

THE ANALYSIS OF PHYSICAL, DIELECTRIC, AND THERMAL PROPERTIES ON GLASS-CERAMIC OXIDE $30\text{B}_2\text{O}_3$: $22.5\text{V}_2\text{O}_5$: 22.5MoO_3 : 15TeO_2 : $10\text{Li}_2\text{O}$

Peerapong Yamchumporn^{1,2}, Kitipun Boonin^{1,2}, Narit Triamnak³, Thanapong Sareein⁴, Narong Sangwaranatee^{5,*}, and Jakrapong Kaewkhao^{1,2}

Received: July 25, 2024; Revised: September 03, 2024; Accepted: October 11, 2024

Abstract

In this study, the dielectric and thermal properties of ceramic materials are examined to provide the thermoelectric performance of $30\text{B}_2\text{O}_3$: $22.5\text{V}_2\text{O}_5$: 22.5MoO_3 : 15TeO_2 : $10\text{Li}_2\text{O}$ samples that were synthesized utilizing the melt-quenching process. Archimedes' Principle was used to determine the physical properties of the sample, showing a density of 3.07 g/cm^3 , and the molar volume of the sample was measured at $39.35\text{ cm}^3/\text{mol}$. Bragg's law uses an X-ray diffractometer to analyze the glass-ceramic structures. The FTIR spectroscopy spectra identified characteristic vibrations of VO_5 , TeO_4 , BO_4 , and BO_3 units. The real part of the permittivity and the loss tangents were investigated and shown on 1.65×10^2 and 0.083 at the frequency range of 1 MHz at room temperature measurement. Thermal analysis such as thermogravimetry and differential scanning calorimetry was investigated in the $25\text{--}800^\circ\text{C}$ of the temperature range. Materials studied in this work can be thermoelectric materials utilizing their dielectric and thermal characteristics.

Keywords: Melt-Quenching; The Permittivity; Thermal Analysis; Thermoelectric

¹ Physics Program, Faculty of Science and Technology, Nakhon Pathom Rajabhat University, Muang, Nakhon Pathom 73000, Thailand. E-mail: peerapong_bk11@hotmail.com; kboonin@hotmail.com; mink110@hotmail.com

² Center of Excellence in Glass Technology and Materials Science, Nakhon Pathom Rajabhat University, Muang, Nakhon Pathom 73000, Thailand. E-mail: peerapong_bk11@hotmail.com; kboonin@hotmail.com; mink110@hotmail.com

³ Department of Materials Science and Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom, 73000, Thailand. E-mail: triamnak_n@su.ac.th

⁴ Division of Industrial Materials Science, Faculty of Science and Technology, Rajamangala University of Technology Phra Nakhon (North Bangkok Campus), 1381 Pracha Rat 1 Rd., Wong Sawang, Bang Sue, Bangkok, 10800, Thailand. E-mail: thanapong.s@rmup.ac.th

⁵ Applied Physics, Faculty of Science and Technology, Suan Sunandha Rajabhat University, Bangkok, Thailand. E-mail: narong.sa@ssru.ac.th

* Corresponding author

Introduction

Thermoelectric materials are capable of directly converting heat into electrical energy and vice versa. The thermoelectric properties of these materials depend on their electrical and thermal characteristics. An effective thermoelectric material should exhibit high electrical power output and low thermal conductivity. Glass-ceramics have significant potential as thermoelectric materials due to their ability to reduce thermal conductivity through the formation of crystalline phases. Thus, glass-ceramics hold promise for the development of thermoelectric materials with thermal and electrical properties for thermoelectric applications (Gonon and Dupla, 2021). The investigation of the specific composition 30B₂O₃: 22.5V₂O₅: 22.5MoO₃: 15TeO₂: 10Li₂O in this study represents a novel exploration, as this combination has not been extensively studied previously, particularly in the context of thermoelectric applications. The study of its dielectric and thermal properties adds new knowledge to the field of glass-ceramics. The components in the glass matrix indicate the crucial part of its properties. Boron oxide (B₂O₃) is known for its excellent glass-forming ability and contributes to the structural network, enhancing the thermal and chemical stability of the glass (Rao *et al.*, 2008). Vanadium pentoxide (V₂O₅) is an essential component for semiconducting properties and has been extensively studied for its role in enhancing the dielectric properties and electrical conductivity of glasses. Due to the some of the infrared vibrational bands of the structural groups of these ions sit in the same area as those of the BO₃ and BO₄ structural units, it is envisaged that vanadium ions will dissolve easily in the borate glass matrices (Elalaily, and Mahamed 2002). Molybdenum trioxide (MoO₃) contributes to forming non-bridging oxygens, which are crucial for modifying the glass network and influencing the thermal and dielectric behavior (Chowdari *et al.*, 1998). Tellurium dioxide (TeO₂) improves thermoelectric efficiency with low phonon energy (Ibrahim *et al.*, 2023). Lastly, lithium oxide (Li₂O) is added to modify the glass network, enhancing the electrical conductivity and thermal properties (Dalal *et al.*, 2015). The combination of these oxides results in a complex glass network with unique properties. This research addresses the ongoing need for low-cost and efficient thermoelectric materials. The investigated glass-ceramic, composed of readily available oxides, offers a potential solution to the cost aspect. While the direct thermoelectric performance is not thoroughly evaluated in this work, the characterization of

thermal and dielectric properties lays the groundwork for further exploration in this direction. Additionally, this study provides insights into the influence of each oxide component on the material's properties. This understanding can guide future compositional modifications to enhance specific properties, such as reducing thermal conductivity or improving electrical conductivity, which are crucial for thermoelectric applications. The Archimedes Principle was utilized to calculate the physical parameters, including density and molar volume. X-ray diffraction (XRD) analysis using Bragg's law reveals the glass-ceramic structures, which are crucial for understanding the crystallization behavior and phase composition. The vibrational bands of the structural groups of different ions inside the glass network, which are described in the wavenumber range of 500-4,000 cm⁻¹, are analyzed with the FTIR spectrum. The material's potential in electronic applications was demonstrated by determining its dielectric characteristics using an LCR Meter in the frequency range of 10²-10⁶ Hz. Specifically, the real part of the permittivity (ϵ') and loss tangents ($\tan \delta$) were detected. Thermal analysis, including thermogravimetry (TG) and differential scanning calorimetry (DSC), over a temperature range of 25-800°C, provides a comprehensive understanding of the material's thermal stability and thermal reactivity of the material. These analysis are essential for determining the suitability of the thermoelectric material for high-temperature applications.

In conclusion, the melt-quenching method was used to synthesize the 30B₂O₃: 22.5V₂O₅: 22.5MoO₃: 15TeO₂: 10Li₂O materials for the evaluation of their thermal and dielectric characteristics. The glass-ceramic oxide system is aimed at exploring its potential as a thermoelectric material. The characteristic combination of its components, coupled with thorough characterization offers insights into its applicability in thermoelectric applications.

Materials and Methods

The glass-ceramic samples with the composition 30B₂O₃: 22.5V₂O₅: 22.5MoO₃: 15TeO₂: 10Li₂O were synthesized using the conventional melt-quenching method, ensuring that the purity of all chemical powders was at least 99.99%. The powdered compound that had been weighed was mixed in a porcelain crucible and melted for 1 h at 1,473 K in an electric furnace. At normal

temperatures, the molten liquid was poured into a graphite mold. The molded samples were then put back into an electric furnace and annealed at 473 K for 2 h. Using a variety of measuring techniques, the samples were ready for examination once they had cooled to about room temperature and polished to the appropriate size for inspection with various equipment. Using water as the immersion medium and Archimedes' principle, the density of the sample was ascertained. Equation (1) uses this number to get the molar volume.

$$V_m = \frac{M_w}{\rho_g} \quad (1)$$

where V_m is the molar volume, M_w is molecular weight or molar mass, and ρ_g is the density of the sample. A portion of the glass-ceramic sample was ground into powder for structural measurement using X-ray diffraction using an instrument Shimadzu XRD-6100 with Cu K α radiation accelerated in a 2θ range of 10-80 degrees. FTIR spectroscopy (500-4,000 cm^{-1}) using Cary-630 FTIR Spectrometer. The sample was produced as disks with a thickness of 1.0 mm to determine the dielectric characteristics via an LCR Meter (4284A Precision, Keysight, USA) with a frequency range of 10^2 Hz-1 MHz. The prepared samples were ground into powder for thermogravimetric (TGA) and differential scanning calorimetric (DSC) analysis. The report data of spectra shown in the temperature range of 25-800°C was obtained on a simultaneous thermal analyzer (STA 449 F3 Jupiter, NETZSCH, Germany).

Results and Discussion

The X-ray diffraction (XRD) method was used to confirm the sample's structure. The broad arc in the $2\theta = 15^\circ$ to 35° is characteristic of an amorphous glass matrix. However, within this region, we observed a subtle peak corresponding to the diffraction peak of the LiV_3O_8 phase, as referenced from the standard crystal database (JCPDS No. 01-072-1193). Although the noise level makes it difficult to identify using XRD alone, this peak at $2\theta = 28^\circ$ indicates the formation of LiV_3O_8 crystals, as shown in Figure 1. These results are consistent with the structure reported in the study of Ramaraghavulu *et al.* (2012); they synthesized LiV_3O_8 ceramic powders to investigate their structural and dielectric properties (Ramaraghavulu *et al.*, 2012) and found that the LiV_3O_8 phase contributed to the intrinsic polarization mechanism of the material, resulting in improved dielectric

properties. Archimedes' Principle was used to calculate the physical parameters, including density and molar volume, which were found at 3.07 g/cm^3 and 39.35 cm^3/mol , respectively.

In Figure 2, the FTIR spectrum shows various transmission bands, indicating the presence of different functional groups within the glass matrix. The bands at 1,637, 2,263, 2,358, and 3,203 cm^{-1} are attributed to the O-H bending mode of vibration. The broad band around 3202 cm^{-1} suggests the presence of hydroxyl groups (O-H), which can influence the glass's dielectric properties and thermal stability due to their polar nature (Abo-Naf *et al.*, 2004; Ouis *et al.*, 2019). The band at 1,416 cm^{-1} corresponds to the asymmetric stretching vibrations of B-O bonds in BO_3 triangular units. The 1,193 cm^{-1} band indicates B-O bond stretching vibrations from diborate groups, which alter the structural and thermal characteristics of the BO_4 tetrahedra (Marimuthu *et al.*, 2009). The 1,088 cm^{-1} band is indicative of VO_5 polyhedra, while the

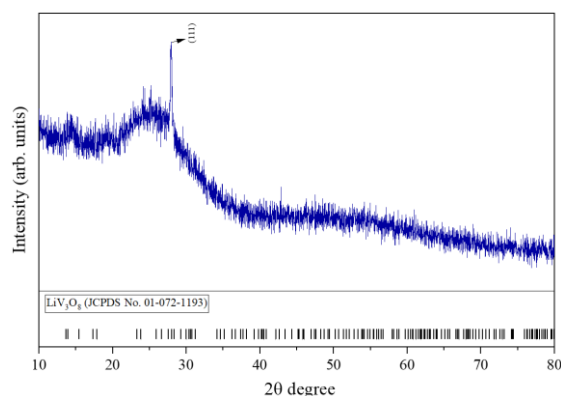


Figure 1. X-ray diffraction phase of LiMoVBT glass-ceramic

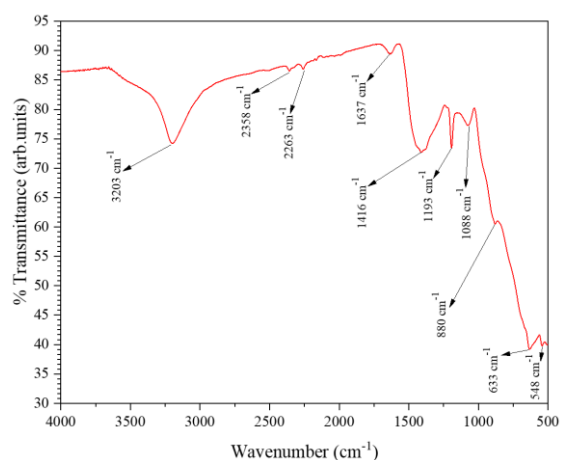


Figure 2. FTIR spectrum of LiMoVBT glass-ceramic

880 cm⁻¹ band is associated with V-O-V chains. The 548 cm⁻¹ band corresponds to the V=O double bond or the stretching mode of an oxygen atom between three vanadium atoms. Although vanadium ions can exist in the V²⁺ and V³⁺ states, they are typically found in the V⁴⁺ and V⁵⁺ states in glass matrices. The low V⁴⁺/V⁵⁺ ratio and electrical conductivity, ranging from 10⁻³ to 10⁻⁵ (Ωcm)⁻¹, are characteristic of vanadate glasses, which are known for electron hopping between V⁴⁺ and V⁵⁺ ions, identifying them as n-type semiconductors (Rao and Veeraiiah, 2004; Srinivas *et al.*, 2021). The 633 cm⁻¹ band indicates Te-O-Te bridges between four-coordinate tellurium atoms [TeO₄] (Ardelean *et al.*, 2000). Incorporating various metal oxides influences the thermal stability and glass transition temperatures, as observed in the DSC and TG analyses.

The DSC and TG analyses provide crucial insights into the thermal behavior and stability of the glass oxide composite 30B₂O₃: 22.5V₂O₅: 22.5MoO₃: 15TeO₂: 10Li₂O, which is essential for its potential application in thermoelectric materials. In Figure 3, the DSC analysis identifies several glass transition temperatures (*T_g*) at 120°C, 290°C, 320°C, 470°C, and 550°C, indicating multiple endothermic reactions.

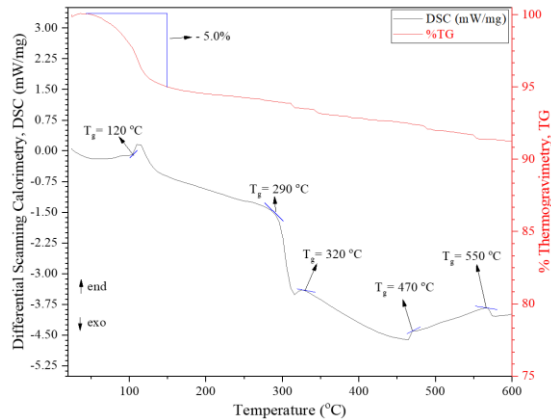


Figure 3. Thermal analysis of LiMoVBT glass-ceramic

The transitions seen here signify a state change from V⁴⁺ to V⁵⁺ as a result of different structural relaxations and rearrangements brought about by the glass matrix absorbing heat. Examining at a higher temperature causes modifications in the neighboring bonds as well. This causes the material to change from a stiffer to a more flexible condition when the oxidation state goes from V⁴⁺ to V⁵⁺. The absence of significant exothermic peaks suggests that the material remains amorphous, without undergoing crystallization or other heat-releasing

phase changes (Saiter *et al.*, 2007). The TG analysis reveals an initial mass loss of 5% at 150°C due to the evaporation of adsorbed moisture. Above this temperature, a gradual mass loss continues up to 800°C, with a total weight reduction of about 15%. This indicates the release of structural water and oxides. For AC measurements the dielectric properties are shown in Figure 4.

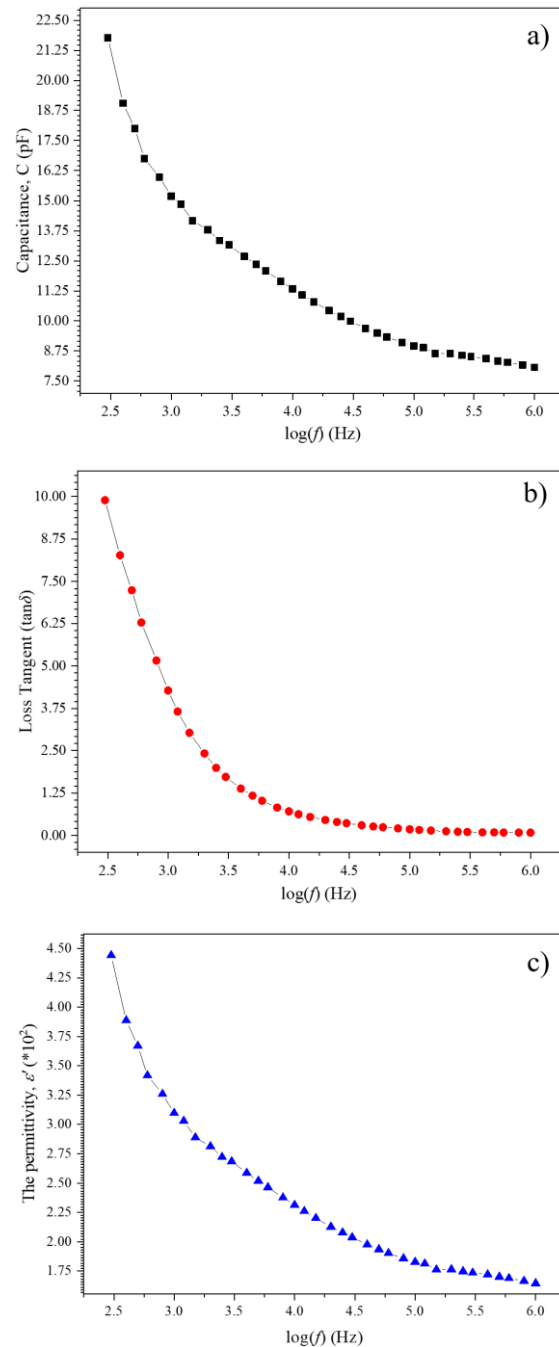


Figure 4. Dielectric properties of LiMoVBT glass-ceramic a) Capacitance, b) Loss Tangent, and c) The permittivity

The capacitance (C) shows a decreasing trend with increasing frequency at lower frequencies, the dipoles have enough time to align with the alternating field, resulting in higher capacitance. As the frequency increases, the dipoles cannot keep up with the rapid changes, leading to a decrease in capacitance. This behavior indicates good dielectric properties at lower frequencies, which is beneficial for applications requiring high capacitance at low frequencies. The loss tangent ($\tan \delta$) also decreases with increasing frequency, reaching a minimum before slightly increasing at higher frequencies. The loss tangent represents the energy lost in the dielectric material. A lower $\tan \delta$ at higher frequencies indicates lower energy loss and better insulating properties. However, the low loss tangent at higher frequencies suggests that the LiMoVBT glass-ceramic with the LiV_3O_8 phase indicated low dielectric losses, making it suitable for high-frequency applications (Ramaraghavulu *et al.*, 2012). The real part of the permittivity (ϵ') decreases as the frequency increases due to the inability of the dipoles to orient themselves quickly enough with the applied field that was similar to the capacitance. The high permittivity value at low frequencies indicates strong polarization within the material, which is desirable for capacitive applications, and a comparison of the dielectric properties with another research is presented in Table 1.

The loss tangent of LiMoVBT glass-ceramic is significantly low at higher frequencies. This is a significant advantage over materials, which may exhibit a higher loss tangent and consequently greater energy loss. The low loss tangent at high frequencies suggests that LiMoVBT glass-ceramic has superior insulating properties and minimal energy dissipation, making it highly suitable for high-frequency applications. The permittivity of LiMoVBT glass-ceramic also decreases with increasing frequency, aligning with the behavior of typical dielectric materials. However, LiMoVBT glass-ceramic may exhibit higher permittivity at lower frequencies compared to other materials. This higher permittivity at low frequencies is beneficial for applications that require strong polarization and high permittivity values. Considering both the dielectric and thermal properties, the LiMoVBT glass-ceramic shows potential as a thermoelectric material. This material may efficiently convert

thermal energy into electrical energy while exhibiting minimal energy loss. Additionally, its thermal stability ensures effective performance in high-temperature environments, making it a strong candidate for various thermoelectric materials.

Conclusions

The glass-ceramic samples with the composition $30\text{B}_2\text{O}_3$: $22.5\text{V}_2\text{O}_5$: 22.5MoO_3 : 15TeO_2 : $10\text{Li}_2\text{O}$ were synthesized using the conventional melt-quenching method. The density and molar volume are shown at 3.08 g/cm^3 and $39.35 \text{ cm}^3/\text{mol}$, respectively. The LiV_3O_8 peak was investigated by X-ray diffraction indicating the glass-ceramic. FTIR spectra are shown in the bonding vibration of the hydroxyl groups (O-H) where the presence of broad bands around $3,202 \text{ cm}^{-1}$ indicates the existence of hydroxyl groups, which can affect the glass's dielectric properties and thermal stability due to their polar nature. The DSC analysis identifies several glass transition temperatures (T_g) at 120°C , 290°C , 320°C , 470°C , and 550°C , indicating multiple endothermic reactions. The TG analysis reveals a total weight reduction of about 15% indicating the release of structural water and oxides. The presence of crystalline phases, such as LiV_3O_8 , contributes to polarization mechanisms within the material, increasing the dielectric constant. This is because crystalline regions can generate localized electric fields that interact with the amorphous matrix, enhancing dielectric permittivity. Moreover, the microstructure, including the size and distribution of the crystalline phases within the matrix, plays a crucial role in determining the overall dielectric behavior. In the results and discussion section, it was observed that samples with a higher degree of crystallinity exhibited a higher dielectric constant and lower dielectric loss, indicating improved energy storage capabilities. Strikethrough text

Acknowledgement

N. Sangwaranatee would like to thank Suan Sunandha Rajabhat University for supporting this research. The author would like to thank everyone

Table 1. The comparative analysis of the dielectric properties of the LiMoVBT glass-ceramic with another material at 1 MHz

Composition	Permittivity, ϵ'	Loss Tangent ($\tan \delta$)	Ref:
$35.14\text{Li}_2\text{O}-31.66 \text{ B}_2\text{O}_3-33.2\text{SiO}_2$	6.4×10^3	0.003	Hagemann and Ihrig (1979)
$35 \text{ B}_2\text{O}_3-25\text{SrO}-5\text{Al}_2\text{O}_3-35\text{SiO}_2$	5.7×10^3	0.002	Kim <i>et al.</i> (2019)
LiMoVBT	1.6×10^2	0.083	This work

who helped define the specimen's attributes. Kitipun Boonin and Jakrapong Kaewkhao thank the National Research Council of Thailand (NRCT) and Thailand Science Research and Innovation (TSRI) for funding this study.

References

- Abo-Naf, S.M., Ghoneim, N.A., and El-Batal, H.A. (2004). Preparation and characterization of sol-gel derived glasses in the ternary Na₂O-Al₂O₃-P₂O₅ system. *Journal of Materials Science: Materials in Electronics*, 15(5):273-282. <https://doi.org/10.1023/B:JMSE.0000024226.51362.de>
- Ardelean, I., Ciorcas, F., Peteanu, M., Bratu, I., and Ioncu, V. (2000). The structural study of Fe₂O₃-TeO₂-B₂O₃-SrF₂ glasses by EPR and IR spectroscopies. *Modern Physics Letters B*, 14(17-18):653-661. <https://doi.org/10.1142/S0217984900000087>
- Chowdari, B.V.R., Tan, K.L., and Ling, F. (1998). Synthesis and characterization of xCu₂O.yTeO₂ (1-x-y)MoO₃ glass system. *Solid State Ionics*, 113-115:711-721. [https://doi.org/10.1016/S0167-2738\(98\)00334-8](https://doi.org/10.1016/S0167-2738(98)00334-8)
- Dalal, S., Khasa, S., Dahiya, M.S., Yadav, A., Agarwal, A., and Dahiya, S. (2015). Optical and thermal investigations on vanadyl doped zinc lithium borate glasses. *Journal of Asian Ceramic Societies*, 3(3):234-239. <https://doi.org/10.1016/j.jascer.2015.03.004>
- Elalaily, N.A. and Mahamed, R.M. (2002). Effects of fast neutron and gamma irradiation on electrical conductivity of some borate glasses. *Journal of Nuclear Materials*, 303(1):44-51. [https://doi.org/10.1016/S0022-3115\(02\)00810-3](https://doi.org/10.1016/S0022-3115(02)00810-3)
- Gonon, M. and Dupla, F. (2021). Glass-ceramics and their applications. *Encyclopedia of Materials: Technical Ceramics and Glasses*, 2:709-727. <https://doi.org/10.1016/B978-0-12-818542-1.00008-4>
- Hagemann, H.-J. and Ihrig, H. (1979). Valence change and phase stability of 3d-doped BaTiO₃ annealed in oxygen and hydrogen. *Physical Review B*, 20:3871-3878. <https://doi.org/10.1103/PhysRevB.20.3871>
- Ibrahim, S.E., El-Mallawany, R., and Abouhaswa, A.S. (2023). Structural, optical and dielectric properties of tellurite borate glasses doped with cerium oxide. *Journal of Inorganic and Organometallic Polymers and Materials*, 33(8):2319-2330. <https://doi.org/10.1007/s10904-023-02682-0>
- Kim, M., Kim, G.H., Lee, T.K., Choi, I.W., Choi, H.W., Jo, Y., Yoon, Y.J., Kim, J.W., Lee, J., Huh, D., Lee, H., Kwak, S.K., Kim, J.Y., and Kim, D.S. (2019). Methylammonium chloride induces intermediate phase stabilization for efficient perovskite solar cells. *Joule*, 3(9):2179-2192. <https://doi.org/10.1016/j.joule.2019.06.014>
- Marimuthu, K., Babu, S.S., Muralidharan, G., Arumugam, S., and Jayasankar, C.K. (2009). Structural and optical studies of Eu³⁺ ions in alkali borate glasses. *Physica Status Solidi (A) Applications and Materials Science*, 206(1):131-139. <https://doi.org/10.1002/pssa.200824198>
- Ouis, M.A., Taha, M.A., El-Bassyouni, G.T., and Azooz, M.A. (2019). Thermal, mechanical and electrical properties of lithium phosphate glasses doped with copper oxide. *Bulletin of Materials Science*, 42(5):246. <https://doi.org/10.1007/s12034-019-1897-y>
- Ramaraghavulu, R., Sivaiah, K., and Buddhudu, S. (2012). Structural and dielectric properties of LiV₃O₈ ceramic powders. *Ferroelectrics*, 432(1):55-64. <https://doi.org/10.1080/00150193.2012.707843>
- Rao, P.V., Satyanarayana, T., Reddy, M.S., Gandhi, Y., and Veeraiah, N. (2008). Nickel ion as a structural probe in PbO-Bi₂O₃-B₂O₃ glass system by means of spectroscopic and dielectric studies. *Physica B: Condensed Matter*, 403(19-20):3751-3759. <https://doi.org/10.1016/j.physb.2008.07.001>
- Rao, R.B. and Veeraiah, N. (2004). Study on some physical properties of Li₂O-MO-B₂O₃: V₂O₅ glasses. *Physica B: Condensed Matter*, 348(1-4):256-271. <https://doi.org/10.1016/j.physb.2003.12.012>
- Saiter, J.M., Grenet, J., Dargent, E., Saiter, A., and Delbreilh, L. (2007). Glass transition temperature and value of the relaxation time at T_g in vitreous polymers. *Macromolecular Symposia*, 258:152-161. <https://doi.org/10.1002/masy.200751217>
- Srinivas, B., Hameed, A., Srinivas, G., Chary, M.N., and Shareefuddin, M. (2021). Influence of V₂O₅ on physical and spectral (optical, EPR & FTIR) studies of SrO-TeO₂-TiO₂-B₂O₃ glasses. *Optik*, 225:165815. <https://doi.org/10.1016/j.ijleo.2020.165815>