PROCESSING LOW THERMAL EXPANSION GLASS-CERAMIC FROM LITHIUM ALUMINOSILICATE (LAS) GLASS

A THESIS

Submitted by

VENKATESWARAN C.

for the award of the degree

of

DOCTOR OF PHILOSOPHY

SCHOOL OF ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY MANDI

HIMACHAL PRADESH-175075, INDIA

MARCH 2021

Dedicated to ISRO, my Family & Friends

Preface

The present Ph.D. thesis is submitted in candidacy for a Ph.D. degree from Indian Institute of Technology (IIT), Mandi. The work presented herein was carried between August 2014 and August 2020 at Glass and Electronic Materials Division (GEM), Materials and Metallurgy Group (MMG), Materials and Mechanical Entity (MME), Vikram Sarabhai Space Centre (VSSC) under the supervision of Dr. Sharad Chandra Sharma, VSSC, Dr. Rahul Vaish and Dr. Vishal Singh Chauhan of School of Engineering.

The project was fully funded by the Department of Space (DoS), Indian Space Research Organisation (ISRO), Vikram Sarabhai Space Centre (VSSC). The main goal of the project was to explore the development of low thermal expansion glass-ceramics (LEGCs) from lithium aluminosilicate glass with improved properties.

Declaration

I hereby declare that the entire work embodied in this thesis is the result of investigations carried out by me in the ***Glass and Electronic Materials Division***, Vikram Sarabhai Space Centre (VSSC) and ***School of Engineering,*** Indian Institute of Technology (IIT), Mandi, under the supervision of Dr. Sharad Chandra Sharma, VSSC, Dr. Vishal Singh Chauhan and Dr. Rahul Vaish, IIT-Mandi**,** and that it has not been submitted elsewhere for any degree or diploma. In keeping with the general practice, due acknowledgements have been made wherever the work described is based on the finding of other investigators.

Place:	Thiruvananthapuram	Signature:	
Date:	19th March 2021	Name:	Venkateswaran C (ERPD1401)

Certificate

This is to certify that the thesis entitled **“Processing Low Thermal Expansion Glass-Ceramic from Lithium Aluminosilicate (LAS) glass”** submitted by **VENKATESWARAN C**, an External Research Scholar (ERPD1401) in the School of Engineering, Indian Institute of Technology, Mandi, for the award of the degree of **DOCTOR OF PHILOSOPHY**, is a record of an original research work carried out by him under my supervision and guidance. The thesis has fulfilled all the requirements of the Vikram Sarabhai Space Centre (VSSC). The results embodied in this thesis have not been submitted to any other University or Institute for the award of any degree or diploma.

शरद चन्द्र शर्मा

Sharad Chandra Sharma
Associate Director, R&D
Vikram Sarabhai Space Centre,
Indian Space Research Organisation,
Thiruvananthapuram, Kerala, PIN-695022

Place: Thiruvananthapuram

Date: 19th March 2021

THESIS CERTIFICATE

This is to certify that the thesis entitled **"PROCESSING LOW THERMAL EXPANSION GLASS-CERAMIC FROM LITHIUM-ALUMINOSILICATE (LAS) GLASS"** submitted by **VENKATESWARAN C** to the Indian Institute of Technology, Mandi for the award of the degree of **Doctor of Philosophy** is a bonafide record of research work carried out by him under my supervision. The thesis has fulfilled all the requirements as per the regulations of the Institute. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

Rahul Vaish
Associate Professor
School of Engineering
Indian Institute of Technology Mandi
Himachal Pradesh, PIN—175075

Vishal Singh Chauhan
Associate Professor
School of Engineering
Indian Institute of Technology Mandi
Himachal Pradesh, PIN—175075

Place: Kamand, Mandi

Date: 19th March 2021

PUBLICATIONS AND PRESENTATIONS

PUBLICATIONS

1. Venkateswaran, C. *et al.,* “Near-zero thermal expansion transparent lithium aluminosilicate glass-ceramic by microwave hybrid heat treatment." *Journal of the American Ceramic Society* 101, no. 1 (2018): 140-150.
2. Venkateswaran, C. *et al.,* “Crystallisation studies on site-saturated lithium aluminosilicate (LAS) glass." *Thermochimica Acta* 679 (2019): 178311.
3. Venkateswaran, C. *et al.*, “Processing Li_2O-Al_2O_3-SiO_2 (LAS) glass-ceramic with and without P_2O_5 through bulk and sintering route”, *Journal of Non-Crystalline Solids*, (2020): 120289.
4. Venkateswaran, C. *et al.*, “Crystallisation and sintering studies on an anomalous las glass towards making tunable expansion ceramic”, *International Journal of Applied Glass Science*, (2021) IJAG15917.
5. Venkateswaran, C. *et al.*, “Lithium aluminosilicate (LAS) ceramic: A review of recent Progress”, International Materials Review, IMR696 (Under review).

PRESENTATIONS IN CONFERENCE, SYMPOSIUMS & TECHNICAL MEETING

1. Near-Zero thermal expansion materials from microwave hybrid heating, International Conference on Advances in Glass Science and Technology (ICAGST)-2017, CSIR-Central Glass and Ceramic Research Institute, Kolkata, 23rd-25th January 2017 *(Received Best Poster Award).*
2. Nanoindentation studies on lithium aluminosilicate glass and glass-ceramic, Indian Institute of Metals (IIM) - Research Scholar Symposium on materials Science and Engineering, 6th April 2018.
3. Crystallisation behaviour of lithium aluminosilicate glass, Indian Institute of Metals (IIM) - Research Scholar Symposium on materials Science and Engineering, 3rd April 2019.
4. Effect of Phosphorus Pentoxide (P_2O_5) in processing lithium aluminosilicate glass-ceramic through bulk and sintering route, International Conference on Advanced Thermostructural Materials & Thermal Protection System-2020, Thiruvananthapuram, 19th -21th January 2020 *(Received Best Paper Award).*
5. C. Venkateswaran, Processing of low expansion glass-ceramic, Annual Technical Meeting-2020, Materials Research Society of India, Thiruvananthapuram, 7th March 2020. (*Receievd Best Presentation Award).*

ACKNOWLEDGEMENTS

Foremost, I am very grateful to GOD ALMIGHTY for grace and blessing.

I would like to sincerely thank Chairman, ISRO, Director, VSSC and Academic Committee for providing me with all the opportunities.

My sincere gratitude to my PhD guides Dr. Rahul Vaish and Dr. Vishal S. Chauhan of IIT-Mandi, and Dr. S. C. Sharma, AD (R&D), VSSC who have paved my research career. Special thanks to Dr. Rahul Vaish, who inspired me a lot through his diligent involvement in research without his follow-up this thesis would not have been possible.

My sincere thanks to my Doctoral Committee for intellectual questions and guidance.

My travel towards this thesis would not be possible without support from number of people. I am grateful to all of them. Some, however, deserve special mention:

Faculties at IIT-Mandi: Dr. Sudhir Pandey, Dr. Vishwanath B., Dr. Venkata Krishnan and my Co-guide Dr. V. S. Chauhan who educated me various aspects of Materials Science and Engineering during the course work.

Dr. P.V. Venkitakrishnan, Director, CBPO/ISRO & Dr. Sam Dayala Dev D., Director, IISU – for encouraging this work from its inception.

My Senior colleagues: Dr. Roy M. Cherian, AD, VSSC, Dr. M. Mohan, Deputy Director, VSSC (MME), Dr. Bhanu Pant, Group Director, MMG/VSSC, and Dr. H. Sreemoolanadhan – for their honest cooperation, faith, encouragement and support.

Dr. S. A. Ilangovan DD, (PCM) MME and unknown reviewers of my manuscripts – for their constructive review comments.

International Commission on Glass (ICG) and Team, CGCRI – for the tutorial programme on glass science & technology.

Smt. Mariamma Mathew – for faith and freedom.

Enni Krishna and K.R. Narayanan Kutty – for performing laser generation studies.

All the 'Ignited Minds of INSTEF', Dr. Davinder and Dr. Rohit Patak – for their friendship.

All my Colleagues, Contract staffs, Trainee and Project students in GEM and AMCD – for helping me during experiments.

Dr. Sivaprakash, Dr. Chakravarthy, Dr. Sudhakar, Dr. Suresh, Arjunraj, Sadhik & Somu– for their positive influence.

Ezhilan, Karthick and Sandy – for just being around.

Doctor Manish Agarwal – for preserving my knee.

I also acknowledge all my Teachers with a deep sense of reverence.

I am indebted to my Lovely Family for the absolute love, help and support that they have extended. And finally, I acknowledge my wife, Divya, who sacrificed a lot during this Journey.

ABBREVIATIONS AND NOTATIONS

ABBREVIATIONS

CTE – Coefficient of thermal expansion
DSC – Differential scanning calorimeter
DTA – Differential thermal analyser
GC – Glass-ceramic
HQSS – High or β-quartz solid solution
JMA – John-Mehl-Avrami
KSS – Keatite solid solution
LEGC – Low thermal expansion glass-ceramic
LAS – Lithium aluminosilicate
LTCC – Low temperature co-fired ceramic
NTE – Negative thermal expansion
PTE – Positive thermal expansion
SEM – Scanning electron microscope
SOFC – Solid oxide field cell
s.s. – solid solution
TA – Thermo-analytical
TE – Thermal expansion
TMA –Thermo-mechanical analyser
TEM – Transmission electron microscope
ULEGC–Ultra-low thermal expansion glass-ceramic
XRD – X-ray diffraction
ZTE – Zero thermal expansion

NOTATIONS

T_0 – 300 K
ΔG_D –Activation energy for transfer/diffusion of a species through the melt-nucleus interface
Δh^* –Activation enthalpy of volume or enthalpy relaxation
η_s –Activation enthalpy of shear viscosity
E_{ac} –Activation energy of electrical conductivity
E_n –Activation energy for nucleation
E_c –Activation energy for crystal growth
E_g –Activation energy of glass transition
ω –Angular frequency
K_B –Boltzmann constant ($1.38064852 \times 10^{-23}$ m^2 kg s^{-2} K^{-1})
θ –Bragg angle
r^* –Critical radius of the nucleus
x –Crystallized fraction at time t
T_c –Crystallisation onset temperature
$\propto$ –Coefficient of thermal expansion
ρ –Density
a_o –Diffusion jump distance or mean crystal size
σ_c –Electrical conductivity
E_f –Electric field intensity inside the material
E –Effective overall activation energy or activation energy of crystallisation

K	–Effective overall reaction rate or dimensionless shape factor
W^*	–Free energy change due to the creation of the interface
ΔG	–Free enthalpy of motion
ν	–Frequency factor
g'	–Geometric or shape factor
F	–Glass fragility index
T_g	–Glass transition temperature
P	–Heat dissipated per unit volume of a dielectric
α	–Heating rate
m	–Integer or half-integer denoting the dimensionality of the growth
D	–Mean size of the particle crystal
T_m	–Melting temperature /start of meting range
I_υ	–Nucleation frequency per unit volume
$I_{\upsilon 0}$	–Nucleation rate at steady-state (I_o)
T_n	–Nucleation temperature
σ	–Optical attenuation/turbidity coefficient
T_P	–Peak crystallisation temperature
n	–Refractive index or Avrami exponent/parameter
ε_r	–Relative permittivity
T_S	–Softening point
C_p	–Specific heat capacity
f	–Surface site fraction
T	–Temperature
u	–The crystal growth rate
ε''	–The imaginary part of the permittivity
$\tan\delta$	–The loss tangent of the material
ε'	–The real part of permittivity
TS	–Thermal stability of the glass
t	–Time
R	–Universal gas constant
ε_0	–Vacuum permittivity
η	–Viscosity of glass
λ	–Wavelength of light
β	–XRD machine constant

ABSTRACT

The material with dimensional and thermal stability manifested their importance in widespread applications in kitchen to cosmos. The material of choice for applications which demand very high dimensional stability is lithium aluminosilicate (LAS) based low thermal expansion glass-ceramic. This doctoral thesis work explored the possibility of realizing an ultra-low expansion, transparent glass-ceramic (GC) for its potential use in space applications.

Chapter 1 introduces the field of research, background motivation and objective of the thesis.

Literature Review presented in Chapter 2 is targeted to discuss the structural features of different LAS crystal system including their polymorphs and solid-solutions, the origin of unusual properties, the role of chemical constituents and additives, significant results of thermo-analytical studies, current commercial applications, recent trends, emerging technologies and future research perspectives. This review offers adequate fundamental, and recent progress in the LAS system with significant emphasise on processing low thermal expansion glass-ceramic (LEGC), ceramic matrix composite, low temperature co-fired ceramics and associated technologies.

Chapter 3 brings out the process optimisation procedure adopted for realising transparent and nanocrystalline ultra-low thermal expansion glass-ceramic using microwave-assisted (hybrid)crystallisation of LAS glass realised from conventional melt quenching route. The experimental strategy involved two stages (i) identification of the optimum crystallisation temperature (T_c) under a microwave field and (ii) optimisation of microwave-assisted crystallisation process to achieve near-zero coefficient of thermal expansion (CTE). Optimum heat treatment schedules for nucleation and crystallisation under a microwave environment were found to be 720 °C/ 24 h and 775 °C/0.3 h respectively. The optimised heat treatment condition revealed the efficacy of the microwave hybrid heating, by producing nanocrystalline

(35-50 nm) and transparent (>82%) ultra-low thermal expansion glass-ceramic (ULEGC) having a linear coefficient of thermal expansion of –0.03 $\times 10^{-6}$ °C^{-1} (0-50 °C).

In Chapter 4, crystallisation parameters of the LAS glass composition were studied using non-isothermal DSC and thermoanalytical (TA) methods. Available sites for nucleation has to reach a saturated condition, that is a primary validity criterion for employing conventional TA methods. The activation energy of crystallisation for a thermally stable LAS composition was determined after the prenucleation process, and it was found to be 371 ± 14 kJ/mol. A heat treatment programme for controlled crystallisation process was designed to result in a transparent (>80%), nanocrystalline, low expansion (CTE: –0.31$\times 10^{-6}$ °C^{-1} between –60 to +60 °C) GC. Crystal growth at 775 °C was determined to be in the range 2.56–3.53 $\times 10^{-11}$ m/s and viscosity of glass near the growth front was predicted to vary between 1.28 $\times 10^{5}$ and 2.82 $\times 10^{5}$ N. s. m^{-2}.

In Chapter 5, the LAS glass compositions with P_2O_5 content varying between 0 – 6.8 mol% were prepared through the conventional melt-quenching route. From high-temperature dilation results, it was found that different amount of P_2O_5 in the LAS glass greatly influences phase transformation characteristics, the softening and melting points. Two LAS glass systems, namely 3.1 mol% of P_2O_5 (P3.1) and without P_2O_5 (P0) were considered further towards making low expansion GC using bulk and sintering route due to their contrary thermal behaviour. The optimum nucleation temperature for P0 and P3.1 glass system was determined to be 640 and 700 °C, respectively using the Marotta method. Effect of heat-treatment temperature on the thermal expansion behaviours of the LAS GC was explained in detail. Negative thermal expansion (NTE) and low expansion GCs were produced from bulk and sintering route. Transparent β–quartz s.s. based ultra-low thermal expansion (0.04 $\times 10^{-6}$ °C^{-1} between –60 and 400 °C) GC was produced.

Chapter 6 presents the crystallisation behaviour of unconventional LAS (1: 1.2: 7) composition having MgO, BaO, K_2O, and ZrO_2. Crystallisation parameters were determined using thermo-analytical models based on Differential Scanning Calorimetry (DSC). The activation energy of crystallisation, E, and frequency factor, ν were calculated to be 354.40 kJ mol^{-1} K^{-1} and 1.63×10^{15}, respectively. Effect of sintering temperature on density, phase constitution, thermal expansion, and microstructure are reported herein. The temperature range between 1373 K and 1473 K was found to be the optimum window for sintering the glass particles. GC with CTE matching the Fe-Ne superalloy is reported herein. Considering the LAS glass system's better sinterability, efforts were made towards sintering alumina with LAS glass as a sintering aid. The 5 wt.%. LAS/Al_2O_3 composite was prepared with density: 3.6 g/cm^3, relative permittivity 10.5, and dielectric loss tangent 2.45×10^{-3}. This composition was found to be a potential CTE compensator material while processing tailorable CTE ceramic or polymer-based composites.

Limitation of the present work, summary and future scope of work are presented in Chapter 7.

Keywords: lithium aluminosilicate, glass-ceramic, low thermal expansion, negative thermal expansion

TABLE OF CONTENTS