Gamma ray induced decomposition of barium and strontium nitrates dispersed in sulphate and carbonate matrices in solid state

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The G(NO₃⁻) values in gamma radiolytic decomposition of barium and strontium nitrates are enhanced by their respective sulphate and carbonate additives, their concentration and the absorbed dose. The enhancement is more significant at > 95 mol % of the additive after which the increasing trend is not so significant. Thermoluminescence and ESR spectral studies suggest the formation of radical species such as SO₄⁻, SO₃⁻, O₂⁻, CO₃⁻, CO₂⁻, etc. which may interact with the radical species of nitrates (NO₃⁻, NO₂⁻ etc) causing enhanced decomposition by energy transfer. A comparison of the carbonate and sulphate additives shows the former to be more efficient medium of energy transfer.

Gamma radiolysis of inorganic nitrates is affected by many factors such as nature and size of cation, water of crystallization, free space volume in the crystal lattice, lattice energy, absorbed dose, nature and concentration of the additives. Khare and Johnson first investigated the energy transfer in several systems composed of KNO₃ in alkali halides, metal oxides etc. and found that G(NO₃⁻) values are enhanced by 100 times compared to pure salt in the concentration range 0.005-5.0 wt% of the nitrate. In our laboratory, extensive studies on gamma radiolysis of alkali metal nitrates with halide, sulphate, carbonate and phosphate additives have shown enhanced decomposition. It has been suggested that energy transfer involving radical species may occur. In the present study, we report on the gamma radiolytic decomposition of barium and strontium nitrates dispersed in respective sulphate and carbonate matrices in the concentration range 0.5-80 mol % of the nitrate up to an absorbed dose of 250 kGy.

Materials and Methods

All the nitrate salts and other chemicals were of AR/GR grade. Sulphates and carbonates of barium and strontium were prepared by precipitation from chloride salts with concentrated sulphuric acid and aqueous solution of ammonium carbonate. The precipitate was washed thoroughly and dried.

The binary mixtures of the nitrates with respective sulphate and carbonate additives were prepared by grinding together the weighed amounts in an agate mortar. Samples were sieved (50 mesh) to get uniform particle size and irradiated in unsealed Corning glass tube in a ⁶⁰Co Gamma Chamber-900 at a dose rate of 0.80 kGy h⁻¹. Dose rate was assayed by Fricke dosimeter using G(Fe³⁺) = 15.6 and alanine dosimeter. Radiolytic product NO₂⁻ was estimated spectrophotometrically using modified Shin's method of diazotization by employing Shimadzu UV-240 spectrophotometer. G-values were calculated on the basis of corrected dose obtained on the base of its electron fraction in the total system i.e.

\[
\frac{(\text{absorbed dose}) \times (\text{mol fraction of nitrate})}{\text{electrons per mol in the nitrate}} \times \frac{\text{electrons per mol in the total system}}{\text{electrons per mol in the nitrate}}
\]

Thermoluminescence glow curves of the gamma irradiated solid samples were recorded by heating at a linear heating rate of 150 K min⁻¹, using Indotherm temperature controller in conjunction with a RCA-931A photomultiplier and a millivolt recorder. ESR spectra of the gamma irradiated samples were recorded on a Brucker ESP-800 ESR X band spectrometer using microwave frequency of 9.74 GHz and DPPH as the field marker.

Results and Discussion

Gamma radiolytic decomposition of barium and strontium nitrates and their binary mixtures at varying concentrations were studied at various doses.

In Fig. 1 are plotted the variations of G(NO₃⁻) with mol % of strontium nitrate in the binary mix-
Table 1 — Gamma ray induced decomposition of Ba(NO$_3$)$_2$ and Sr(NO$_3$)$_2$ with respective sulphate and carbonate matrices at various compositions.

<table>
<thead>
<tr>
<th>Mol % of nitrate</th>
<th>Ba(NO$_3$)$_2$ + BaSO$_4$, 250 kGy</th>
<th>Sr(NO$_3$)$_2$ + SrCO$_3$, 100 kGy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[NO$_2^-$], ppm</td>
<td>G(NO$_2^-$)</td>
</tr>
<tr>
<td>0.5</td>
<td>1433 ± 22</td>
<td>396 ± 2.2</td>
</tr>
<tr>
<td>1.0</td>
<td>1398 ± 16</td>
<td>194 ± 2.2</td>
</tr>
<tr>
<td>5.0</td>
<td>1321 ± 16</td>
<td>35.6 ± 2.3</td>
</tr>
<tr>
<td>20.0</td>
<td>1008 ± 17</td>
<td>8.9 ± 1.0</td>
</tr>
<tr>
<td>60.0</td>
<td>1096 ± 14</td>
<td>1.9 ± 0.10</td>
</tr>
<tr>
<td>100.0</td>
<td>969 ± 10</td>
<td>0.82 ± 0.06</td>
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</table>

Fig. 1 — Variation of G(NO$_2^-$) with mol % of Sr(NO$_3$)$_2$ in SrSO$_4$ matrix at 50, 100 and 200 kGy.

Fig. 2 — Dependence of G(NO$_2^-$) with mol % of Sr(NO$_3$)$_2$ in SrCO$_3$ at absorbed doses of 50, 170 and 230 kGy.

Fig. 3 — Variation of G(NO$_2^-$) with absorbed dose for Sr(NO$_3$)$_2$ in SrCO$_3$ matrix at different nitrate compositions.
Thermoluminescence (TL) glow plots were recorded for irradiated samples of pure sulphates and carbonates and its binary mixtures with 1 mol % of respective nitrates at several doses. Typical TL glow curves for BaSO$_4$ + Ba(NO$_3$)$_2$ at 100 kGy, SrSO$_4$ + Sr(NO$_3$)$_2$ at 170 kGy and BaCO$_3$ + Ba(NO$_3$)$_2$ at 270 kGy are shown in Fig. 4.

Enhancement in the G(NO$_2^-$) values in alkali and alkaline earth metal nitrates by the additives such as alkali metal halides$^{17-20}$, silica$^{21}$, metal oxides$^{17-20}$ etc. is well known in literature. Earlier we have observed that addition of respective sulphate and carbonate$^{6,9}$ in the alkali metal nitrates increases its decomposition by several folds. Further, the decomposition was found to be composition and dose dependent. Khare and Johnson$^7$ have proposed an energy transfer mechanism involving excitons. On the other hand, Sagert and Robinson$^{21}$, and Wong and Willard$^{22}$ explained energy transfer process in terms of electron migration. Nitrate ion absorbs energy and it requires a minimum of -4.0 eV to cause dissociation. Therefore, only the matrix materials having an energy gap > 4 eV are effective in causing the energy transfer. In continuation of our earlier work$^{8,9}$, we have investigated the effect of sulphate and carbonate additives in strontium and barium nitrates at various doses and compositions.

Decomposition of barium and strontium nitrates in sulphate matrix

A perusal of data in Table 1 and Fig. 1 shows that G(NO$_2^-$) values are enhanced by sulphate matrix in both cases of barium and strontium nitrates at all doses and compositions. The figure also shows that G(NO$_2^-$) values are very high for <20 mol % of Sr(NO$_3$)$_2$ and Ba(NO$_3$)$_2$ in respective sulphates at all the doses. The inset of this figure further indicates that in low concentration range up to 10 mol % of the nitrate, G(NO$_2^-$) values decrease rapidly and beyond that only slowly. Further, it has been observed that at low concentrations up to 5 mol % of the nitrate, G(NO$_2^-$) is higher by two or three orders of magnitude as compared to the pure nitrate. With decreasing amount of sulphate additives, the enhancement in G(NO$_2^-$) is much smaller. It appears that the mechanism of radiolytic decomposition is different for lower concentration range of 0.5 to 5 mol % than for higher concentration range of >20 mol % sulphate. This observation could possibly be attributed to the different modes of interaction of radical species or defect centres formed$^{23}$ in the sulphate matrix with the nitrate ions. Even though in both cases energy is transferred from the sulphate matrix to the nitrate but in the low concentration range the defect centres seem to play a dominating role. At low concentrations of nitrates (i.e. >95 mole % sulphate), NO$_3^-$ may be in close contact with the sulphate matrix leading to the formation of lattice defects. In such cases, energy transfer may take place at the interfacial boundaries of the particles of two components thus enhancing decomposition. However, at higher concentration range of nitrate (i.e. <80 mole % sulphate) energy is transferred through excitons. It is well known that on gamma irradiation of sulphate, different radical species such SO$_4^-$, SO$_2^-$, SO$_2^-$, etc. are formed$^{24-26}$.

Mass spectrometric studies of $\gamma$-irradiated SrSO$_4$ have shown the excess of SO$_3^-$ and SO$_2^-$ formed by irradiation and interaction of electrons trapped in SrSO$_4$ lattice with the radical ion SO$_4^-$ (ref. 27). Gromov and Karaseva$^{28}$ studied ESR
spectra of Sr$^{35}$SO$_4$ and Ba$^{35}$SO$_4$ and γ-irradiated non-radioactive powders and observed signals for paramagnetic species such as SO$_3^-$ and SO$_4^{2-}$. ESR spectra of γ-irradiated sodium and strontium nitrates show the presence of radical species NO$_3^-$ and NO$_2$ (ref. 29). Similarly ESR spectra of γ-irradiated barium nitrate show signals for NO, NO$_3^-$ and O$^-$ (ref. 30). In order to identify the radical species in γ-irradiated systems, ESR spectra of BaSO$_4$ and BaSO$_4$ + 0.5 mol % Ba(NO$_3$)$_2$ were recorded at an absorbed dose of 200 kGy. The g-values and identification of radical species are listed in Table 2. Thermoluminescence measurements of γ-irradiated BaSO$_4$ and SrSO$_4$ along with their respective binary mixtures with 1 mol % nitrates at different absorbed doses of 100, 170 and 250 kGy further support the formation of radical species. Figure 4 shows a shoulder at 385 K and a peak at ~450 K, which may be assigned to radical species SO$_3^-$ and O$_2^-$ respectively$^{26}$. At higher doses the shoulder disappears. However, TL peak intensity at 450 K though decreases with increasing dose but the intensity is always higher w.r.t. binary mixture with 1 mol % nitrates at all doses during decomposition process. These evidences suggest that SO$_4^{2-}$ radical species are totally consumed whereas a part of O$_3^-$ species are also used up by interacting with NO$_3^-$ at all doses during decomposition process. The mechanism of decomposition involving interaction of radical species SO$_4^{2-}$, SO$_3^-$, and O$_3^-$ may be represented as follows:

**Primary process:**

\[ \text{SO}_4^{2-} \rightarrow \text{SO}_3^-, \text{SO}_2^-, \text{O}_3^- , e^- , \text{etc.} \]  \hspace{1cm} (1)

\[ \text{NO}_3^- \rightarrow \text{NO}_2^-, \text{NO}_3^-, \text{NO}_2^-, \text{NO}_2^-, \text{etc.} \]  \hspace{1cm} (2)

**Secondary process:**

\[ \text{SO}_3^- + \text{NO}_3^- \rightarrow \text{NO}_2^- + \text{SO}_2^- \]  \hspace{1cm} (3)

\[ \text{SO}_4^- + \text{NO}_3^- \rightarrow \text{NO}_4^+ + \text{SO}_2^- \]  \hspace{1cm} (4)

\[ \text{O}_3^- + \text{NO}_2^- \rightarrow \text{NO}_2^- + \text{O}_2 \]  \hspace{1cm} (5)

\[ \text{SO}_2^- + \text{NO}_3^- \rightarrow \text{NO}_2^- + \text{SO}_3^- \]  \hspace{1cm} (6)

\[ \text{NO}_3^- + \text{NO}_3^- \rightarrow 2\text{NO}_2^- + \text{O}_2 \]  \hspace{1cm} (7)

\[ \text{NO}_2^- + e^- \rightarrow \text{NO}_2^- \]  \hspace{1cm} (8)

\[ \text{SO}_4^- + e^- \rightarrow \text{SO}_2^- + \text{h} \nu \]  \hspace{1cm} (9)

\[ \text{NO}_3^- + \text{hv} \rightarrow \text{NO}_2^- + \text{O} \]  \hspace{1cm} (10)

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### Table 2

<table>
<thead>
<tr>
<th>System</th>
<th>Probable radical species</th>
<th>g&lt;sub&gt;av&lt;/sub&gt; Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaSO$_4$</td>
<td>SO$_3^-$</td>
<td>2.003</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>O$_2^-$</td>
<td>1.999</td>
<td>24</td>
</tr>
<tr>
<td>BaSO$_4$ + 0.5 mol %</td>
<td>SO$_3^-$</td>
<td>2.003</td>
<td>26</td>
</tr>
<tr>
<td>Ba(NO$_3$)$_2$</td>
<td>NO$_3^-$</td>
<td>2.001</td>
<td>24</td>
</tr>
</tbody>
</table>

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A comparison of the present observations with those of our earlier studies on alkali metal nitrates$^{9,12,13}$ suggests decrease in decomposition of alkaline earth metal nitrates. Similarly a comparison amongst two sulphates suggests BaSO$_4$ to be more effective medium for energy transfer compared to SrSO$_4$ in the decomposition of respective nitrates. It seems that besides anionic radical species and defect centres, the nature and size of cation also seems to play an important role in the decomposition process.

**Decomposition of barium and strontium nitrates in carbonate matrix**

It has been observed that decomposition of nitrates in respective carbonate additives in general, is enhanced for all the compositions and at all the doses. Figure 2 shows the decreasing trends of G(NO$_2^-$) with mol % of SrCO$_3$. Inset shows intercrossing of the plots suggesting decomposition process to be dose sensitive and dual role of the mechanisms of energy transfer. G(NO$_2^-$) values decrease rapidly for the lower mol % of the nitrates (~ 5 mol %). For higher concentration range, however, decreasing trend becomes slow. Again, similar to the case of sulphate system, different mechanism seems to operate in the lower...
A cursory look at the data in Table 1 suggests manifold increase (by 2-3 orders of magnitude) in G(NO$_3^-$) values on adding large amounts of carbonate. Enhancement in G(NO$_3^-$) is more significant in 0.5-5 mol % of the nitrate in both the cases. Also the rate of decrease in G(NO$_3^-$) becomes slow at higher absorbed doses (Fig. 3). This decreasing trend may be explained due to building up of trapped defect species in carbonate lattice. The number of defect species increases with absorbed dose and reach saturation at a certain dose depending upon concentration of the nitrate in the binary mixture. At this stage, radiation annealing may occur causing decrease in G values$^6$. Therefore, energy transfer ability of the additive may cease beyond an absorbed dose when saturation level reaches. ESR spectra of γ-irradiated SrCO$_3$ and SrCO$_3$ + 0.5 mol % Sr(NO$_3$)$_2$ systems at 50 kGy in Fig. 6 confirm the presence of CO$_2$ (g$_{av}$=1.9980)$^{31}$ and NO$_3^-$ (g$_{av}$=2.010)$^{34}$ radical species. Natarajan et al.$^{31}$ have observed the formation of radical species CO$_2^-$, O$_2^-$ and CO$^-$ for irradiated BaCO$_3$. In order to further confirm the formation of radical species in strontium and barium carbonates and their respective binary mixtures with 1 mol % nitrate, TL studies were carried out at different doses (Table 3). Earlier, Natarajan et al.$^{31}$ observed the TL peaks at 383, 430 and 570 K in gamma irradiated BaCO$_3$ and assigned to the formation of O$_2^-$, CO$_2^-$ and CO$^-$ respectively. We have observed three peaks at 380, 430 and 570 K for BaCO$_3$ at 270 kGy (Fig. 4C) in confirmation with the observations of Natarajan et al.$^{31}$. However, in the case of binary mixture with 1 mol % Ba(NO$_3$)$_2$ (Fig. 4C) a third peak at 605 K was observed which may be due to CO$_2^-$.

They have suggested that CO$_2^-$ could be stable even after 570 K. Thus, all these evidences suggest the formation of radical species CO$_2^-$, CO$_2^-$ and O$_2^-$ in both the carbonate matrices. These radical species may interact with NO$_3^-$ causing enhanced decomposition.$^6$ A probable mechanism may be represented as follows:

**Primary process:**

$$\text{CO}_2^- \rightarrow \text{CO}_2^-, \text{CO}_2^- , \text{O}_2^- , \text{e}^- \text{ etc.} \quad \ldots (11)$$

**Secondary process:**

$$\text{NO}_3^- + \text{CO}_2^- \rightarrow \text{NO}_3^+ + \text{CO}_2^- \quad \ldots (12)$$

$$\text{CO}_2^- + \text{NO}_3^- \rightarrow \text{NO}_2^- + \text{CO}_3^- \quad \ldots (13)$$

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Table 3—Peak temperatures and intensities in TL glow curves of gamma irradiated sulphates and carbonates and their binary mixtures with 1 mol % nitrates

<table>
<thead>
<tr>
<th>System</th>
<th>Dose (kGy)</th>
<th>Peak temperature (± 10 K)</th>
<th>Intensity/10 mg × 10$^{-7}$</th>
<th>Probable radical species</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrSO$_4$</td>
<td>100</td>
<td>425</td>
<td>30</td>
<td>O$_2^-$</td>
<td>26</td>
</tr>
<tr>
<td>SrSO$_4$ + Sr(NO$_3$)$_2$</td>
<td>100</td>
<td>420</td>
<td>33</td>
<td>O$_2^-$</td>
<td>26</td>
</tr>
<tr>
<td>BaCO$_3$</td>
<td>270</td>
<td>430 (shoulder)</td>
<td>36</td>
<td>CO$_2^-$</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>570</td>
<td>50</td>
<td>CO$_2^-$</td>
<td>31</td>
</tr>
<tr>
<td>BaCO$_3$ + Ba(NO$_3$)$_2$</td>
<td>270</td>
<td>450 (shoulder)</td>
<td>28</td>
<td>CO$_3^-$</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>605</td>
<td>85</td>
<td>CO$_2^-$</td>
<td>31</td>
</tr>
</tbody>
</table>
Thus, carbonates are better media for energy transfer than sulphates. This is in accordance with our earlier observations for alkali metal nitrates,\(^9\) and of magnitude compared to respective sulphates. Table 4 suggests order of magnitude for nitrate. ESR and carbonates and the nitrate. ESR and phates due to the interaction of the radical species of sul-

The enhancement in decomposition is explained due to the interaction of the radical species of sulphates/carbonates and the nitrate. ESR and Ti evidences support the formation of radical species.

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