MULTIFUNCTIONAL $\text{Cr}_x\text{Ca}_{(10-x)}\text{Al}_{30}\text{Si}_{60}$ GLASSES, ELECTRICAL CONDUCTIVITY AND THERMOLUMINESCENCE

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ABSTRACT

The SiO$_2$ glasses embedded with Cr$^{3+}$ ions are notable for solid state optical resource, which are useful in various opto-electronic and semiconducting applications. However, the available thermoluminescent resource, which include different electronic and semiconducting materials, need some refinement in their structure, luminescence, and electronic properties towards development of advanced glass resource. In this vision, Cr$_x$Ca$_{10-x}$Al$_{30}$Si$_{60}$ glassy materials have planned for synthesis and testing. The GT, and GC phase transition points, and thermal stability (~1.2639) of test samples are identified. Structural vibrations are identified with the help of FT-IR spectra. The order of electrical conductivity (~1.657x10$^{-4}$ ohm$^{-1}$ cm$^{-1}$), and A.E. (~0.3669 eV) of test samples reveal their electrical strength. The symmetry (~0.576%) factor, frequency (1.1172 X 10$^{20}$ S$^{-1}$) factor, and A.E. (0.682 eV) of the test samples are recorded under 30 kGy irradiation. Overall, the results, which include structure, electrical and luminescence of the test samples suggest the materials might be useful electrically conductive and thermal stimulated light resource.

Keywords: CaO-Al$_2$O$_3$-SiO$_2$-Cr$_2$O$_3$Glasses, X-Ray Diffraction, DTA, FT-IR, Electrical Conductivity, Thermoluminescence.

INTRODUCTION

Inherently, the glass with silicon dioxide chemical constitutes is highly non-corrosive, transparent, and thermally stable. Their anticipated properties, such as high refractive index and luminescence, will make them needful optoelectronic industrial applications. Since many years to present, there have been wide-ranging research on a glasses with SiO$_2$ chemical constitutes due to their abnormal structure, and spectroscopic results. The aluminum oxide is not a conventional glass former, but add-on Al$_2$O$_3$ to the glasses with SiO$_2$ improves their elastic nature, thermal stability, non-corrosion properties. And also increase of Al$_2$O$_3$ in the SiO$_2$ glass host lead to more microhardness and thermal stability. SiO$_2$ embedded with Al$_2$O$_3$ glasses have a high order of thermally stimulated luminescence, which will highly useful for radiation dosimetry process. The addition of CaO to the silicate glass substances enhance the refractive index, and optical inertness. Calcium silicate glasses embedded with different transition metal oxides are the most favorable candidates in the current semiconducting sectors and finds plentiful usage in the area of thermoluminescent and D.C. Conductivity applications. The addition of Al$_2$O$_3$ also influence SiO$_2$ ions, which further improves the strength, chemical endurance, mechanical and spectroscopic properties to a considerable extent of the overall glass network. The CaO, and Al$_2$O$_3$ in the silicate glass host stimulates Cr$^{3+}$ ions for better optical output. The metal oxide like Cr$_2$O$_3$ is a well-known nucleation agent, which involves tri-valent oxidation states in silica glass matrix to enhance thermoluminescence and D.C. conductivity properties. Usually, Cr$^{3+}$ ions have a substantial effect on the glass lattice, further which lead to advance in thermoluminescence and D.C. conductivity properties. The glass with silicon dioxide chemical constitutes enclosing mixed valence states of Cr$^{3+}$ ions are of recent interest as a thermoluminescence and cathode resource in rechargeable batteries as of their abnormal energy density and capacitance.
Subsequently, in the existing work, Cr$_2$O$_3$ doped calcium aluminum silicate materials were synthesized and report for their suitability regarding thermoluminescent and D.C. conductivity behavior. Potential functions such as abnormal thermoluminescent and D.C. conductivity, etc., are achievable by improving tremendously advantageous solid-state glass resource that have fascinated extensive attention. Because of this, the current research aimed to prepare solid-state glass materials of chemical composition Cr$_{10-x}$Ca$_3$Al$_{30}$Si$_6$O$_{92}$ and to study the (x)Cr$_2$O$_3$+(10-x)CaO composite influence on electrical conductivity, and TL characteristics of Al$_2$O$_3$+SiO$_2$ glasses.

**EXPERIMENTAL**

The chemicals of Cr$_{10-x}$Ca$_3$Al$_{30}$Si$_6$O$_{92}$ have been used for the preparation of samples (where, 0.0 ≤ x ≤ 1.0, step size = 0.2 mol%). The 99% Pure AR grade chemicals such as Cr$_2$O$_3$, CaO, Al$_2$O$_3$, and SiO$_2$ have been chosen in agate mortar for fine grinding. Finely ground powder, in required mol% is taken in crucible with a 25 ml volume for form a glass. The furnace operated upto 1470°C temperature. Obtained melt allowed for rapid cooling on brass cast to achieve a test glass. Immediately, the achieved test glass annealed at 490°C with help of other furnace. Refined, and dimensionally prepared test samples are taken for structure, electrical, and luminescence studies. The melt technique is used to develop the test samples. The composition of test glasses given as follows Cr-0.0 (Cr$_{10}$Ca$_3$Al$_{30}$Si$_6$O$_{92}$), Cr-0.2 (Cr$_{9.8}$Ca$_3$Al$_{30}$Si$_6$O$_{92}$), Cr-0.4(Cr$_{9.6}$Ca$_3$Al$_{30}$Si$_6$O$_{92}$), Cr-0.6(Cr$_{9.4}$Ca$_3$Al$_{30}$Si$_6$O$_{92}$), Cr-0.8(Cr$_{9.2}$Ca$_3$Al$_{30}$Si$_6$O$_{92}$), and Cr-1.0 (Cr$_{1}$Ca$_3$Al$_{30}$Si$_6$O$_{92}$).

**RESULTS AND DISCUSSION**

Figure-1 reports the X-ray diffraction recording of Cr$_x$Ca$_{10-x}$Al$_{30}$Si$_6$O$_{92}$ glasses. The analysis suggest glassy behavior of all the test samples. Figure-2 reports chemical analysis of the glass with 0.8 mol% Cr$_2$O$_3$ concentration. Results obtained signify Ca, Al, Si, O, and Cr with their atomic weight %. Figure-3 reports, DTA spectra of the Cr$_x$Ca$_{10-x}$Al$_{30}$Si$_6$O$_{92}$ glasses. The glass transition ($T_g$), and crystallization ($T_c$) temperature positions are identified from the spectra. And thermal stabilities of glasses are computed with the help of glass transition ($T_g$), and crystallization ($T_c$) temperature. The variation in values of thermal stability of glasses with ion concentration projected in the inset of the same figure. Observed results reveal a glass with 0.8 mol% Cr$_2$O$_3$ concentration exhibiting the highest in the values of thermal stabilities of current glasses.

All the exothermic and endothermic thermograms variations are observed highest for the glass with 0.8 mol% Cr$_2$O$_3$ concentration, due to enthalpy change. Figure-4 reports the FT-IR spectra of Cr$_x$Ca$_{10-x}$Al$_{30}$Si$_6$O$_{92}$ glasses. Observed spectra exhibited well resolved following bands due to silicate, lanthanum, and Cr$^3+$ units at different wavenumber regions. The Ca–O (~1575 cm$^{-1}$) linkages, AlO$_4$ (~415 cm$^{-1}$) linkages, AlO$_6$ (~710–775 cm$^{-1}$) linkages, Si–O–Si Asymmetrical (~1015 to 1023 cm$^{-1}$) stretching, Si–O–Si Symmetrical (~842 to 851 cm$^{-1}$) stretching, Si–O–Si Rocking /bending (~461 to 473 cm$^{-1}$) vibrations, Cr–O Specific (~415 cm$^{-1}$) stretching vibrations. The glass with a 0.8 mol% Cr$_2$O$_3$ concentration found to be highest in the Cr$_x$Ca$_{10-x}$Al$_{30}$Si$_6$O$_{92}$ glasses exhibiting the highest shift in
wavenumber positions of all the silicate, aluminum, calcium and chromium structural units. The FT-IR analysis supports all the existence various chemicals such as Si–O–Si asymmetrical, Si–O–Si symmetrical, Si–O–Si bending, AlO$_6$ distorted octahedral and Cr–O specific stretching vibrational units.

Glass with a 0.8 mol% Cr$_2$O$_3$ concentration found to be highest in the Cr$_x$Ca$_{(10-x)}$Al$_{30}$Si$_{60}$ glasses exhibiting the highest shift in wavenumber positions of all the silicate, aluminum, calcium and Cr$^{3+}$ structural units due to steady inter-ionic forces between Cr$^{3+}$ ions to Si$^{4+}$, Al$^{3+}$, and Ca$^{2+}$ ions. The tetrahedrons in SiO$_2$ geometry are observed to be interconnected with mutual corners sharing. Usually, SiO$_2$ in its amorphous form will be preferred for glass production. Usage of Al$_2$O$_3$ in SiO$_2$ glasses improves the hardness, refractive index, and density of optical glasses. It is also used to improve thermo and piezoelectric characteristics of SiO$_2$ glass. SiO$_2$ glass phosphors, conductive ceramics, and dielectrics inclusive of Al$_2$O$_3$ are valuable photoelectronic resources. Naturally, Al$_2$O$_3$ has Cr$_2$O$_3$ hexagonal symmetry at low temperatures. The addition of CaO and Cr$_2$O$_3$ actively involves with Ca$^{2+}$ and Cr$^{3+}$ ions produce Ca-O-Si and Cr-O-Si linkages, which further influence all other Si$^{4+}$, Al$^{3+}$, and Ca$^{2+}$ ions within the glass network and improves non-bridging oxygen’s.

**Electrical Conductivity**

Figure-6 illustrates electrical conductivity variations with the inverse of increasing temperature. Observed results are almost linear. Insect (a), and (b) of the figure signifies the variation in electrical conductivity and A.E. with Cr$_2$O$_3$ increasing concentration. Observed electrical conductivity increased up to 0.8 mol% Cr$_2$O$_3$ concentration. Whereas analyzed, A.E. found to be decreasing until 0.8 mol% Cr$_2$O$_3$ concentration increasing concentration. All the evaluations concerning electrical conductivity measurements are
observed to be highest for the Cr-0.8 glass code. The detailed information concerning electrical conductivity measurements of the Cr$_x$Ca$_{(10-x)}$Al$_{30}$Si$_{60}$ glasses are furnished in Table-1.

Linear relation between electrical conductivity with increased inverse temperature in the present Cr-series of materials suggesting that the linear thermally exciting movement of the charge carriers for conduction An increase in the values of electrical conductivity and decrease in the values of A.E. up to 0.8 mol% Cr$_2$O$_3$ suggest a higher rate of polaron hopping and ionic transport phenomenon within the present Cr-series of materials. Mixed ionic and electronic conduction effects cause an increase in the value of electrical conductivity and a decrease in the values of A.E. up to 0.8 mol% Cr$_2$O$_3$ concentration. In comparison, decreasing electrical conductivity and decrease in the values of A.E. after 0.8 mol% Cr$_2$O$_3$ concentration. Both analyses suggest dissimilar conduction phenomena on the two sides of the present chemical composition. Such variations in the values of both electrical conductivity and A.E. of the present Cr-series of materials due to conformed mobility of both Ca$^{2+}$ and Cr$^{3+}$ ions.

<table>
<thead>
<tr>
<th>Glass</th>
<th>DC Conductivity at 300 K ($\times 10^{-4}$ ohm$^{-1}$ cm$^{-1}$)</th>
<th>A.E. (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-0.0</td>
<td>0.755</td>
<td>0.7215</td>
</tr>
<tr>
<td>Cr-0.2</td>
<td>0.915</td>
<td>0.4015</td>
</tr>
<tr>
<td>Cr-0.4</td>
<td>0.997</td>
<td>0.3912</td>
</tr>
</tbody>
</table>

Fig.-5: Proposed Molecular Structure of Cr$_x$Ca$_{(10-x)}$Al$_{30}$Si$_{60}$ Glasses

Fig.-6: Variation of Electrical Conductivity with 1/T for Cr$_x$Ca$_{(10-x)}$Al$_{30}$Si$_{60}$ Glass Materials, (where, 0.0 ≤ x ≤ 1.0, step size = 0.2 mol %). The inset 8(a) represents variation in activation energy with concentration and inset 8(b) variation in electrical conductivity with concentration of Cr$_2$O$_3$. Table-1: Data on Electrical Conductivity of Cr$_x$Ca$_{(10-x)}$Al$_{30}$Si$_{60}$ Series of glass materials, (where, 0.0 ≤ x ≤ 1.0, step size = 0.2 mol %).
Thermoluminescence

Thermoluminescence of the CrₓCa₉(10-x)Al₃₀Si₆₀ glasses were recorded from room temperature to 300 °C without γ-irradiation, and under 30 minutes of γ-irradiation (~30 kGy), these reports are shown in Fig.-7. In both situations the luminescence intensity is increasing as increasing upto 0.8 mol% Cr₂O₃ concentration.

Fig.-7: Thermoluminiscence Analysis of CrₓCa₉(10-x)Al₃₀Si₆₀ Series of Glass Materials, (where, 0.0 ≤ x ≤ 1.0, step size = 0.2 mol %).

The luminescence graph shows two intensity peaks for every glass sample one is at low temperature and other is at high temperature, the intensity peak at low temperature disappears quickly compare to intensity at high temperature. The trap-depth factors of glass samples were calculated by subsequent equations.²¹⁻²²

\[
E_x = C_x \left( \frac{KT_m^2}{x} \right) - b_x (2KT_m)
\]

\[
E_y = C_y \left( \frac{KT_m^2}{y} \right)
\]

\[
E_z = C_z \left( \frac{KT_m^2}{z} \right)
\]

Frequency Factor = \( \frac{\beta E}{KT_m} \left( \frac{\exp \left( \frac{E}{KT_m} \right)}{1 + (b - 1) \exp \left( \frac{E}{KT_m} \right)} \right) \)

Where, \( T_m \) is temperature at peak intensity,
\( T_1 = \) half maximum intensity intercepts at left and right side on the TL curve, and \( K \) is Boltzmann constant.

\( x = T_m - T_2, y = T_2 - T_1, z = T_2 - T_1 \) and Symmetry ratio(\( \eta \)) = \( \frac{y}{z} \)

\( C_x = 1.510 + 3(\eta - 0.42), C_y = 0.976 + 7.3(\eta - 0.42) \) and
\( C_z = 2.52 + 10.2(\eta - 0.42), b_x = 1.58 + 4.2(\eta - 0.42) \)

The trap depth factors such as activation-energies \( E_x, E_y \) and \( E_z \) and shape symmetry ratios without γ-irradiation and under 30 minutes of γ-irradiation witnessed from thermoluminescence investigation are initiate to be best for the glass sample of 0.8 mol% of Cr₂O₃ and the conforming data was provided in Table-2. The TL measurements of the CrₓCa₉(10-x)Al₃₀Si₆₀ glasses found to be increased, and the Cr-0.8 glass code found to be best in the results. Generally, Al₂O₃ exhibits (Al/Si)-O tri-clusters. Ca²⁺ ions and octahedral (Al/Si)-O₆ tri-clusters dislocate silicate linkages and induce binding defects. The addition of Al₂O₃ improves the structural defects within the glass network. Suitable applied external heat or thermal energy, lead to liberation of electrons, which also increase the Al³⁺, Cr³⁺, Si⁴⁺, and Ca²⁺ ions with in the
samples. The irradiation on surface of sample induce trap centers. Which will increase in increasing with irradiation dose. Later on the thermal moment with in the samples lead to electron trapping with trap centers with in the materials. In this view, the sample with 08Cr2O3 mol% concentration observed to be highest in TL grades.

Table-2: Summary on Thermoluminescence Studies of CrxCa10-xAl30Si60 Glass Materials, (where, 0.0 ≤ x≤ 1.0, step size = 0.2 mol %).

<table>
<thead>
<tr>
<th>Glass</th>
<th>Tm (K)</th>
<th>u</th>
<th>Ex (eV)</th>
<th>Er (eV)</th>
<th>Ez (eV)</th>
<th>Eavg (eV)</th>
<th>Frequency Factor (s-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-0.0</td>
<td>428</td>
<td>0.5</td>
<td>2.366</td>
<td>2.191</td>
<td>2.288</td>
<td>2.282</td>
<td>4.5288 X 10^10</td>
</tr>
<tr>
<td>Cr-0.2</td>
<td>463</td>
<td>0.473</td>
<td>2.974</td>
<td>2.785</td>
<td>2.899</td>
<td>2.886</td>
<td>1.0143 X 10^12</td>
</tr>
<tr>
<td>Cr-0.4</td>
<td>465</td>
<td>0.44</td>
<td>2.714</td>
<td>2.554</td>
<td>2.652</td>
<td>2.640</td>
<td>2.0836 X 10^13</td>
</tr>
<tr>
<td>Cr-0.6</td>
<td>466</td>
<td>0.392</td>
<td>1.973</td>
<td>1.928</td>
<td>1.969</td>
<td>1.957</td>
<td>2.7914 X 10^14</td>
</tr>
<tr>
<td>Cr-0.8</td>
<td>471</td>
<td>0.333</td>
<td>1.839</td>
<td>1.744</td>
<td>1.819</td>
<td>1.800</td>
<td>6.6342 X 10^15</td>
</tr>
<tr>
<td>Cr-1.0</td>
<td>467</td>
<td>0.375</td>
<td>3.028</td>
<td>2.834</td>
<td>2.951</td>
<td>2.938</td>
<td>1.7510 X 10^16</td>
</tr>
</tbody>
</table>

Under 30 kGy Irradiation

<table>
<thead>
<tr>
<th>Glass</th>
<th>Tm (K)</th>
<th>u</th>
<th>Ex (eV)</th>
<th>Er (eV)</th>
<th>Ez (eV)</th>
<th>Eavg (eV)</th>
<th>Frequency Factor (s-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-0.0</td>
<td>440</td>
<td>0.52</td>
<td>2.623</td>
<td>2.464</td>
<td>2.561</td>
<td>2.549</td>
<td>5.1879 X 10^16</td>
</tr>
<tr>
<td>Cr-0.2</td>
<td>455</td>
<td>0.5</td>
<td>2.945</td>
<td>2.810</td>
<td>2.905</td>
<td>2.886</td>
<td>4.5008 X 10^17</td>
</tr>
<tr>
<td>Cr-0.4</td>
<td>457</td>
<td>0.538</td>
<td>1.957</td>
<td>1.902</td>
<td>1.951</td>
<td>1.937</td>
<td>4.8809 X 10^18</td>
</tr>
<tr>
<td>Cr-0.6</td>
<td>458</td>
<td>0.535</td>
<td>1.456</td>
<td>1.324</td>
<td>1.420</td>
<td>1.400</td>
<td>7.1121 X 10^19</td>
</tr>
<tr>
<td>Cr-0.8</td>
<td>461</td>
<td>0.576</td>
<td>0.821</td>
<td>0.505</td>
<td>0.721</td>
<td>0.682</td>
<td>1.1172 X 10^20</td>
</tr>
<tr>
<td>Cr-1.0</td>
<td>459</td>
<td>0.6</td>
<td>1.181</td>
<td>1.014</td>
<td>1.130</td>
<td>1.109</td>
<td>8.906 X 10^21</td>
</tr>
</tbody>
</table>

The order of trap centers, and the outer most orbital (3d) degeneracy of Cr3+ ions lead to few order of covalence, which also results in good order of thermoluminescence with in the samples. The octahedral CrO6 units act as modifiers induce non bridging oxygens, could lead to enhanced TL emission. The increase in Cr2O3 mol % from 0 to 0.8 mol % improves octahedral tendency of samples, which lead to variation in intensities of thermoluminescence glow curves. Thereafter TL results follows reverse trend. The existence of Ca3+ ions with in the samples also another the reason to for better thermoluminescence results of samples. The developed octahedral behavior added advantage to high order of TL emission.23-24 The larger atomic radius of Cr3+ ions, tri-valent coordination of Cr3+ ions, octahedral tendency of Cr3+ ions, maximum intermolecular force between the ions, and short range periodic order with in the glasses are the reasons for the enhanced properties of the present glasses.

CONCLUSION

In the present work, we have synthesized the CrxCa10-xAl30Si60 glasses, (where, 0.0 ≤ x≤ 1.0, step size = 0.2 mol %). The structure of the glasses studied by means of X-ray diffraction, DTA and FT-IR characterization. Under DTA Studies, evaluated thermal stabilities of glasses observed to be highest for Cr-0.8 glass code, which reveal, high order of octahedral Cr3+ ions. The electrical conductivity and thermoluminescence studies of glasses also reported: Observed, dc conductivity (~1.657 x 10^-4 ohm^-1 cm^-1), and A.E. (~0.3669 eV) evaluations of glass with 0.8 mol% Cr2O3 concentration is a beneficial glass in electronics. The TL results such as shape symmetry factor and low AE’s of Cr-0.8 glass code under thermoluminescence studies is a useful TL asset. The larger atomic radius of Cr3+ ions, tri-valent coordination of aluminum ions, octahedral tendency of Cr3+ ions, maximum intermolecular force between the ions, and short range periodic order with in Cr-0.8 glass code is the reason for the enhanced properties. Based on structure, electrical and thermoluminescent studies of the glasses recommend that the Cr-0.8 glass code is a desirable resource for electrical and thermoluminescent use.

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REFERENCE
