208-231.

[8] P. Nandi, M. Goswami, A. Arya, M. Krishnan, Study of crystallization kinetics, microstructure and optical properties of Ce: YAG glass-ceramics for white LED applications; Journal of Thermal Analysis and Calorimetry. 2021. https://doi.org/10.1007/s10973-021-10690-w.